



# Characterization of carbonation-cured cement paste using X-ray photoelectron spectroscopy

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## HIGHLIGHTS

- X-ray photoelectron spectroscopy was effective in studying microstructure of cement pastes cured by carbonation.
- Carbonation curing of the pastes promoted silicate polymerization at the early-age and long-term.
- Higher polymerization of silicates and accelerated reaction of C<sub>2</sub>S increased the strength of the pastes cured by carbonation.
- C<sub>2</sub>S was more reactive with CO<sub>2</sub> than C<sub>3</sub>S as evident by QXRD.

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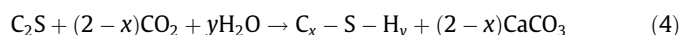
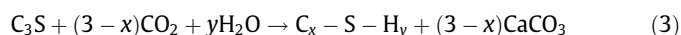
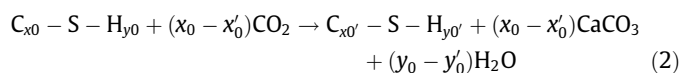
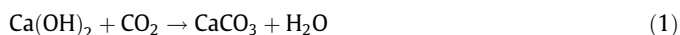
## ABSTRACT

X-ray photoelectron spectroscopy (XPS) was used to examine the microstructure of cement pastes following early-age CO<sub>2</sub> curing. The samples were hydrated for 18 h, and, then, were exposed to high-purity gaseous CO<sub>2</sub> at a pressure of 0.15 MPa for 6 h. They were subsequently hydrated until the age of 28 d. The samples were tested right after the carbonation process at the age of 1 d, as well as after the subsequent hydration. The results were compared with those obtained for the reference cement pastes which were not exposed to the carbonation curing. It was found that the calcium-silicate-hydrate (C-S-H) produced by the early-age carbonation had a more disordered and highly polymerized structure compared to that in the conventionally hydrated cement paste. The subsequent hydration significantly changed this structure, and resulted in the incorporation of additional calcium ions. The improved compressive strengths at both test ages were attributed to the higher polymerization of silicates in the cement pastes due to the early-age carbonation curing. Based on the quantitative X-ray diffraction results, more than 40% of C<sub>2</sub>S phase of cement was reacted in early carbonation at the age of 1 d. This accelerated reaction appeared to be a primary mechanism of the higher compressive strength at both early and late ages.

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## 1. Introduction

Reducing the carbon emission from concrete production is becoming increasingly important in the construction industry. The early-age carbonation of concrete, which involves the reaction of gaseous CO<sub>2</sub> with concrete within the first 24 h after casting, is considered as one of the promising approaches to reach this goal [1]. Concrete at this early-age includes the unreacted as well as hydrated phases of cement. Both these could react with gaseous CO<sub>2</sub>, and produce carbonate-based precipitates. The main reactions occur according to Eqs. (1)–(4):



The early-age carbonation of concrete, in addition to providing environmental advantages, could benefit the concrete performance. It accelerates the strength-gain of ordinary Portland cement (OPC) paste at the early-ages while maintaining high strength in the long-term [2]. Rostami et al. [3] also suggested that concrete samples that were exposed to 2 h of early-age carbonation after 2 h of steam curing had improved durability compared to those produced by 4 h of steam curing.

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Several studies have been performed in the last few decades to characterize the microstructure of concrete produced by the early-age carbonation and understand the mechanisms underlying its mechanical performance and durability [3–6]. Despite documented progress, the nature of the cementitious phases formed during the early-age carbonation and their contribution to the concrete performance are not fully resolved. Application of advanced techniques to provide a better understating of the characteristics of these phases appears to be essential. The primary cementitious phase of concrete is calcium-silicate-hydrate (C-S-H). Characterizing the structure of C-S-H in cement paste by the X-ray diffraction (XRD) technique is challenging due the low crystallinity of this phase. Analytical techniques which are not dependant of structural order, therefore, should be used for this purpose. Examples of these techniques include nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR). Rostami et al. [4] used  $^{29}\text{Si}$  NMR to characterize OPC paste exposed to 2 h of carbonation after 18 h of initial hydration. They suggested that the carbonated sample had higher value of  $Q^2/Q^1$  ratio compared to that in the conventionally hydrated sample. No  $Q^3$  was detected in these samples. Subsequent hydration of the carbonated sample until the age of 28 d did not significantly affect the degree of polymerization. Lerigoleur [5] also performed similar experiments with the carbonation time increased from 2 h to 24 h. An increase in the  $Q^2/Q^1$  ratio and the formation of a small  $Q^3$  peak were reported in the spectra of the sample tested right after the carbonation. In addition, Shao et al. [6] suggested that the early-age carbonation process increased the  $Q^2/Q^1$  ratio in the Portland limestone cement paste. The Si-O band in the FTIR spectra of this sample also shifted from  $975\text{ cm}^{-1}$  to  $1020\text{ cm}^{-1}$ .

X-ray photoelectron spectroscopy (XPS) is another powerful analytical technique which can be used for the surface characterization of materials independent of their crystallinity. It allows quantitative analysis of the surface elements and their chemical environments. XPS has shown great potential for the analysis of hydrated cement clinkers and synthetic C-S-H systems [7–13]. Few investigations, however, have been performed on the application of XPS for the chemical analysis of Portland cement paste as a multiphase system. The main objective of the current study is to use the XPS technique to elucidate the structural composition of the Portland cement paste produced by the early-age carbonation. Both conventionally hydrated cement paste and that produced by the early-age carbonation were tested by the XPS technique. The results were analyzed along with those obtained by the Quantitative X-ray diffraction technique. In addition, the compressive strength of the samples was measured at the ages of 1 d and 28 d. Mechanisms of the improved strength of the samples produced by the early-age carbonation were proposed.

## 2. XPS theory and application in cement studies

The XPS technique involves irradiating the sample surface by a focused beam of X-rays. This results in the emission of photoelectrons from the topmost surface of the sample (typically 1 to 10 nm). The kinetic energy and the number of photoelectrons are measured. The kinetic energy that remains on the emitted electrons ( $K.E._{XPS}$ ) is related to their binding energy, i.e. the energy required to promote the electrons from their inner-shells orbitals to the free state, according to:

$$K.E._{XPS} = E_{ph} - B.E._{XPS} - \phi_{XPS} \quad (5)$$

where  $E_{ph}$  is the initiating photon energy,  $B.E._{XPS}$  is the binding energy of the atomic orbital from which the electron originates, and  $\phi_{XPS}$  is the spectrometer work function [14]. Each element has a unique set of binding energies [15]. It is, therefore, possible

to determine the elemental composition of materials surfaces by XPS. The chemical bonding environments can also be studied based on the variations in the binding energies or chemical shifts.

The XPS technique has been useful in studying cement-based materials. It has been used to determine variations of the Ca/Si ratio and change in the bonding structure of pure calcium silicates upon hydration [16]. Rheinheimer and Casanova [7,8] studied the hydration of  $C_3S$  and  $\beta\text{-}C_2S$  thin films by the XPS technique. An increase in B.E. of Si 2p was observed as a result of the polymerization of silicates. Broadening of Si 2p peak was also detected due to the disordering of silicate structure related to the C-S-H formation. In addition, Black et al. [9] examined the Si 2p spectra of fresh and aged powdered  $\beta\text{-}C_2S$  samples. The fresh sample had a B.E. of 100.8 eV. This peak shifted to 102.44 eV in the aged sample, and a new small peak appeared at 100.51 eV. The peak at lower energies was related to unreacted  $\beta\text{-}C_2S$ , while the peak at the higher B.E. was assigned to a “calcium-depleted C-S-H phase” in the aged sample [9].

Black et al. [10–12] used the XPS technique for the study of synthetic C-S-H systems with various Ca/Si ratios. The results showed that Si 2p binding energy of synthetic C-S-H systems is related to the polymerization of silicates in these systems. C-S-H systems with higher degree of silicate polymerization and lower Ca/Si ratio had higher values of Si 2p B.E. [10]. It was also suggested that the average surface composition of nanocrystalline C-S-H systems determined by the XPS well agreed with the bulk composition obtained by the XRD. Black et al. [17] also studied the structural change of synthetic C-S-H systems exposed to weathering carbonation using XPS. In addition, Yousuf et al. [18] used the XPS technique in studying the carbonation of Type V Portland cement paste. They suggested that the Si 2p B.E. increased from 100.8 eV in the unhydrated cement to 102.2 eV in the 28-day old samples. No difference was observed in the Si 2p B.E. of the samples cured in air or under gaseous  $\text{CO}_2$ . In addition, the B.E. values were much lower than that detected for the silica gel (104.1 eV). These researchers suggested that the carbonation possibly “promoted polymerization with silicate tetrahedron being reorganised in a different mode as opposed to tridimensional arrangements in silica gel”. In the current study, the XPS technique was used for the characterization of cement paste samples prepared by a curing regime including 18 h of hydration followed by 6 h of carbonation and 27 d of subsequent hydration. This curing regime was selected as it would appear to provide adequate long-term performance of the paste based on previous research by Rostami et al. [3]. The structure of cement paste samples right after the early-age carbonation process and after the subsequent hydration was assessed using XPS as well as QXRD. The compressive strength of the samples was also measured. The results were compared with those obtained for the conventionally hydrated cement paste samples.

## 3. Experimental procedure

### 3.1. Materials

Canadian Standards Association (CSA) Type GU Portland cement was used for the preparation of cement paste samples. The chemical composition of cement is presented in Table 1. The mass percentage of  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  phases of the cement was 59.78%, 12.98%, 6.85% and 8.55%, respectively, as estimated using Bogue formulas.

### 3.2. Sample preparation

A total of 48 cement paste samples in four different series were prepared. The first series of samples, labeled as H1, were hydrated

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