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Microstructural changes in alkali-activated slag mortars induced by accelerated carbonation

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A B S T R A C T

This study investigated microstructural changes in alkali-activated slag (AAS) mortars after carbonation using XRD, FTIR, DTG, ^{1}H NMR and SEM examinations. The results showed that decalcification of C-S-H was the main reaction in carbonation of AAS. The C-S-H with a low Ca/Si was more vulnerable to decalcification in AAS samples activated by waterglass. Besides, AAS mortars demonstrated a lower $CaCO_3$ formation compared to Portland cement mortars. Calcite and vaterite were the major $CaCO_3$ polymorphs produced by carbonation of AAS precipitated mainly in gel pores and spaces in C-S-H interlayers. Meanwhile, the carbonation also caused a certain volume of contraction in AAS mortars.

1. Introduction

Carbonation includes complex physical and chemical reactions that can reduce durability of alkali-activated slag (AAS) at a rate higher than that of Portland cement (PC) concrete [1–3]. Many studies have investigated the carbonation and its governing mechanisms in ordinary Portland concrete. Carbonation of PC takes place when CO_2 from the atmosphere diffuses into the pore network of the matrix and reacts with calcium hydroxide (CH), calcium silicate hydrate (C-S-H), calcium aluminate hydrate (C-A-H) and ettringite promoting the formation of calcium carbonate polymorphs through a decalcification process [4]. The carbonation can be different in alkali-activated slag as it belongs to a Me_2O-MeO-Me_2O_3-SiO_2-H_2O system, in which hydration products mainly consist of C-S-H gel with a lower Ca/Si compared to that of PC. Song et al. [5] reported compressive strength loss in carbonated AAS due to formation of a low cohesive silica gel with a soft matrix; and a larger shrinkage as a result of C-S-H decalcification. They showed that the decalcification of C-S-H was the main reaction in the carbonation as the low Ca/Si of the binders reduced the nucleation and crystal growth of CH. Aperador et al. [6] illustrated that during exposure of specimens to CO_2, Na^+ slowly spoiled AAS matrix by forming more soluble compounds such as natron. With the absence of CH, Ca^{2+} from the C-S-H gel was the principal source of calcium ions in the pore solution to restrain the pH. Considering comparatively lower Ca/Si in AAS than that in PC, it can be concluded that AAS has a lower capacity to maintain pH of the pore solution than PC. Due to destabilization of C-S-H in a low pH environment, the Ca^{2+} from C-S-H in AAS concrete was transformed into $Ca(OH)_2$, and ultimately to $CaCO_3$ on exposure to CO_2 [7,8]. Although it is convinced that carbonation takes place directly in the C-S-H gel in AAS binders, effects of carbonation on microstructure of AAS mortars are not sufficiently clear.

Alkali activation of slag with sodium hydroxide/waterglass was recommended by researchers due to production of C-S-H with a lower Ca/Si resulting in formation of a very cohesive and homogeneous structure [9,10]. During carbonation, however, the low Ca/Si may adversely affect the microstructure of AAS as the decalcification process mostly targets the C-S-H. According to He et al. [11], carbonation decreased Ca/Si from an original value of 1.1–1.2 to 1.0 in C-S-H from activation of slag. The decrease in Ca/Si by carbonation was also reported in [12,13] resulting in shrinkage and an increase in the number of gel pores and micropores. Shi et al. [10] also showed a remarkable shrinkage and increased porosity in AAS which were related to the low Ca/Si of C-S-H. They also reported that almost no crystal phase formed by carbonation. However, the effect of activator type and dosage on the carbonation of AAS is still dubious due to dissimilar Ca/Si from C-S-H as well as secondary products generated by different activators. Puertas et al. [8] reported higher accelerated carbonation depths in AAS mortars activated with sodium silicate than that of sodium hydroxide. In their study, C-S-H had a lower Ca/Si ($\sim$0.8) in waterglass-activated AAS than those activated with NaOH-only solution (Ca/Si ratio $\sim$1.2). They concluded that the higher Ca/Si, along with a reduced silicate chain length observed in NaOH-activated slag, favored the formation and precipitation of a higher amount of carbonation products which filled pore spaces and decreased the diffusivity of CO_2 within the material. Higher alkalinity of activators also decreased the carbonation rate by modifying the rendered C-S-H [5,14]. Authors stated that the

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increased alkalinity was beneficial in dissolution and poly-condensation of the species from the slag, which accelerated precipitation of C-S-H gel in the system. Song et al. [5] also suggested that an increase in the activator dosage led to a higher formation rate of C-S-H at an accelerated pace, which increased compaction, compressive strength and carbonation resistance of the microstructure. As the Na_2O content in the activator was fixed, the carbonation rate of AAS slowed down as the modulus of waterglass increased from 0.75–1.0 [15,16]. This may be due to an increased reaction degree of the available slag caused by the increase in the activator content. Based on the available literature, it can be stated that the carbonation of AAS depends on C-S-H characteristics varying with type and concentration of activators.

There is also uncertainty about type of carbonation products as well as effects of secondary products of activation on carbonation when different activator types are used. During the carbonation process, natron and calcium carbonate polymorphs namely; calcite, vaterite and aragonite were identified as the main carbonation products of waterglass-activated slag binders [8]. However, Bernal et al. [15] reported that calcite was the only calcium carbonate polymorph in carbonated waterglass-activated slag. He et al. [11] reported the formation of calcite and vaterite, but no aragonite was detected in the carbonated waterglass-activated slag. Hydrotalcite is a secondary reaction product observed in slag activated with NaOH and waterglass [17,18]. However, reflections corresponding to hydrotalcite were detected after one day in the NaOH-activated slag, whereas such reflections were clearly identified in the NaOH/waterglass-activated slag after 6 months [17,18]. On account of a faster reaction rate in the early stage of NaOH-activated slag, large hydrotalcite crystals formed in NaOH-activated slag although the chemical compositions were similar in both NaOH or waterglass-activated slag materials [17]. Hydrotalcite was also observed during accelerated carbonation of NaOH/waterglass-activated slag using high CO_2 concentrations [19]. León et al. [20] found that the formation of double layered hydroxides with a hydrotalcite-type structure increased CO_2 absorption. Bernal et al. [21] also reported that the larger formation of hydrotalcite significantly contributed to enhancing performance of AAS binders when exposed to high CO_2 concentrations.

Several studies focused on the carbonation rate and mechanisms, however, microstructural changes of AAS after carbonation received less attention. The overarching purpose of this study is to investigate the effect of activator type and concentration on microstructural changes of AAS with comparison to PC. The compressive strength, microstructure of the main reaction products and pore structure of these cements before and after carbonation were investigated. Findings of this study can further improve understanding of the characteristics and mechanism of carbonation in AAS.

2. Materials and methods

2.1. Materials

A vitreous ground granulated blast furnace slag from a local steel company was used. Portland cement PI 42.5 in compliance with Chinese standard GB 175-2007 was also used as a reference. The chemical composition of slag and cement was determined by X-ray fluorescence (XRF) and shown in Table 1. The particle size distribution was determined by laser particle size analyzer as shown in Fig. 1. Fig. 2 shows the XRD pattern of the GGBS indicating its dominant amorphous

Table 1
Chemical composition of blast-furnace slag and cement, wt%.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	Fe_2O_3	Na_2O	SO_3	LOI
Slag	33.81	14.78	38.81	7.09	0.44	0.36	0.26	2.49	1.40
Cement	21.90	4.81	65.15	1.95	–	3.41	0.65	0.51	1.62

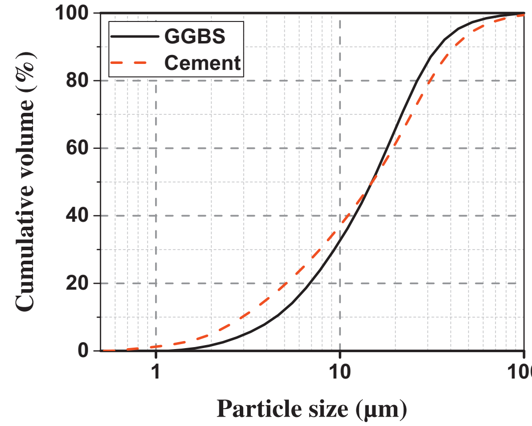

Fig. 1. Particle size distribution of GGBS and cement.

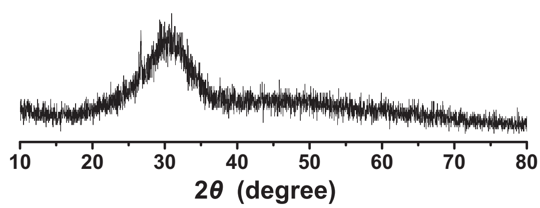

Fig. 2. XRD pattern of GGBS.

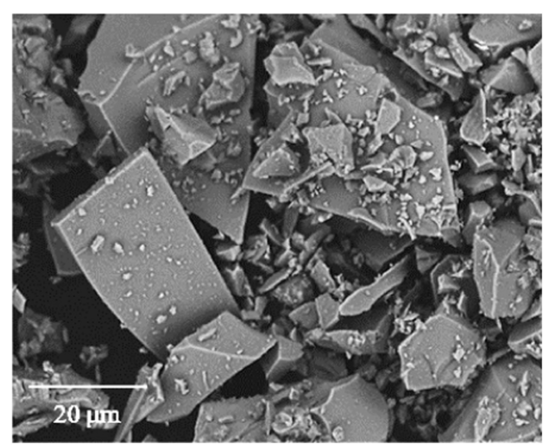

Fig. 3. SEM picture of GGBS particles.

phase. The GGBS particles had angular shape as shown in Fig. 3.

River sand with a maximum particle size of 2.36 mm, a fineness modulus of 2.75, and apparent density of 2530 kg/m^3 was used to prepare mortar samples. In this study, sodium hydroxide and sodium silicate solution were used as alkaline activators. Sodium hydroxide (NaOH) in pellet-form was an industrial-grade with purity of 99 ± 1%. Also, sodium silicate solution used was an industrial grade sodium with a chemical composition of 8.3% Na_2O, 26.5% SiO_2 and 65.2% H_2O. The alkaline activator consisted of sodium silicate and sodium hydroxide with a molar modulus (SiO_2/Na_2O molar ratio) of 0 (NaOH-only solution), 0.5, 1.0, 1.5 prepared 24 h prior to use.

2.2. Mixture proportions and sample preparation

The slag was activated by mixing with the alkaline activator at a water-to-binder ratio of 0.47 by mass of slag. For all groups, Na_2O in activator was kept constant at 4% of mass of slag, while SiO_2 content was changed to reach the proposed modulus. The sand to binder ratio of 2.25 was used. The mixture proportions of AAS and PC mortars are