Article

Phase Analysis of Alkali-Activated Slag Hybridized with Low-Calcium and High-Calcium Fly Ash

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Abstract: This paper investigates the hydrated phase assemblage, microstructure, and gel composition of sodium hydroxide (NaOH)-activated fly ash–slag blends with either low-calcium or high-calcium fly ash. The results show that the nature of precipitated calcium–aluminosilicate–hydrate (C-A-S-H) and alkali aluminosilicate-hydrate (N-A-S-H) depends on the fly ash composition and slag-to-fly ash ratio. However, regardless of fly ash composition and slag-to-fly ash ratio, a universal linear compositional relationship exists between Al/Ca ratio and Si/Ca ratio in precipitated gels. This indicates that there exists a structural limitation on the incorporation of Al 3+ for Si 4+ in the tetrahedral silicate of C-A-S-H, N-A-S-H, or metastable N-C-A-S-H gels. In a hybrid slag–fly ash system, the framework structure of precipitated gels is an assemblage of aluminosilicate units with heterogeneous Ca 2+ and Na + distribution. The amount and reactivity of calcium and alkalis seem to play a critical role in determining the structure and properties of precipitated gels in hybrid systems. The low cementitious capability in alkali-activated high-calcium fly ash may be attributed to the unstable N-C-A-S-H gel structure with concurrent high Na and Ca contents.

Keywords: alkali-activated binder; geopolymer; alternative cementitious materials; fly ash; blast furnace slag

1. Introduction

Pulverized fly ash is an industry byproduct of the combustion of pulverized coal in thermal power plants, which comprise heterogeneous spherical particles with glassy and crystalline phases (e.g., mullite and quartz). Although the bulk of fly ash is mainly made up of silicon, aluminum and iron oxide, it can be further categorized into Class F (FA-F) or Class C fly ash (FA-C) depending on its composition. In particular, FA-F has low calcium content and exhibits pozzolanic properties, while FA-C contains up to 20% CaO and exhibits cementitious properties [1,2]. On the other hand, ground-granulated blast furnace slag is an amorphous by-product of iron industry, and relatively richer in calcium and lower in aluminum as compared with fly ash [2,3]. The alkaline activation of sole slag (i.e., without fly ash incorporation), FA-F, FA-C, or fly ash-slag blends as novel binders have gained significant attention recently since contemporary environmental concerns and economic realities demand these industrial byproducts be effectively re-utilized [4–7]. For instance, alkali-activated slag binders have demonstrated ultrahigh strength [8,9], anti-fire-induced explosive capacity [10,11], remarkable chloride durability [12,13] and sulfate attacks [14,15]. Alkali-activated FA-F binders are featured with outstanding acid resistance and thermal stability [16,17]. Since fly ash and slag are the most popular choices as raw materials in the production of alkali-activated binders, their combined use can potentially provide engineering properties and performances that are more favorable than using them solely. For instance, a small amount of slag incorporation can considerably shorten the setting time of NaOH-activated fly ash at room temperature [18]. However, due to the
differences in reactivity and composition among raw slag, FA-F, and FA-C, the chemistry of an alkali-activated hybrid slag-fly ash system is complex.

The main hydrated phase in pure alkali-activated slag (AAS) is calcium–aluminosilicate-hydrate (C-A-S-H) with a strong structural similarity to tobermorite minerals [19,20]. The main hydrated phase in alkali-activated pure FA-F is alkali–aluminosilicate–hydrate (N-A-S-H), where tetrahedral units of silicates (Si\(^{4+}\)) and aluminates (Al\(^{3+}\)) are connected to create a three-dimensional spatial structure, with alkaline (Na\(^+\)) and/or calcium (Ca\(^{2+}\)) cations compensating the electrical charge imbalance associated with substituted Al\(^{3+}\) [21]. The N-A-S-H is a zeolite precursor and may be able to crystallize as a result of continued condensation, polymerization, and reorganization [22,23]. As the composition of FA-C locates it between FA-F and slag, the coexistence of C-A-S-H and N-A-S-H in alkali-activated pure FA-C has been reported [24,25]. In addition, for hybrid slag and FA-F systems with intermediate levels of Ca and Al, the coexistence of C-A-S-H and N-A-S-H is manifested during alkaline activation [24,26]. In addition, metastable N-C-A-S-H as a hybrid-type phase of N-A-S-H and C-A-S-H can exist in these systems [27]. The nature of precipitated C-A-S-H and N-A-S-H in an alkali-activated FA-C system or hybrid slag-fly ash system is different than the respective C-A-S-H or N-A-S-H formed in pure AAS or alkali-activated FA-F. Many attempts have been made towards a better understanding of the nature of, and compatibility among, the co-existing C-A-S-H and N-A-S-H in alkali-activated FA-C or fly ash–slag blend systems [28–30]. For example, it has been reported that Ca, although it significantly modifies the composition of N-A-S-H, probably via ionic exchange with Na, does not alter the gel structure of N-A-S-H [29,30]. Alternatively, although the geopolymeric gel incorporating a substantial percentage of Ca (i.e., N-C-A-S-H), being similar to the composition of C-A-S-H, can have different molecular structures than C-A-S-H [5]. Recent advances in thermodynamic modeling allows the prediction and management of phase assemblage and gel composition based on raw binder composition [31]. Nevertheless, the nature of precipitated gels in hybrid slag–fly ash systems has not been fully understood.

Alkali-activated sole FA-C has been shown to have a poor cementitious capability and low compressive strength and hence is not recommended for producing building materials [32]. As such, most of FA-C are currently dumped in landfill or utilized for soil stabilization. The causes of low cementitious and mechanical properties in alkali-activated FA-C have not been exclusively investigated, although it has been postulated to be associated with the chemical forms of calcium in FA-C [24]. It remains unclear how the chemical composition of fly ash affects the phase formation and microstructure development of alkali-activated hybrid slag–fly ash systems, the knowledge of which allows better and optimized utilizations of FA-C in green concrete construction. Therefore, examining the relationship between the composition of the starting reactants, nature of precipitated gels, and the engineering properties of alkali-activated binders will result in significant advancements in material selection and mixture design.

The objective of this paper is to investigate the hydrate assemblage and composition in a NaOH-activated hybrid slag–fly ash system with varying fly ash compositions and slag-to-fly ash ratios. This study aims to contribute to a better understanding of the nature of precipitated gels in hybrid slag–fly ash systems, as well as the reactivity and compatibility of C-A-S-H and N-A-S-H.

2. Materials and Methods

Grade 120 ground-granulated blast furnace slag (SL), Class F fly ash (FA-F), and Class C fly ash (FA-C) were used in this study. The major chemical composition of SL is: 43.8% CaO, 30.1% SiO\(_2\), 12.7% Al\(_2\)O\(_3\), and 4.8% MgO; FA-F is 2.5% CaO, 48.7% SiO\(_2\), 25.1% Al\(_2\)O\(_3\), 0.9% MgO, and 16.08% Fe\(_2\)O\(_3\); while FA-C is 19.2% CaO, 43.6% SiO\(_2\), 18.7% Al\(_2\)O\(_3\), 4.4% MgO, and 5% Fe\(_2\)O\(_3\). The granulometric size distributions of these three raw SL, FA-F, and FA-C materials are displayed in Figure 1. The X-ray powder diffractograms for all the raw materials used are shown in Figure 2. It can be seen that raw slag contains a primarily amorphous structure (see the humps in 20 = 30° to 31.6° as a result of the short range order
of CaO-SiO$_2$-Al$_2$O$_3$-MgO glass [20]) with a trace amount of gypsum and alite. For FA-F and FA-C, they both are basically amorphous materials (see the huge diffraction humps at $2\theta = 20$–35°), with some amounts of quartz and mullite. In contrast to FA-F, FA-C also contains some amount of hatrurite.

This study investigates NaOH-activated hybrid fly ash–slag binders, with all mixtures having an initial liquid (alkaline activator)-to-solid (i.e., raw FA-F or FA-C, and slag) volumetric ratio maintained at 0.75. The initial volumetric ratio in starting solid phases between raw fly ash (FA-F or FA-C) and slag were set to be 100/0, 80/20, 50/50, 20/80, and 0/100. The compositions of starting solid materials (a total of nine different mixtures) are listed in the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O ternary diagram in Figure 3. The activator used in this study was a 6 M NaOH solution with a pH of 14.7 and a density of 1.13 g/cm$^3$. The effects of the activator (e.g., pH and dissolved silicate) on the hydrates assemblage and composition of hybrid fly ash–slag systems have been reported in other studies [19,33–35] and are hence not considered in this study. Each mixture was poured into 100 mL containers after mixing, which was further sealed by parafilm and stored in ambient condition (~20°C) till further characterization.
X-ray diffraction (XRD) was utilized to characterize the phase assemblages of samples, using a PANalytical Empyrean diffractometer in a conventional Bragg–Brentano θ–2θ configuration. CuKα X-ray (λ = 1.5418 Å) was generated using 40 mA and 45 kV operating conditions. The grinded samples powders were frontally filled into a zero-background plate and scanned continuously between 5° and 43° 2θ (0.033453 degree/second). The total acquisition time of XRD diffractogram for each sample is about 15 min. The samples were characterized after hydration for 1d and 28d, during which the time-resolved phase evolution can be observed.

Scanning electron microscopy equipped with energy-dispersive spectroscopy (SEM/EDS) was used to characterize the composition of hydrates at 28D, using FEI ESEM Quanta 200. Prior to chemical analysis, the samples were epoxy impregnated and surface polished down to 1 µm. To reduce the random errors of EDS acquisition, about 50 data points were collected and analyzed for each polished specimen.

3. Results and Discussion
3.1. X-Ray Diffractometry

Figures 4–7 show the XRD diffractograms of alkali-activated hybrid fly ash–slag paste samples at 1D and 28D, and Table 1 lists the X-ray diffractometry information for major peaks identified in hybrid blast furnace slag and Class C fly ash-based geopolymer samples. It should be noted that some crystalline phases (e.g., quartz) originally exist in the raw materials and are mainly inert during the alkaline activation. As such, the remnant crystalline phases would not be explicitly labeled and the emphasis would be placed on the difference in hydrates assemblage and evolution due to the difference from starting material composition.

Figure 3. The CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O ternary diagram for the composition of starting solids materials.
The introduction of large amounts of aluminum into the C-S-H (I) structure (i.e., forming C-A-S-H) can inflate the thickness between silicate layers [38].

**Figure 4.** XRD diffractograms of alkali-activated 100% slag, FA-F or FA-C at 1D and 28D.

| d-Spacing | Reacted Phase | Typical d-Spacing | Theoretical Value (h k l) |
|-----------|---------------|-------------------|--------------------------|
| 14.47–14.48 | Sodium Aluminosilicate Hydrate (Na2Al2Si2.5O9·6.2H2O) | - | 14.47 (1 1 1) |
| 3.81 | - | 3.81 (5 3 3) |
| 12.83–13.18 | C-S-H (I) (CaO·SiO2·H2O) | - | 11.48–11.59 [35] a, 12.50–12.57 [24] b 12.50 (0 0 2) [37] |
| 3.06–3.07 | - | 3.07–2.97 [35] a 3.07 (1 1 *) [37] c |
| 2.78–2.80 | - | 2.79–2.82 [24] b 2.80 (2 0 *) [37] c |
| 1.83–1.84 | - | 1.83 (0 2 *) [37] c |
| 9.64–9.80 | Ettringite (Ca6Al2S3O50H64) | - | 9.72 (1 0 0) |
| 5.61–5.62 | - | 5.61 (1 1 0) |
| 4.99–5.00 | - | 4.97 (1 1 2) |
| 4.70 | - | 4.70 (1 0 4) |
| 3.88 | - | 3.88 (1 1 4) |
| 3.24–3.25 | C-S-H (Ca1.5SiO3.5·xH2O) | - | 3.04 |
| 1.82 | - | 1.82 |

**Figure 5.** XRD diffractograms of alkali-activated hybrid (80% FA + 20% SL) at 1D and 28D.

On the other hand, a coexistence of two types of C-S-H gels (i.e., C-S-H (I) and C-S-H) and a partial transformation from C-S-H (I) to C-S-H is observed in FA-C–slag blends.
Figure 5. XRD diffractograms of alkali-activated hybrid (80% FA + 20% SL) at 1D and 28D.

Figure 6 shows the XRD diffractograms for alkali-activated hybrid 50% slag and 50% fly ash system. It can be seen that most of the crystalline zeolite-type phases have disappeared. This indicates that the dissolution and reaction processes of slag and fly ash are not independent but interactive. Instead, fly ash–slag micro-scale interactions exist during alkaline activation or geopolymerization, which can chemically, structurally, and kinetically affect the hydrates assemblages and microstructure formation [33].

Figure 6. XRD diffractograms of alkali-activated hybrid (50% FA + 50% SL) at 1D and 28D.

Figure 7. Comparison of the C-S-H (I) and C-S-H XRD diffractograms in alkali-activated hybrid 50% FA-C and 50% slag mixtures at three different ages (i.e., 1 h, 1D, and 28D).

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Figure 7. Comparison of the C-S-H (I) and C-S-H XRD diffractograms in alkali-activated hybrid 50% FA-C and 50% slag mixtures at three different ages (i.e., 1 h, 1D, and 28D).

Figure 4 shows the XRD diffractograms for the alkali-activated 100% slag, 100% FA-F, and 100% FA-C. For AAS, the main hydrates are alumina-modified C-S-H (I), C-S-H, hydrotalcite-type phase, portlandite, and some amount of sulfate-bearing phase due to the presence of gypsum [33,36]. In comparison with the C-S-H, C-S-H (I) has a relatively high ordered structure and presents a diffusive basal reflection corresponding to the mean interlayer in its layered silicate structures [36,37]. The introduction of large amounts of aluminum into the C-S-H (I) structure (i.e., forming C-A-S-H) can inflate the thickness between silicate layers by lowering the coherent domain [38].

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Table 1. X-ray diffractometry information for main diffraction peaks identified in the hybrid blast furnace slag and Class C fly ash-based geopolymer samples.

| d-Spacing in This Study | Reacted Phase | Typical d-Spacing       | Theoretical Value | (h k l) |
|-------------------------|---------------|-------------------------|-------------------|--------|
| 14.47–14.48 3.81        | Sodium Aluminosilicate Hydrate (Na₂Al₂Si₅O₁₉·6.2H₂O) | - 14.47           | (1 1 1)          |
| 12.83–13.18             | C-S-H (I)     | 12.50–12.57             | (0 0 2) [37]      |
| 3.06–3.07               | C-S-H (I)     | 3.07–2.97 [35] a        | (1 1 *) [37] c    |
| 2.78–2.80               | C-S-H (I)     | 2.79–2.82 [24] b        | (2 0 *) [37] e    |
| 1.83–1.84               | Ettringite     | 1.83–1.84 [35] a        | (0 2 *) [37] e    |
| 9.64–9.80               | Hydrotalcite-type Phase | 7.63–7.70 [35]       | (0 0 6)          |
| 5.61–5.62               | C-S-H         | 5.61–5.62               | (1 1 0)          |
| 4.99–5.00               | Ettringite     | 4.97–4.97               | (−1 −1 2)        |
| 4.70                    | Ettringite     | 4.70–4.70               | (1 0 4)          |
| 3.88                    | Ettringite     | 3.88–3.88               | (−1 −1 4)        |
| 3.24–3.25               | Ettringite     | 3.24–3.24               | (3 0 0)          |
| 7.13–7.14               | Sodium Aluminosilicate Hydrate (Na₅Al₅Si₅O₁₉·9H₂O) | - 7.11             | (1 1 0)          |
| 6.67–6.78               | Sodium Aluminosilicate Hydrate (Na₅Al₅Si₅O₁₉·9H₂O) | - 6.68             | (0 0 1)          |
| 4.87–4.88               | Sodium Aluminosilicate Hydrate (Na₅Al₅Si₅O₁₉·9H₂O) | - 4.87             | (1 1 1)          |
| 3.14                    | Sodium Aluminosilicate Hydrate (Na₅Al₅Si₅O₁₉·9H₂O) | - 3.14             | (2 2 1)          |
| 4.15–4.16               | Sodium Aluminosilicate Hydrate (Na₅Al₅Si₅O₁₉·9H₂O) | - 4.15             | (0 2 1)          |
| 4.14                    | Sodium Aluminosilicate Hydrate (Na₅Al₅Si₅O₁₉·9H₂O) | - 4.14             | (2 2 0)          |

Note: a—alkali-activated blast furnace slag; b—pure NaOH-activated blast furnace slag and alkali-activated Class C fly ash; c—(h k *) denotes a band head related to two-dimensional lattice.

For alkali-activated fly ash, it can be seen that the type of precipitated zeolite-type crystalline phases and shapes of the amorphous hump (corresponding to N-A-S-H gels) appreciably evolve as a function of fly ash composition and age. First, a shift in the position of the hump ascribed to the amorphous glass phase in the initial fly ash to slightly higher angular values at around 25–40° indicates the formation of geopolymeric N-A-S-H gels [25,39]. The difference in shapes of the humps between alkali-activated FA-F and FA-C indicates that the structures of vitreous N-A-S-H gels in these materials are different since the XRD profiles of these two kinds of raw fly ash are rather similar. At 28D, different types of zeolite-type phases and crystalline geopolymeric sodium–aluminosilicate-hydrates (N-A-S-H) can be clearly detected, which is however mainly absent at the early age. This suggests the transformation of amorphous N-A-S-H gels into crystalline phases during geopolymerization as a result of continued condensation, polymerization, and reorganization [22]. Contrary to FA-F, the alkali-activation of FA-C creates a magnified hump at around 30°, indicating the formation of C(-A)-S-H. This C(-A)-S-H in alkali-activated FA-C is more amorphous than the C-S-H (I) in AAS, which may be attributed to a different composition, nanostructure, or degree of crystallinity. In addition, strong peaks corresponding to hydrotalcite-type phases are detected in the FA-C system, due to the high magnesium content in the raw FA-C composition.

Figure 5 shows the XRD diffractograms for alkali-activated hybrid 20% slag and 80% fly ash system. It can be seen that the precipitation of zeolite-type crystalline phases is inhibited by the incorporation of slag for FA-F–slag blends. On the contrary, the small amount of slag incorporation does not conspicuously affect the precipitation of zeolite-type
phases in FA-C–slag blends. This observation may indicate that the dissolved Ca from slag can modify the N-A-S-H structure of alkali-activated FA-F, inhibiting its crystallization; while in the FA-C system, the precipitate phase already comprises a significant amount of Ca (see Section 3.2 for SEM/EDS data), which makes it less influenced by the additional Ca dissolved from slag. Moreover, a new hump at around 30° corresponding to C(-A)-S-H has been identified in the FA-F-slag system, as a result of slag hydration. In addition, the hump corresponding to C(-A)-S-H in the FA-C–slag system seems to become wider and more diffusive. It is reasonable since slag itself is a glassy reactive material and its hydration can also promote the formation of C(-A)-S-H.

Figure 6 shows the XRD diffractograms for alkali-activated hybrid 50% slag and 50% fly ash system. It can be seen that most of the crystalline zeolite-type phases have disappeared. This indicates that the dissolution and reaction processes of slag and fly ash are not independent but interactive. Instead, fly ash–slag micro-scale interactions exist during alkaline activation or geopolymerization, which can chemically, structurally, and kinetically affect the hydrates assemblages and microstructure formation [33].

On the other hand, a coexistence of two types of C-S-H gels (i.e., C-S-H(I) and C-S-H) and a partial transformation from C-S-H(I) to C-S-H is observed in FA-C–slag blends, as shown in Figure 7. It can be seen that the gradual conversion from C-S-H(I) to C-S-H is accompanied by a simultaneous enlargement in basal spacing (i.e., distance between two layers). In term of C-S-H(I), the degree of crystallinity tends to decrease and the basal spacing, if present, also decreases with an increase in Ca/Si ratio, according to Taylor [37]. However, given that the composition of C-S-H and basal peak shown in XRD patterns are not strongly correlated [40], it is impossible to postulate the change in Ca/Si ratio in C-S-H here. Considering that C-S-H(I) is the main detected C-S-H phase in AAS while C-S-H is the main detected C-S-H phase in alkali-activated FA-C, the transformation demonstrates the reactions among various hydrates due to thermodynamic incompatibility.

It is known that the calcium in a C-S-H nanostructure model, particularly in tobermorite-based models [41], is located either in the CaO polyhedra layer (i.e., intralayer) or in the interlayer region as Ca$^{2+}$ ions. The CaO polyhedra layer is a double plane of Ca$^{2+}$ ions 6- or 7-coordinated by central O$^{2-}$ ions, to which disordered silica chains are grafted on each side [41]. It is postulated that the calcium dissolved from slag can contribute to the extensive formation of a CaO polyhedra layer, which is magnified by the strong peak corresponding to the interlayer plane (002 plane) in XRD, whilst the calcium dissolved from FA-C behaves differently and presents mostly as Ca$^{2+}$ absorbing on the surface or interlayers of gels. It is probable that the calcium in the CaO polyhedra layer in some sense affects the overall properties of C-S-H. As such, the high calcium in FA-C may reduce the mechanical strength of materials, while the calcium in slag increases the mechanical strength [24].

Figure 8 shows the XRD patterns for an alkali-activated hybrid 80% slag and 20% fly ash system. It can be seen that regardless of fly ash composition, the basal reflection of C-S-H(I) for hybrid system shifts to higher d-spacing values, compared with that in pure AAS. This may be explained by the insert of a large amount of aluminum from FA-C or FA-F in the C-S-H(I) structure [38]. However, it can be seen that the d-spacing for an FA-C-slag system is slightly larger than that of an FA-F-slag system, although the amount of alumina in FA-F is substantially higher than that in FA-C. This may suggest that the C-S-H(I) from AAS is metastable in the presence of dissolved Ca from FA-C.
The accuracy of implementing EDS in identifying the gel composition in a hybrid system is questionable since the electron beam size for the chemical probe is likely to be larger than the sizes of the homogeneous phases like C-A-S-H and N-A-S-H. However, the present study indicates that, although various types and compositions of gels are likely intermixed with each other, the framework structure of precipitated gels is an assemblage of aluminosilicate units of varying Ca and Na contents. Depending on the structural roles and binding sites of Ca and Na, the gels may have totally different structures and properties. In term of the gel composition, the heterogeneity of a hybrid system could be a result of the heterogeneous spatial distribution of Ca and Na in the microstructure. It should be noted that this observation may merely be applicable to NaOH-activated systems; while for the system activated by sodium silicates, the heterogeneous dispersion of dissolved silica from the activator may increase the degree of heterogeneity of composition in the microstructure [19,33].
Figure 9. Backscatter SEM images for hybrid slag and high-calcium fly ash (FA-C) pastes with varying percentages of slag. (a) 20% FA-C + 80% SL; (b) 50% FA-C + 50% SL; (c) 80% FA-C + 20% SL; (d) 100% FA-C.

Figure 10. Al/Ca versus Si/Ca atomic ratio in the solid hydrated phases of alkali-activated (a) hybrid FA-F–slag system (b) hybrid FA-C–slag.
Figure 11 shows the relationship between the Na–Si and Ca–Si atomic ratios in solid hydrated phases in an alkali-activated hybrid fly ash–slag system. For an FA-F–slag system, with the increased loading of slag, the N-A-S-H phase gradually converts into a metastable N-C-A-S-H phase with high Na and high Ca contents and wide ranges of Na/Si and Ca/Si ratios. This N-C-A-S-H has a similar Ca–Si ratio to the C-A-S-H in AAS, but with a much higher Na content. For the FA-C–slag system, with the increasing loading of slag, the precipitated gels show a gradually reduced Na–Si ratio with a relatively stable average Ca–Si ratio. However, it should be noted that for mixtures containing FA-C, the composition is greatly heterogeneous. Theoretically, the Ca$^{2+}$ and Na$^+$ will compete with each other to compensate the negative surface charge of silicate due to deprotonation (i.e., $\equiv$SiOH to $\equiv$SiO$^-$), and to balance the change deficiency of Al$^{3+}$ for substituting Si$^{4+}$ (i.e., M$^+$ + Al$^{3+}$ = Si$^{4+}$). However, the concurrent high Na and Ca content in hydrated products of an alkali-activated FA-C system and hybrid slag–fly ash with intermediate proportions may indicate that the precipitated gels are thermodynamically unstable and structurally distorted. This hypothesis can explain the low cementitious properties of alkali-activated FA-C, as well as the reduced compressive strength of a hybrid FA-F–slag system with intermediate proportions. Moreover, it is suggested that the relative amount and reactivity of Ca and Na are critical in determining the nature and properties of the precipitated gels in a hybrid system.

![Graph showing Na–Si versus Ca–Si atomic ratio](image)

**Figure 11.** Na–Si versus Ca–Si atomic ratio in the solid hydrated phases of alkali-activated (a) hybrid FA-F–slag system (b) hybrid FA-C–slag.

4. Conclusions

In this paper, the hydrates assemblage and composition in an alkali-activated hybrid slag–fly ash system with different starting material compositions was studied. The following conclusions can be drawn according to this study:

1. The type and composition of precipitated C-A-S-H, N-A-S-H, and N-C-A-S-H depend on the fly ash composition and slag-to-fly ash ratio.
2. There is a structural limitation on the incorporation of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral silicate chain of C-A-S-H, N-A-S-H, and N-C-A-S-H, regardless of the starting material chemistry.
3. In an NaOH-activated hybrid slag–fly ash system, the framework structure of precipitated gels is an assemblage of aluminosilicate units of varying Ca and Na contents. The heterogeneity of composition in the microstructure could be a result of the heterogeneous spatial distribution of Ca and Na cations.
4. The C-S-H (I) formed in hydrated AAS seems to be reactive with the dissolved (calcium, alumina, silicate) species from fly ash, resulting in a gradual conversion to a
distinct C-S-H with probably different compositions, nanostructures, and degree of crystallinity at an early age.

(5) The low cementitious capability of alkali-activated FA-C may be attributed to the unstable N-C-A-S-H gel structure with concurrent high Na and Ca contents.

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