



# Reactivity and reaction products of alkali-activated, fly ash/slag paste



N.K. Lee, H.K. Lee\*

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

## HIGHLIGHTS

- The amount of added slag affected the formation of reaction product.
- As the amount of added slag increased, the amount of C-S-H gel increased.
- The aluminosilicate gel with the Q4 units was similar to a Ca-based geopolymer.

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## ABSTRACT

Few studies have described the reaction products of an alkali-activated, two-source binder and their characteristics due to the complexity of the mechanism. In this study, the microstructure, reaction products, and reactivity of alkali-activated, fly ash/slag binders synthesized at various mixture ratios of two raw materials were examined using various experimental techniques (NMR, ICP-OES, EDS, FT-IR and TGA) to systematically investigate the complex reaction mechanism of the binders. It was also intended to help assess durability of the binders. It was found that the amount of added slag primarily affected the amount of reaction product and its silicate structure, and as the amount of added slag increased, the amount of C-S-H gel increased and the amount of aluminosilicate gel decreased. Considering chemical composition and silicate structure, the aluminosilicate gel with the Q4 ( $nAl$ ) units was found to be similar to a Ca-based geopolymer (N-C-A-S-H). The chemical composition ratios of the Ca-based geopolymer were nearly the same as those of C-S-H whereas their silicate structures were different.

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## 1. Introduction

Geopolymer materials are known as alternatives to ordinary Portland cement (OPC); the geopolymer binders can reduce CO<sub>2</sub> emissions by 80% compared to the OPC [11]. The main sources of the geopolymers are metakaolin, fly ash, and blast furnace slag. Reaction products formed through an alkali-activation process are completely different depending on chemical composition of the raw sources [24]. The main reaction product of alkali-activated blast furnace slag, which is rich in Ca, is C-S-H gel with a low Ca/Si ratio (0.8–1.1) [24,16,17], whereas the main reaction product of alkali-activated metakaolin or fly ash, which is rich in Si and Al, is amorphous aluminosilicate gel with a three-dimensional framework of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra linked through shared O atoms [35,41,10].

Several studies have reported the alkali-activation of two-source mixtures that consist of fly ash/slag or metakaolin/slag [37]; [47,31,3,38,5,19]. The addition of blast furnace slag in the

one-source mixture was effective for improving the mechanical properties of the geopolymers made with metakaolin [43,44] and fly ash [23]. The authors investigated mechanical properties such as compressive strength, elastic modulus, splitting tensile strength, and setting properties of alkali-activated, fly ash/slag concrete at various slag contents, and concluded that the slag content of 20–30% relative to the total binder weight was optimal considering setting, flowability, and strength [27,28,20].

There are two different reaction products of the alkali-activated, two-source binder; both products had higher reactivity than that of the one-source binder. Puertas et al. [37] showed that two different reaction products existed in alkali-activated pastes. Correspondingly, Buchwald et al. [6] showed in an NMR study that alkali-activated metakaolin/slag binders had higher reactivity than the alkali-activated metakaolin binder, and established the types and quantities of the reaction products. The main reaction products were calcium silicate hydrate rich in Al that contains Na in its structure and alkaline aluminosilicate hydrate with a three-dimensional structure [37]. Yip and Van Deventer [45] and Buchwald et al. [6] concluded, after SEM observations and NMR spectroscopic studies, that the C-S-H and aluminosilicate gel

\* Corresponding author. Tel.: +82 42 350 3623; fax: +82 42 350 3610.

E-mail address: [leeh@kaist.ac.kr](mailto:leeh@kaist.ac.kr) (H.K. Lee).

coexist in the alkali-activated metakaolin/slag binders. In addition, the chemical interaction may arise between the elements released by the dissolution of fly ash and slag particles [25], and the two phases (C-S-H and aluminosilicate) may not only be combined but also may chemically interact [6,25]. On the contrary, the authors stated that the discrete formation of C-S-H gel and aluminosilicate gel in an SEM length scale was not observed from their experiment, and the separation between calcium-rich and calcium-deficient regions was not identified [26]. Nevertheless, if the separation is observed, it may be due to inadequate mixing during the manufacturing process [26]. Recently, it was found that C-A-S-H gel and N-A-S-H gel are reaction products in a fly ash/slag geopolymer [19,5,29], and the N-C-A-S-H gel may be a hybrid-type phase of the N-A-S-H gel and the C-A-S-H gel [19].

The alkali-activation of a two-source mixture has a more complex mechanism than that of a one-source mixture. Few studies have described the reaction products of an alkali-activated, two-source binder and its characteristics due to the complexity of the mechanism [5,38,19]. Quantitatively evaluating the reaction products and reactivity of alkali-activated, fly ash/slag binder synthesized at various mixture ratios of two raw materials is important to figure out the complex mechanism.

In the present study, the microstructure, reaction products, and reactivity of alkali-activated, fly ash/slag binders synthesized at various mixture ratios of two raw materials were examined using various experimental techniques (NMR, ICP-OES, EDS, FT-IR and TGA) in order to systematically investigate the complex reaction mechanism of the binders. The test results will help assess the durability of the alkali-activated, fly ash/slag binders with different amounts of the reaction products and different reactivity levels.

## 2. Experimental program

### 2.1. Materials

Class F fly ash (containing more than 70% pozzolanic compounds ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ ) in accordance with ASTM C618) and blast furnace slag were used as binder materials. The chemical compositions of these materials are listed in Table 1.

Two types of alkali-activators were prepared: sodium silicate powder with a chemical composition of  $\text{SiO}_2$  (53.4%) and  $\text{Al}_2\text{O}_3$  (25.2%), a bulk density of 0.62 g/cm<sup>3</sup> and a molar ratio of 2.18 ( $M_s = \text{SiO}_2/\text{Na}_2\text{O}$ ); and sodium silicate liquid ( $\text{SiO}_2/\text{Na}_2\text{O} = 1.0$ ) mixed with 4 M NaOH and water glass (Korean industrial standards (KS) Grade-3;  $\text{SiO}_2$  (29%),  $\text{Na}_2\text{O}$  (10%),  $\text{H}_2\text{O}$  (61%), specific gravity 1.38 g/mL). Distilled water was used to dissolve the solid NaOH (98%); the latter alkali activator was prepared by mixing the NaOH solution with water glass at the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratios developed by the authors [27].

### 2.2. Mixture proportions

The mixture proportions are provided in Table 2 and are labeled with specific codes. The labels 'P', 'L' and 'S' represent powder, liquid, and slag, respectively. The numbers '10', '30', and '50' refer to the percentage of slag to the total binder (fly ash + slag) by mass.

The method for producing the alkali-activated, fly ash/slag (AFS) paste is as follows: In the case of use of powder sodium silicate, fly ash, slag, and powder sodium silicate were dry-mixed for 2 min to ensure the homogeneity of the mixture. Once water was added to the mixture, it was mixed for an additional 2 min. In the case of

**Table 1**  
Chemical composition of the binder materials.

Oxide (wt.%)	Fly ash (FA)	Blast furnace slag (BFS)
CaO	4.41	42.47
$\text{SiO}_2$	67.26	35.17
$\text{Al}_2\text{O}_3$	14.76	13.93
$\text{Fe}_2\text{O}_3$	4.07	0.58
$\text{SO}_3$	–	2.03
MgO	1.29	4.12
$\text{Na}_2\text{O}$	2.04	0.15
$\text{K}_2\text{O}$	1.39	0.46
LOI	3.57	0.18

**Table 2**  
Mix proportion of alkali-activated fly ash/slag paste.

Sample	Water/binder <sup>a</sup>	$\text{SiO}_2/\text{Na}_2\text{O}$ ratio of sodium silicate	Slag/(fly ash + slag) <sup>a</sup>	Type of sodium silicate
PS10	0.4	2.12	0.1	Powder
PS30	0.4	2.12	0.3	Powder
PS50	0.4	2.12	0.5	Powder
LS10	0.4	0.94	0.1	Liquid
LS30	0.4	0.94	0.3	Liquid
LS50	0.4	0.94	0.5	Liquid

<sup>a</sup> All values are given as mass ratios.

use of liquid sodium silicate, fly ash, and slag were dry-mixed and then the liquid sodium silicate was added to the mixture. The AFS paste samples prepared by the process were immediately cast into 50 mm cubic molds. All of the samples were cured at 20 °C and at a relative humidity of 50% in a room with constant temperature and humidity levels. After one day, the samples were removed from their molds and were stored in a conditioning room until the day of testing.

### 2.3. Experimental details

The AFS samples for the X-ray powder diffraction (XRD) test were prepared by mechanical grinding. The XRD data were recorded on a Rigaku D/MAX-2500 machine using  $\text{Cu K}\alpha$  radiation at a scanning rate of 2°/min from 2° to 160° in 2 $\theta$ .

To analyze the polished surfaces of the samples on a NOVA 230 device (FEI Company), scanning electron microscopy (SEM) with back-scattered electron (BSE) images and energy-dispersive spectroscopy (EDS) analyses were performed. The samples were impregnated by using low-viscosity epoxy resin, polished with SiC paper, and coated with gold.

Powdered AFS samples were dried at 80 °C in an oven for 1 day before the thermogravimetric analyses (TGA). The TGA measurements were applied to the powdered samples under  $\text{N}_2$  gas at 10 K/min up to 900 °C.

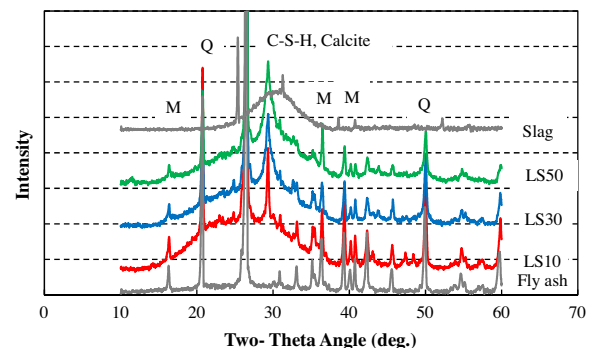
Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the water-soluble silicon, aluminum, calcium, and sodium contents of the AFS samples in distilled water. The powdered AFS samples were sonicated in distilled water for more than 2 h and the amounts of water-soluble elements were then measured by means of ICP-OES. The reactivity of the alkali-activator (sodium silicate powder or liquid) was evaluated indirectly through this quantitative analysis.

<sup>29</sup>Si nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCE 400WB) was used to record the solid-state NMR spectra with the purpose of evaluating the reactivity and content of the reaction products (i.e., C-S-H gel and aluminosilicate gel). The <sup>29</sup>Si resonance frequency was 79.42 MHz and the spinning rate was 5 kHz. All of the measurements were taken at room temperature with tetramethylsilane (TMS) as an external standard. The spectra were acquired using a pulse length of 1.5  $\mu\text{s}$ , and a short repetition time of 20 s was chosen. The powdered samples were also analyzed by Fourier transform infrared (FT-IR) spectroscopy (Model FT-IR 4100, JASCO, Japan).

## 3. Results

### 3.1. X-ray powder diffraction (XRD)

Fig. 1 shows the XRD patterns of the AFS samples, raw fly ash and raw slag. The raw fly ash shows peaks related to the presence



**Fig. 1.** XRD patterns of raw fly ash, raw slag and AFS samples activated by sodium silicate liquid.

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