Fly ash-slag interaction during alkaline activation: Influence of activators on phase assemblage and microstructure formation

Hailong Ye*, Aleksandra Radlińska

Department of Civil and Environmental Engineering, The Pennsylvania State University, 3127

Research Drive, State College, PA, 16801, United States

* Corresponding author. Email: huy131@psu.edu Phone: +001 484-260-4003

Abstract: In this work, the influence of activator on the interaction mechanisms between slag and low-calcium fly ash (FA-F) during alkaline activation was investigated. In particular, the evolution of phase assemblage and microstructure of alkali-activated binary slag and FA-F paste was monitored by means of X-ray diffraction with Rietveld analysis, scanning electron microscopy, and energy-dispersive spectroscopy (SEM/EDS). The results show that the nature of amorphous gels and type of crystalline phases formed are dependent on sample age, initial slag to FA-F ratio, and activator type and dosage. The interaction between FA-F and slag during alkaline activation or geopolymerization is primary demonstrated as: (1) modified nanostructure (e.g. crystallography and lattice parameters) and chemical composition of precipitates, (2) depressing or triggering the formation of some crystalline phases, and (3) spatial heterogeneity of composition in microstructure. The activator is chemically incorporated into interactions between slag and FA-F, and likely affects the dissolution and reaction kinetics.

Keywords: Alkali-activated binder; Geopolymer; Calcium-alumina-silicate-hydrate; Alkali-aluminosilicate-hydrate; Fly ash-slag blends.

1. Introduction

Due to environmental concerns related to cement and concrete production, repurposing of ground-granulated blast furnace slag (GGBFS) and Class F fly ash (FA-F) into infrastructure materials has been gaining wider attention [1, 2]. As GGBFS and FA-F are both industrial by-products with remarkable cementitious or pozzolanic activities, alkali-activated binary FA-F and slag materials have become one of most promising alternative binders to ordinary Portland cement (OPC) [3, 4]. The combined use of FA-F and slag for preparing alkali-activated binders has several advantages over either pure alkali-activated slag (AAS) or pure FA-F-based geopolymer alone. For instance, addition of small dosages of slag into NaOH-activated FA-F-based geopolymer can potentially resolve its setting problems, since NaOH-activated FA-F typically takes much longer time to harden at room temperature than OPC [5]. On the other hand, as AAS has considerable chemical and drying shrinkage [6-8], the incorporation of FA-F in AAS binders can enhance its volumetric stability [9]. With respect to further implementation in construction field, the physical and engineering properties of alkali-activated FA-F/slag binders must be known. There is no doubt that the properties of these binders are inherently controlled by

the main hydration products formed during the activation process [10].

Previous research has revealed that slag and FA-F, when separately activated, exhibit distinct hydration products [11, 12]. Basically, the main hydration product in AAS binders is calcium-alumina-silicate-hydrate (C-A-S-H), while for pure FA-F-based geopolymers, it is rich in alkali-aluminosilicate-hydrate (N-A-S-H) [12]. It has been widely shown that C-A-S-H formed in AAS has a lamellar structure with a strong similarity to the structure of tobermorite [13-15]. The Al^{3+} in C-A-S-H is incorporated in the dreierketten silicate chains and substitutes Si^{4+} , which is charge balanced by alkali or Ca^{2+} cations [16]. In case of N-A-S-H, Si^{4+} and Al^{3+} are arranged in tetrahedral forms to create 3D structures, with alkaline cations (e.g. Na^+) compensating the charge balance associated with Al^{3+} . In addition, the Al/Si ratio in N-A-S-H varies and typically ranges from 0.28 to 0.36 [17]. Similarities between N-A-S-H gel structure and the structure of zeolites have been reported in numerous papers [17-19]. For alkali-activated FA-F/slag binary materials, the main hydration product is in a $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system, and the hydrated products are reported to contain both N-A-S-H, C-A-S-H, and potentially N-C-A-S-H [20]. Recent study has shown that there may exist chemical interactions between slag and FA-F during alkaline activation and geopolymerization process [21, 22]. In addition, it was reported that the nature of hydrated products formed in binary systems are influenced by the FA-F/slag ratio [20, 22, 23], temperature [24], alkaline activator (e.g. pH, dissolved silica) [25].

Despite an extensive previous investigation, the interaction mechanism between slag and FA-F, as well as the influence of activator on this interaction remains unclear. Recent investigators attempted to explore the potential interaction mechanisms between slag and FA-F, including reaction mechanisms [26], chemical composition [20], gel structure [22], and pore structure [27]. For example, Lee et al. found that although the geopolymeric gel can contain a considerable amount of Ca (i.e. N-C-A-S-H), which has nearly the same chemical composition as C-A-S-H, their silicate structures are different [22]. Ismail et al. reported that a hybrid N-C-A-S-H gel can be identified as part of the Ca released by slag dissolution is incorporated into the N-A-S-H type gel resulting from fly ash activation [20]. Provis et al. found that low calcium content (i.e. low slag/FA-F ratio) can not induce the formation of specific Ca-rich gel phases, and suggests some extent of incorporation of Ca into the N-A-S-H gels [27]. It can be seen that the exact mechanism between slag and FA-F during alkaline activator and the influence of activator on this interaction still remain unknown.

This study aims to illuminate the interaction mechanisms between slag and FA-F by monitoring the phase assemblage and microstructural evolution of the alkali-activated FA-F/slag binary materials. In addition, the influence of the dissolved silica ($[\text{SiO}_2]_{\text{aq}}$) and pH of the activator solutions on the early-age interaction during activation or geopolymerization process is explored. Particularly, X-ray diffraction with Rietveld semi-quantitative analysis, scanning electron

microscopy, and energy-dispersive spectroscopy (SEM/EDS) were implemented to monitor the evolution of hydrated phases, microstructure, and chemical composition of binary system as a function of age, slag/FA-F ratio, and activator. Furthermore, a series of ternary phase diagrams combined with statistical composition distribution were analyzed, to further understand the interaction mechanisms.

2. Experimental procedures

2.1 Materials

Class F fly ash (ASTM C 618-08) and Grade 120 ground-granulated blast-furnace slag (ASTM C989M-12a) were utilized in this study. The chemical compositions, specific gravity, and particle size distributions of these two raw materials are listed in Table 1 and Figure 2, respectively. To prepare activator solution, a combination of sodium silicate and NaOH solutions was used. The sodium silicate ($\text{Na}_2\text{O} \cdot (\text{SiO}_2)_{1.6} \cdot (\text{H}_2\text{O})_x$) had a modulus of 1.6 (by molar), pH of 13.7, and specific gravity of 1.60 at 20°C. The NaOH solution was prepared using pellets and distilled water. The activators were dissolved in distilled water prior to the mixing in order to have a homogenous distribution, further sealed in airtight containers to prevent carbonation and evaporation, and then cooled to room temperature ahead of mixing time.

101 Table 1 Oxide compositions and specific gravity of FA-F and raw slag (mass %)

	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃ ^a	S ²⁻	Fe ₂ O ₃	Na ₂ O	K ₂ O	P ₂ O ₅	MnO	TiO ₂	LOI	Specific gravity
Slag	43.83	30.04	12.74	4.79	3.11	0.85	1.16	0.24	0.40	0.08	0.22	-	2.56	2.89
FA-F	2.53	48.67	25.13	0.86	1.46	-	16.08	1.04	1.97	0.26	0.04	1.03	1.58	2.50

102 Note: a: The element compositions were measured by ICP-AES method, the relatively high SO₃
103 content in slag is primarily due to the presence of gypsum

104

105
106 Figure 1 Particle size distribution of raw slag and FA-F obtained by laser diffraction

107

108

2.2. Mixture design and sample preparation

In this study, FA-F/slag-based geopolymer pastes prepared by three different activators were investigated. Volumetric mixture proportioning was implemented by keeping the initial liquid (activating solution) to solid (FA-F and slag) volumetric ratio constant at 0.75 for all samples, as shown in Table 2. The selection of this volumetric ratio ensured that all mixtures have the same initial porosity although the workability would vary. Considering the different densities between FA-F and slag, as well as among various activators, the mass ratio for each mixture varies. Additionally, three different types of solutions, namely sodium silicate (NS), 6M NaOH (HN), and 2M NaOH (LN) were used as activators. The initial volumetric ratio between raw FA-F and slag were set to be 100/0, 80/20, 50/50, 20/80, for each individual type of activator. The pure AAS binder was neglected in this study, since a systematic study on the phase evolution and microstructure characteristics for the same slag with a broad range of activator type/dosage have been reported by the authors previously [8]. After mixing, each sample was cast in a sealed plastic container to prevent evaporation and carbonation, and was further kept at constant temperature of $23 \pm 0.5^\circ\text{C}$, until reaching the desired age (i.e. 1 day, 7 days, and 28 days) for further characterization as described below.

Table 2 Mixture proportions for alkali-activated binary FA-F/slag-based geopolymer pastes

Mixture ID	Activator/Binder (by vol.)	NaOH Molarity (M)	Sodium silicate/NaOH (by mass)	Slag/FA-F (by % vol.)
FA00S-NS				0/100
FA20S-NS		6	2	20/80
FA50S-NS				50/50
FA80S-NS				80/20
FA00S-HN				0/100
FA20S-HN	0.75	6	0	20/80
FA50S-HN				50/50
FA80S-HN				80/20
FA00S-LN				0/100
FA20S-LN		2	0	20/80
FA50S-LN				50/50
FA80S-LN				80/20

128

129

130 *2.3 X-ray diffraction with Rietveld analysis*

131 Prior to X-ray diffraction (XRD) test, paste samples were crushed and immersed into isopropyl

132 alcohol to stop further hydration at the desired age, and then vacuum-dried before milling to fine

size. Furthermore, 3%-4% crystalline Nickle powder was admixed in each sample as an internal standard for Rietveld analysis. The samples were further front-filled into a zero-background plate and continuously scanned between 5° and $70^\circ 2\theta$ under the conditions as follows.

XRD data was collected using a PANalytical Empyrean diffractometer in a conventional Bragg-Brentano θ - 2θ configuration using $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) with a diffractometer radius of 240 mm. $\text{CuK}\alpha$ X-ray was generated using 40 mA and 45 kV operating conditions. Incident beam Soller slits of 0.04° were used, and the incident divergence and anti-scatter slits were fixed at 0.25° and 0.5° , respectively. Air scattering was reduced using a beam knife. The beam width was 10 mm and no receiving slit was used, but an anti-scatter slit was fixed at 0.25° and the Soller slits limiting the axial divergence to 0.04 radians were positioned in the diffracted beam path. Instead of using monochromators, a beta-filter Nickle was used to eliminate the β diffraction spectrums. A PIXcel3D 1x1 solid-state detector with a total of 255 active channels and an active length of 3.3473° was used for data acquisition.

Rietveld semi-quantitative analysis was implemented in this research to determine the quantities of crystalline and amorphous components in alkali-activated FA-F/slag binary materials. The principle of Rietveld method is to minimize the inconsistency between measured and calculated powder diffraction patterns, by adjusting numerous parameters in particular structural models [28, 29]. The structural model in Rietveld method can account for various systematic errors in

experimental data (e.g. preferred orientation(s), peak broadening, and peaks overlap) [28]. In case of alkali-activated FA-F/slag binary materials, a challenge of quantifying such complex material is due to the presence of amorphous phases in considerable amounts, including both unhydrated raw materials and disorderly formed gels. In order to relatively accurately obtain the amorphous content, a known amount of crystalline Nickle was added as mentioned before. The Rietveld quantitative analysis was performed by Jade software (Material Data Inc.).

2.4 SEM/EDS

Prior to SEM/EDS, samples were first cut into small slices and immersed into isopropyl alcohol at desired age to stop hydration. The samples were further subjected to vacuum-drying, epoxy impregnation, followed by polishing down to $\frac{1}{4}$ μm , and carbon-coating. The SEM/EDS were performed on FEI Quanta 200 at an accelerating voltage of 20 kV, equipped with solid-state backscattered detector and X-ray microanalysis system. The backscattered electron (BSE) images were acquired, in which the contrast is primarily dependent on the average atomic number of the area being examined.

For EDS microanalysis, about 50-100 spots were analyzed at different representative locations on the hydrated products (i.e. excluding unreacted slag or/and FA-F particles) for each sample to reduce random errors. Considering the semi-quantitative nature and limited probing length scale of EDS, the X-ray microanalyses may relate to mixtures of phases (e.g. C-A-S-H, N-A-S-H,

C-N-A-S-H) in varying proportions for alkali-activated binary system. In addition, EDS line scanning was implemented to obtain the chemical evolution between slag and FA-F.

3. Results and Discussion

3.1 XRD mineralogical analysis

X-ray powder diffraction patterns for all the materials studied, including the original raw FA-F and slag, are shown in Figures 2 to 5. FA-F is an essentially vitreous material (see halo recorded for $2\theta = 20\sim 35^\circ$), with various crystalline phases, mainly quartz (black solid line), mullite (black dashed line), hematite (black short dotted line), magnetite (light grey solid line), and traces of halite (light grey dashed line). However, blast-furnace slag contains primarily amorphous phases, with trace of gypsum (blue solid line) and alite (blue dashed line).

Figure 2 shows the XRD patterns for pure FA-F activated by various types (i.e. NS, HN, and LN) of activators. Besides the newly precipitated crystalline phases, alkali-activated pure FA-F has a different background profile than unhydrated FA-F, indicating the alteration in amorphous structures and formation of poorly crystalline sodium aluminosilicate hydrate (N-A-S-H) phases. It can be seen that different activators can affect the types of N-A-S-H gels. For sodium silicate-activated FA-F, no strong additional peak is observed, while for NaOH-activated FA-F regardless of pH, various new crystalline phases, including N-A-S-H, Zeolite X-type phases, and

Chabazite can be detected at later age. In particular, two types of N-A-S-H were detected: one is $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$, preferably found in HN-activated system, another one is $\text{Na}_{1.4}\text{Al}_2\text{Si}_{3.9}\text{O}_{11.5} \cdot \text{H}_2\text{O}$ in LN-activated system. These strong crystalline N-A-S-H peaks appear and magnify (i.e. increasing peak intensity) as age increases, indicating an ongoing activation and structural evolution (e.g. reorganization and crystallization) is taking place.

The different types of crystalline N-A-S-H phases between HN- and LN-activated systems, imply that the initially formed amorphous and gelled structure at the initial stage of activation is also different, since the nature of predominant geopolymeric gel closely relates to the ending crystalline phases (as a result of amorphous-crystalline transformation [30]). Basically, the amorphous or semi-crystalline N-A-S-H gel in geopolymer is characterized in literature is a zeolite-precursor [17], and tends to crystallize [30]. This research supports it and further illustrates that the structure of geopolymeric gels is significantly influenced by the activator type and dosage. In addition, there is an evidence that high pH increases the crystallization of geopolymeric gel, while dissolved silica ($[\text{SiO}_2]_{\text{aq}}$) promotes a more structural disorder in hydrated phases. This is reasonable, since sodium silicate itself is an amorphous material and can be involved during the activation processes. This finding is consistent with the research focused on the influence of different activators on the hydrated phases in pure AAS [8, 31].

Figure 3 shows the XRD patterns for binary 80% FA-F with 20% slag activated by various

solutions. Similarly to alkali-activated pure FA-F, various N-A-S-H phases can be observed when activated by NaOH solutions, which are absent in the NS-activated system. In contrast to the pure alkali-activated FA-F, small incorporation of slag triggers the formation of a broad and diffusive hump at around $29^{\circ}\sim 31^{\circ}$. This new hump corresponds to C-S-H, which is primarily from the hydration of slag. As further characterized by EDS-ternary diagram analysis (see Section 3.4), the small incorporation of slag renders some regions in $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ phase diagram where the detected chemical composition is similar to C-A-S-H. It likely indicates that a small amount of C-A-S-H is occasionally and unevenly formed in this system. In addition, the number and intensity of crystalline N-A-S-H and other zeolite-type phases decrease because of slag incorporation. It is probably due to the incorporation of Ca into the N-A-S-H phase by ion exchange between Ca^{2+} with Na^{+} , which suppresses the crystallization. It may indicate that the hydration process of slag and FA-F are not linearly independent but an interaction exists between slag and FA-F.

Figure 4 shows the XRD patterns for binary 50% FA-F with 50% slag activated by various solutions. Contrary to Figure 2 and Figure 3, no strong crystalline N-A-S-H and zeolite-type peaks can be observed after 28 days curing in alkali-activated FA-F with 50% slag replacement. Instead, a series of strong broad and diffusive humps appearing around 30° can be detected, which is believed to be due to the extensive generation of C-A-S-H. Similar to pure AAS [8, 32], primarily two types of C(-A)-S-H gels (i.e. C-S-H(I) and C-S-H) can be detected by XRD. In

comparison to C-S-H, C-S-H (I) has a more ordered structure in XRD pattern and presents a broad, basal reflection corresponding to the mean interlayer thickness. It should be noted that this C-S-H (I) is actually C-A-S-H, as evidenced by the chemical composition (EDS) and structural modifications (XRD) due to Al substitution. As shown in Table 2, the interlayer thickness of C-S-H (I) shifts to a d-spacing value of around 1.283-1.298 nm, which is much higher than that in pure AAS binders (around 1.250 nm [8, 33]). According to previous findings, the introduction of large amounts of aluminum into the C-S-H structure can inflate the interlayer thickness by decreasing the coherent domain [16]. This phenomenon is more evident in Figure 5 by comparing the XRD patterns of C-S-H (I) in pure AAS and AAS with a small replacement of FA-F activated by HN. This proves that there exists an interaction between FA-F and slag during activation and geopolymerization process. In addition, Figure 5 shows that HN promotes the formation of C-S-H (I) with a co-existence with C-S-H, while no strong evidence of C-S-H (I) can be observed in NS- and LN-activated systems. This indicates that the nanostructure of C-A-S-H formed in the binary FA-F/slag system is considerably affected by the activator type. Besides, LN can significantly promote the generation of sodium calcium aluminum sulfate hydrate (NCASH) phase (The source of sulfate comes from the composition of slag as shown in Table 1). It is noticed that this sulfate-bearing phase gradually decomposes over time and completely absent in HN-activated mixtures, suggesting that sulfate-bearing phase is unstable in high alkalinity or high pH environments.

Figure 5 shows the XRD patterns for binary 20% FA-F with 80% slag activated by various solutions. First, consistent with the findings in Figure 4, LN solution promotes the extensive formation of sulfate-bearing phase while HN promotes C-S-H (I). Additionally, a much stronger peak corresponding to hydrotalcite-type phase is also observed in HN-activated system, probably indicating that hydrotalcite is preferably formed at high pH.

Figure 2 X-ray diffraction patterns of pure alkali-activated FA-F with various types of activators at different ages (i.e. 1, 7, and 28 Days).

Figure 3 X-ray diffraction patterns of alkali-activated binary 80% FA-F and 20% slag with various types of activators at different ages (i.e. 1, 7, and 28 Days).

Figure 4 X-ray diffraction patterns of alkali-activated binary 50% FA-F and 50% slag with various types of activators at different ages (i.e. 1, 7, and 28 Days).

Figure 5 X-ray diffraction patterns of alkali-activated binary 20% FA-F and 80% slag with various types of activators at different ages (i.e. 1, 7, and 28 Days).

Table 2 X-ray diffractometry data for identification of main peaks in binary FA-F/slag-based geopolymer pastes

Observed d-Spacing in this study (Å)	Phase	Theoretical d-spacing (Å) (h k l)
---	-------	--

14.47	Zeolite X-type Phase	14.43	(1 1 1)
9.36	Chabazite	9.32	(1 0 0)
6.35-6.37	Sodium Aluminosilicate Hydrate (Na ₆ (AlSiO ₄) ₆ ·4H ₂ O)	6.35	(1 1 0)
3.67		3.66	(2 1 1)
2.59-2.60		2.59	(2 2 2)
7.09	Sodium Aluminosilicate Hydrate (Na _{1.4} Al ₂ Si _{3.9} O _{11.5} ·H ₂ O)	7.10	(1 1 0)
4.10-4.11		4.10	(1 1 2)
3.18-3.19		3.18	(3 1 0)
3.03-3.04	Calcium Silicate Hydrate C-S-H	3.04	-
1.82	(Ca _{1.5} SiO _{3.5} ·xH ₂ O)	1.82	-
12.83-12.98		12.50	(0 0 2)
3.06-3.07	Calcium-Silicate Hydrate C-S-H (I)	3.07	(1 1 *) ^a
2.78-2.80	(CaO·SiO ₂ ·H ₂ O)	2.80	(2 0 *) ^a
1.83-1.84		1.83	(0 2 *) ^a
10.03		10.03	(0 0 3)
5.01	Sodium calcium aluminum sulfate hydrate (NaCa ₄ Al ₂ O ₆ (SO ₄) _{1.5} ·15H ₂ O)	5.01	(0 0 6)
4.46		4.45	(1 0 3)
3.53		3.53	(1 0 6)
2.88		2.87	(1 1 0)

2.49		2.49	(1 1 6)
2.24		2.24	(1,0,12)
<hr/>			
7.72-7.61		7.84	(0 0 6)
3.86-3.88		3.91	(0 1 8)
	Hydrotalcite-type Phase		
2.60-2.61		2.61	(0 2 4)
	$(\text{Mg}_{0.67}\text{Al}_{0.33}(\text{CO}_3)_{0.17}(\text{OH})_2(\text{H}_2\text{O})_{0.5})$		
			(0 2
2.30-2.32		2.31	10)
<hr/>			

Note: a: hk* denotes a band head given by an essentially two-dimensional lattice

3.2 Rietveld semi-quantitative-X-ray diffraction analysis

Table 3 shows the results of Rietveld quantitative analysis in binary FA-F/slag-based geopolymer paste samples. Most of the phases are amorphous, accounting for about 71.1%~98.6%, depending on the age, activator type/dosage and FA-F/slag ratio. It should be noted that it is impossible to differentiate the vitreous unhydrated phases from amorphous hydrated products (i.e. C-A-S-H and N-A-S-H gels) based solely on the Rietveld method. It can be seen that the HN-activated materials have up to 10.1% crystalline C-S-H (I), 3.3% crystalline C-S-H, 1.7% crystalline N-A-S-H, and 13.7% hydrotalcite, while LN solution can have up to 10.6% crystalline C-S-H, 13.4% NCASH, and 2.7% hydrotalcite. In addition, the relative proportion of crystalline C-S-H gel increases from 1% to about 11%, with increasing slag portion from 0.2 to

0.8 for NH-activated system. The percentage of hydrotalcite also increases with increasing relative portion of slag, especially at high pH binders. The Rietveld quantitative analysis results are consistent with the findings reported in Section 3.1.

Table 3 Rietveld quantitative phase analysis of binary slag and Class F fly ash-based geopolymer samples at different ages (by mass %)^d

Mixture ID	Age	Zeolite-type										NCA		
		Minerals in raw FA-F				Crystalline		Crystalline C-S-H		Amorphous		Hydrotalcite-type		NCA
						Phases				Phase ^a		Phase		SH
														Phase
		Quartz	Mullite	Hematite	Magnetite	Chabazite	Zeolite-X	N-A-S-H ^b	N-A-S-H ^c	C-S-H	C-S-H (I)			
	1D	0.4	0.6	0.3	0.4	-	-	-	-	-	-	98.2	-	-
FA00S-NS	7D	0.4	0.3	0.3	0.4	-	-	-	-	-	-	98.6	-	-
	28D	0.3	0.8	0.4	0.5	-	-	-	-	-	-	97.9	-	-
	1D	0.4	0.5	0.3	0.4	-	-	-	-	1.0	-	97.3	-	-
FA20S-NS	7D	0.4	0.5	0.3	0.5	-	-	-	-	1.1	-	97.1	-	-
	28D	0.3	0.6	0.4	0.5	-	-	-	-	0.9	-	97.2	-	-
FA50S-NS	1D	0.2	0.2	0.2	0.3	-	-	-	-	1.9	-	97.2	-	-

	7D	0.2	0.4	-	0.2	-	-	-	-	0.5	-	98.6	-	-
	28D	0.2	0.6	-	0.3	-	-	-	-	2.5	-	96.4	-	-
	1D	-	-	-	0.4	-	-	-	-	3.6	-	92.2	3.7	-
FA80S-NS	7D	-	2.8	-	0.3	-	-	-	-	6.0	-	86.4	4.4	-
	28D	-	1.4	-	0.3	-	-	-	-	11.9	-	82.5	3.8	-
<hr/>														
	1D	0.5	0.6	0.4	0.6	trace	trace	0.7	-	-	-	97.1	-	-
FA00S-HN	7D	0.5	1.0	0.5	0.8	-	-	1.2	-	-	-	95.9	-	-
	28D	0.7	1.5	0.6	1.0	-	-	1.7	-	-	-	94.5	-	-
	1D	0.3	0.4	0.3	0.3	-	-	1.0	-	1.1	-	96.5	-	-
FA20S-HN	7D	0.4	0.5	0.4	0.3	-	-	0.8	-	1.1	-	96.4	-	-
	28D	0.3	0.5	0.4	0.4	-	-	0.4	-	0.7	-	97.2	-	-
	1D	0.3	0.4	-	0.3	-	-	-	-	0.9	0.3	96.4	1.3	-
FA50S-HN	7D	-	0.9	-	0.3	-	-	-	-	3.3	-	93.8	1.7	-
	28D	-	0.9	-	0.3	-	-	-	-	1.5	0.4	95.4	1.5	-
	1D	-	3.4	-	1.8	-	-	-	-	-	10.1	71.1	13.7	-
FA80S-HN	7D	-	2.3	-	3.2	-	-	-	-	-	9.2	72.5	12.7	-
	28D	-	1.6	-	0.7	-	-	-	-	-	6.8	79.6	11.3	-
<hr/>														
	1D	0.7	1.0	0.6	1.1	-	-	-	0.2	-	-	96.3	-	-
FA00S-LN	7D	0.8	1.0	0.7	1.0	-	-	-	0.6	-	-	95.7	-	-

	28D	0.6	0.8	0.8	0.8	-	-	-	2.0	-	-	94.9	-	-
	1D	0.5	0.7	0.4	0.4	-	-	-	-	1.1	-	96.8	-	-
FA20S-LN	7D	0.5	0.7	0.4	0.4	-	-	-	-	0.8	-	97.1	-	-
	28D	0.6	0.8	0.6	0.5	-	-	-	-	1.3	-	96.1	-	-
	1D	-	2.9	-	1.2	-	-	-	-	7.3	-	76.0	0.7	11.9
FA50S-LN	7D	-	5.6	-	1.8	-	-	-	-	5.8	-	71.4	2.1	13.4
	28D	-	1.3	-	0.3	-	-	-	-	0.9	-	94.6	1.1	1.7
	1D	-	1.0	-	0.0	-	-	-	-	10.6	-	75.2	1.8	11.4
FA80S-LN	7D	-	0.4	-	0.0	-	-	-	-	5.9	0.2	87.0	2.7	3.7
	28D	-	1.1	-	0.3	-	-	-	-	4.2	-	82.6	2.4	9.3

Notes: a: It includes both the amorphous structures in unhydrated raw materials and the generated amorphous structures in hydrated phases, mainly N-A-S-H gel and C-A-S-H gel.

b: It is the detected sodium aluminosilicate hydrate ($\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$).

c: It is the detected sodium aluminosilicate hydrate ($\text{Na}_{1.4}\text{Al}_2\text{Si}_{3.9}\text{O}_{11.5} \cdot \text{H}_2\text{O}$)

d: The estimated errors for the Rietveld semi-quantitative analysis are less than $\pm 5\%$.

3.3 SEM microstructure characterization

Figures 6-8 show the SEM-BSE images of polished alkali-activated FA-F/slag-based geopolymer paste samples at 28 days. It can be seen that the addition of slag considerably modifies the

microstructure of FA-F-based geopolymer by reducing coarse pores and homogenizing morphology, which is in agreement with the previous research [20, 34]. Additionally, activator type/dosage also shows a significant influence on the microstructural characteristics of the binders. The use of NS as a activator results in a much homogenous and denser microstructure regardless of the FA-F/slag ratio, which supports the previous findings that $[\text{SiO}_2]_{\text{aq}}$ can homogenize the microstructure [8, 20]. It can also be noticed that although both slag and $[\text{SiO}_2]_{\text{aq}}$ tend to densify the microstructure as shown in SEM, their mechanisms of influence are different. It is reasonable to deduce that it is the calcium dissolved from slag that makes slag different than $[\text{SiO}_2]_{\text{aq}}$. Previous research regarding the role of externally-added calcium-enriched components on microstructural modification of FA-F-based geopolymer are available, which generally argue that calcium from slag can promote the generation of C-A-S-H gels, which reduces the setting time and densifies the microstructure [4]. This argument is also supported by the changes in the chemical composition of the hydrated phases as discussed in the following section.

(a)

(b)

(c)

(d)

Figure 6 SEM-BSE images on polished binary FA-F/slag samples activated by NS solutions
(a) 100% FA-FA; (b) 80% FA-F and 20% slag; (c) 50% FA-F and 50% slag; (d) 20% FA-F and 80% slag

332

333

334

(a)

(b)

335

336

(c)

(d)

337 Figure 7 SEM-BSE images on polished binary FA-F/slag samples activated by HN solutions
338 (a)100%FA-FA; (b) 80%FA-F and 20%slag; (c) 50%FA-F and 50%slag; (d) 20%FA-F and
339 80%slag

(a)

(b)

(c)

(d)

Figure 8 SEM-BSE images on polished binary FA-F/slag samples activated by LN solutions (a) 100%FA-FA; (b) 80%FA-F and 20%slag; (c) 50%FA-F and 50%slag; (d) 20%FA-F and 80%slag

3.4 EDS chemical composition analysis

Figures 9-11 show the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ and $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-H}_2\text{O}$ ternary phase diagrams for the hydration products formed in the matrix of FA-F/slag-based geopolymer samples activated by NS, HN, and LN solutions, respectively. Considering the large spot size of EDS, the measured chemical composition may represent a mixture of C-A-S-H, N-A-S-H, N-C-A-S-H, with other minor phases. The $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ diagram can be segmented into various regions, each of which represents a chemical boundary for each phase. For example, the Region I represents the N-A-S-H-rich region, in which the $0.08 < \text{Al/Si} < 0.5$ and $0 < \text{Ca/Si} < 0.3$ in N-A-S-H [35]. Similarly, Region II is where C-A-S-H is the primary phase. It is observed that the incorporation of slag can drastically alter the chemical composition of the gels formed in the matrix, regardless of the activator type. With the increase of slag dosage, the chemical composition of the hydration products moves from Region I towards Region II. It demonstrates that C-A-S-H is formed gradually as slag replacement increases, which is consistent with the XRD results. On the other hand, the statistical distribution of the chemical composition as shown in Figure 12 box plots also shows that mean Ca/Si and Na/Al ratios in the hydrated phases tend to increase, while keeping Al/Si approximately constant as slag replacement increases. This is reasonable since raw slag is much richer in calcium and contains less alumina than FA-F. According to the $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-H}_2\text{O}$ ternary diagram in Figs. 9-11, almost all FA-F-rich samples are located in the same region, which indicates the relative stability of alkali content in

the various gels. However, with the increase of slag, all points move slightly towards alkali-rich region, which is probably because of the reduced Si content in the formed gels.

The influence of activator on the chemical composition of FA-F/slag-based geopolymer can also be observed. First of all, NaOH-activated samples have higher average Ca/Si and Al/Si ratios, as well as more heterogeneous chemical distribution, compared with NS-activated samples (see Figure 12). It implies that this highly reactive [SiO₂]aq incorporates into the geopolymerization process and depresses the precipitation of zeolite crystals, as indicated in XRD results. The SiO₂-CaO-Al₂O₃-H₂O diagram shows no points located in the Region II for small slag/FA-F ratio when activated by sodium silicate. It may indicate that when excess [SiO₂]aq is supplied, N-A-C-S-H is preferentially formed rather than C-A-S-H, which agrees with previous research [20]. While activated by sodium hydroxide, SiO₂-CaO-Al₂O₃-H₂O diagram demonstrates that C-A-S-H can form occasionally in the matrix. However, the structure similarity and difference between N-A-C-S-H and C-A-S-H needs further investigation. On the other hand, LN-activated hydration products have higher Ca/Si ratios and more heterogeneous chemical distribution than HN-activated samples, although both of them are [SiO₂]aq-free in activator. It likely indicates that lower pH promotes calcium dissolution from slag, which is well established for Ca(OH)₂ [36], and potentially increases the relative proportion of C-A-S-H gels. This may be the reason why FA-F/slag binary systems with lower pore solution pH have shorter setting times compared to the one with more alkaline pore solutions [37].

389

390 Figure 13 shows the Line EDS results for the elemental distribution between two randomly
391 selected semi-hydrated FA-F and slag particles for FA50S activated by NS, HN, and LN,
392 respectively. In case of NS-activated sample, it is interesting to notice that there exists a reaction
393 rim around the FA-F particle. The chemical analysis indicates a significant reduction in the Si
394 content in this reaction rim compared to unhydrated FA-F, which may indicate that considerable
395 amount of Si is dissolved from FA-F into the matrix. Similar findings are observed in the
396 HN-activated system. In addition, the Ca dissolved from slag considerably increases the Ca
397 concentration around unhydrated FA-F in comparison to the bulk composition of raw FA-F, and
398 probably incorporates into geopolymerization. Analogously, the Al from FA-F can also affect the
399 hydration of slag by increasing the supply of alumina, as confirmed by XRD in Figures 4 and 5.
400 In case of NaOH-activated samples, the results indicate a gradual dissolution of Ca, Al and Mg
401 from raw slag to the matrix to form hydrated phases, while a sudden decrease in Si and Al
402 around FA-F particles. The influential range of dissolved FA-F or slag is merely the limit of
403 aqueous chemical environments around itself, which results in a heterogeneous and localized
404 chemical composition in matrix. It probably also indicates a different reaction process of alkaline
405 activation between FA-F and slag.

406

407

408 *3.5 Interaction between slag and FA-F*

3.5.1 Interaction mechanisms

Combined with XRD, SEM/EDS findings confirm the existence of an interaction between FA-F and slag during activation or geopolymerization process. This interaction mechanism is primarily reflected in three aspects for a certain type of activator:

(1) Modifying the structure and composition of hydrated phases; for instance, the C-A-S-H in pure AAS is modified with a change in lattice parameters even after a small dosage of FA-F loading.

(2) Explicitly depressing or triggering the formation of some crystalline phases; for instance, the early age precipitation of zeolite-type phases in FA-F-based geopolymer can be suppressed or delayed with the addition of slag. This is probably because that calcium from slag can incorporate into the geopolymerization by reacting with N-A-S-H to form N-(C)-A-S-H, resulting in a heterogeneous chemical distribution and inhibiting zeolite crystallization. As further attacked by calcium, N-(C)-A-S-H gels can possibly transform to C-A-S-H gel, since it was reported that calcium can substitute alkalis due to its higher affinity to silicon [38, 39].

(3) Influencing spatial heterogeneity of composition distribution in microstructure; for instance, increasing slag proportion in the mixture seems to increase the degree of heterogeneity of Ca/Si ratio in hydrated phases. It indicates that the interaction between FA-F and slag occurs locally

rather than uniformly. In other words, the interaction mechanism between raw materials is more likely due to interaction and reaction of dissolved chemical elements, which is further influenced by the surrounding aqueous environment. The dissolution of FA-F/slag is time-dependent, indicating that the elemental concentration varies around the unhydrated particles, and the nature and composition of the hydrated gels in the matrix are subjected to evolution as hydration continues. There may exist local phase transformation among N-A-S-H, N(-C)-A-S-H, (N-)C-A-S-H, and C-A-S-H, depending on the FA-F/slag ratio, dissolution/diffusion kinetics, solubility of phases, nature of activator, and local aqueous chemical environment.

3.5.2 Influence of alkaline activator

The interaction between FA-F and slag is strongly affected by activator type and dosage, which is also primarily reflected in analogous aspects, namely, chemistry, structure and kinetics. First of all, the nanostructure or chemical composition of the hydrated gels, as well as the selective formation of other by-products, (e.g. portlandite, sulfate-bearing phases, and hydrotalcite-type phases), is dependent on activators. For instance, various types of C-A-S-H and N-A-S-H gels can be observed if different activators are used. Low pH solutions promote the formation of C-S-H while high pH promotes C-S-H (I), and they have different nanostructures. Secondly, heterogeneity of spatial distribution of composition in microstructure is activator-dependent. For example, as shown in Figure 12, NS-activated samples essentially have more chemically homogenous distributions, which is probably because $[\text{SiO}_2]_{\text{aq}}$ can delay the hydration by

prolonging active FA-F/slag dissolution/diffusion kinetics. Similar observation can be noticed in AAS, in which $[\text{SiO}_2]_{\text{aq}}$ can distribute nucleation sites homogenously at early ages, resulting in slag taking longer time to reach ‘diffusion-controlled’ hydration period [8, 40].

(a)

Figure 9 EDS microanalysis of hydration products formed in binary FA-F and slag samples with various FA-F/slag ratios activated by NS projected on the (a) $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ ternary system diagram (b) $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-H}_2\text{O}$ ternary diagram

(a)

(b)

Figure 10 EDS microanalysis of hydration products formed in binary FA-F and slag samples

465 activated HN with various FA-F/slag ratios projected on the (a) CaO-SiO₂-Al₂O₃-H₂O ternary
 466 system diagram (b) SiO₂-Na₂O-Al₂O₃-H₂O ternary diagram

(a)

(b)

Figure 11 EDS microanalysis of hydration products formed in binary FA-F and slag samples activated LN with various FA-F/slag ratios projected on the (a) CaO-SiO₂-Al₂O₃-H₂O ternary system diagram (b) SiO₂-Na₂O-Al₂O₃-H₂O ternary diagram

(a)

477

(b)

478

479

(c)

480

481

482

483

484

485

486

Figure 12 Box-and-whisker plot showing the statistical distribution of the chemical composition of hydration products formed in NS-, HN- and LN-activated FA-F and slag binders with various FA-F/slag ratios (a) Ca/Si; (b) Al/Si; (c) Na/Al

(a)

487

(b)

488

(c)

489

490 Figure 13 Line EDS results for the elemental distribution between two randomly selected
 491 semi-hydrated FA-F and slag particles for FA50S activated by (a) NS; (b) HN; (c) LN

492

493

494 4. Conclusions

495 In this paper, the influence of activator type/dosage (i.e. $[\text{SiO}_2]_{\text{aq}}$, pH) on the interaction
 496 mechanisms between slag and FA-F is investigated. The following conclusions can be drawn
 497 according to this study:

498

499 (1) The experimental results based on XRD and SEM/EDS support that C-A-S-H and N-A-S-H

gels can co-exist in binary FA-F/slag-based geopolymer. Furthermore, the hydration products consist of various types of C-A-S-H and N-A-S-H gels, and the nature/configuration of the gels, as well as the crystalline phases, are dependent on the mixing proportions (e.g. starting FA-F/slag ratio and type/dosage of activator).

(2) For low slag/FA-F ratio, C-A-S-H is not likely to be formed at early age when activated by sodium silicate, but can be found in sodium hydroxide solutions, based on ternary diagram analysis.

(3) The microstructure of the binary FA-F/slag-based geopolymer is affected by FA-F/slag ratio and type/dosage of the activator. Increasing slag proportion and introduction of $[\text{SiO}_2]_{\text{aq}}$ in activator can both densify the microstructure, while the mechanisms are different.

(4) Sodium silicate-activated mixtures possess structures that are more amorphous than NaOH-activated mixtures, as a result of suppressed formation of crystalline phases. In addition, low pH NaOH solutions promote the formation of more amorphous C-A-S-H (compared to C-S-H (I)) and sulfate-bearing phases, while high pH NaOH solutions promote formation of alumina-modified C-S-H (I) and hydrotalcite-type phases.

(5) For a given type of activator, the interaction mechanisms between FA-F and slag are

primarily reflected in: (i) altering the structure (e.g. crystallography and lattice parameters) of different phases, (ii) suppressing or triggering the formation of some crystalline phases, and (iii) homogeneity of composition and microstructure.

(6) The activator has a considerable impact on the interaction between raw materials chemically, structurally, and kinetically, through influencing in the formation of precipitates and homogeneity of microstructure.

(7) The interaction between FA-F and slag occurs locally rather than uniformly and is likely to be controlled by the dissolution/diffusion kinetics, and solubility/stability of the hydrated gels (C-A-S-H, N-A-S-H, and possible (N-)C-A-S-H gels).

Acknowledgements

The authors gratefully acknowledge the financial support from the U.S. National Science Foundation (NSF) under Award CMMI #1265789. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF.

References

- [1] Juenger M, Winnefeld F, Provis J, Ideker J. Advances in alternative cementitious binders. *Cement and Concrete Research*. 2011;41(12):1232-43.
- [2] Thomas RJ, Ye H, Radlińska A, Peethamparan S. Alkali-activated slag concrete: A closer look at sustainable alternatives to portland cement. *Concrete International*. 2016;38(1):33-8.
- [3] Luo X, Xu J, Bai E, Li W. Systematic study on the basic characteristics of alkali-activated slag-fly ash cementitious material system. *Construction and Building Materials*. 2012;29:482-6.
- [4] Yip CK, Lukey G, Van Deventer J. The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation. *Cement and Concrete Research*. 2005;35(9):1688-97.
- [5] Fernández-Jiménez A, Palomo A. Composition and microstructure of alkali activated fly ash binder: effect of the activator. *Cement and Concrete Research*. 2005;35(10):1984-92.
- [6] Ye H, Cartwright C, Rajabipour F, Radlińska A. Effect of drying rate on shrinkage of alkali-activated slag cements. 4th International Conference on the Durability of Concrete Structure (ICDCS). Purdue University, Indiana, USA2014. p. 254-61.
- [7] Ye H, Radlińska A. A review and comparative study of existing shrinkage prediction models for portland and non-portland cementitious materials *Advances in Materials Science and Engineering*. 2016;2016(2016):Article ID: 2418219.
- [8] Ye H, Radlińska A. Quantitative analysis of phase assemblage and chemical shrinkage of alkali-activated slag. *Journal of Advanced Concrete Technology*. 2016;14:245-60.

560 [9] Lee N, Jang J, Lee H. Shrinkage characteristics of alkali-activated fly ash/slag paste and
561 mortar at early ages. *Cement and Concrete Composites*. 2014.

562 [10] Duxson P, Provis JL, Lukey GC, Mallicoat SW, Kriven WM, Van Deventer JS.
563 Understanding the relationship between geopolymer composition, microstructure and mechanical
564 properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*.
565 2005;269(1):47-58.

566 [11] Pacheco-Torgal F, Castro-Gomes J, Jalali S. Alkali-activated binders: A review: Part 1.
567 Historical background, terminology, reaction mechanisms and hydration products. *Construction*
568 *and Building Materials*. 2008;22(7):1305-14.

569 [12] Li C, Sun H, Li L. A review: The comparison between alkali-activated slag (Si+ Ca) and
570 metakaolin (Si+ Al) cements. *Cement and Concrete Research*. 2010;40(9):1341-9.

571 [13] Richardson I. The nature of CSH in hardened cements. *cement and concrete research*.
572 1999;29(8):1131-47.

573 [14] Richardson I, Brough A, Groves G, Dobson C. The characterization of hardened
574 alkali-activated blast-furnace slag pastes and the nature of the calcium silicate hydrate (CSH)
575 phase. *Cement and Concrete Research*. 1994;24(5):813-29.

576 [15] Taylor HF. *Cement chemistry*: Thomas Telford; 1997.

577 [16] Renaudin G, Russias J, Leroux F, Cau-dit-Coumes C, Frizon F. Structural characterization
578 of C–S–H and C–A–S–H samples—Part II: Local environment investigated by spectroscopic
579 analyses. *Journal of Solid State Chemistry*. 2009;182(12):3320-9.

- 580 [17] Provis JL, Van Deventer JSJ. Geopolymers: structures, processing, properties and industrial
581 applications: Elsevier; 2009.
- 582 [18] Davidovits J. Geopolymers. Journal of Thermal Analysis and Calorimetry.
583 1991;37(8):1633-56.
- 584 [19] Franus W, Wdowin M, Franus M. Synthesis and characterization of zeolites prepared from
585 industrial fly ash. Environmental monitoring and assessment. 2014:1-9.
- 586 [20] Ismail I, Bernal SA, Provis JL, San Nicolas R, Hamdan S, van Deventer JS. Modification of
587 phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash. Cement and
588 Concrete Composites. 2014;45:125-35.
- 589 [21] Lloyd RR, Provis JL, van Deventer JS. Microscopy and microanalysis of inorganic polymer
590 cements. 2: The gel binder. Journal of Materials Science. 2009;44(2):620-31.
- 591 [22] Lee N, Lee H. Reactivity and reaction products of alkali-activated, fly ash/slag paste.
592 Construction and Building Materials. 2015;81:303-12.
- 593 [23] Puligilla S, Mondal P. Role of slag in microstructural development and hardening of fly
594 ash-slag geopolymer. Cement and Concrete Research. 2013;43:70-80.
- 595 [24] Kumar S, Kumar R, Mehrotra S. Influence of granulated blast furnace slag on the reaction,
596 structure and properties of fly ash based geopolymer. Journal of Materials Science.
597 2010;45(3):607-15.
- 598 [25] Ryu GS, Lee YB, Koh KT, Chung YS. The mechanical properties of fly ash-based
599 geopolymer concrete with alkaline activators. Construction and Building Materials.

600 2013;47:409-18.

601 [26] Chithiraputhiran S, Neithalath N. Isothermal reaction kinetics and temperature dependence
602 of alkali activation of slag, fly ash and their blends. Construction and Building Materials.
603 2013;45:233-42.

604 [27] Provis JL, Myers RJ, White CE, Rose V, van Deventer JS. X-ray microtomography shows
605 pore structure and tortuosity in alkali-activated binders. Cement and Concrete Research.
606 2012;42(6):855-64.

607 [28] Rietveld H. A profile refinement method for nuclear and magnetic structures. Journal of
608 applied Crystallography. 1969;2(2):65-71.

609 [29] Warren BE. X-ray Diffraction: Courier Corporation; 1969.

610 [30] De Silva P, Sagoe-Crenstil K. Medium-term phase stability of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$
611 O geopolymer systems. Cement and Concrete Research. 2008;38(6):870-6.

612 [31] Wang S-D, Scrivener KL. Hydration products of alkali activated slag cement. Cement and
613 Concrete Research. 1995;25(3):561-71.

614 [32] Ben Haha M, Le Saout G, Winnefeld F, Lothenbach B. Influence of activator type on
615 hydration kinetics, hydrate assemblage and microstructural development of alkali activated
616 blast-furnace slags. Cement and Concrete Research. 2011;41(3):301-10.

617 [33] Ye H, Radlińska A. Shrinkage mechanisms of alkali-activated slag. Cement and Concrete
618 Research. 2016;(Under Review).

619 [34] Oh JE, Monteiro PJ, Jun SS, Choi S, Clark SM. The evolution of strength and crystalline

620 phases for alkali-activated ground blast furnace slag and fly ash-based geopolymers. Cement and
621 Concrete Research. 2010;40(2):189-96.

622 [35] Garcia-Lodeiro I, Palomo A, Fernández-Jiménez A, Macphee D. Compatibility studies
623 between NASH and CASH gels. Study in the ternary diagram $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Cement and Concrete Research. 2011;41(9):923-31.

624 O. Cement and Concrete Research. 2011;41(9):923-31.

625 [36] Granizo ML, Alonso S, Blanco - Varela MT, Palomo A. Alkaline activation of metakaolin:
626 effect of calcium hydroxide in the products of reaction. Journal of the American Ceramic
627 Society. 2002;85(1):225-31.

628 [37] Lee N, Lee H. Setting and mechanical properties of alkali-activated fly ash/slag concrete
629 manufactured at room temperature. Construction and Building Materials. 2013;47:1201-9.

630 [38] Garcia-Lodeiro I, Fernández-Jiménez A, Palomo A. Variation in hybrid cements over time.
631 Alkaline activation of fly ash-portland cement blends. Cement and Concrete Research.
632 2013;52:112-22.

633 [39] Garcia-Lodeiro I, Palomo A, Fernández-Jiménez A, Macphee D. Compatibility studies
634 between NASH and CASH gels. Study in the ternary diagram $\text{Na}_{2\text{O}}-\text{CaO}-\text{Al}_{2\text{O}_3}-\text{SiO}_2-\text{H}_2\text{O}$. Cement and Concrete
635 Research. 2011;41(9):923-31.

636 Research. 2011;41(9):923-31.

637 [40] Gebregziabihier BS, Thomas R, Peethamparan S. Very early-age reaction kinetics and
638 microstructural development in alkali-activated slag. Cement and Concrete Composites.
639 2015;55:91-102.