

Performance and Mechanism of Alkali-Activated Complex Binders of High-Ca Fly Ash and Other Ca-Bearing Materials

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ABSTRACT

Industrialization leads to the generation and release of large quantity of wastes into the environment. Processes that maximum utilization of wastes, as products, and minimize pollution in the environment are greatly needed. Complex binders were created from high-Ca fly ash and other Ca-bearing materials activated by sodium hydroxide and sodium silicate solution. Hardened binders made only from high-Ca fly ash (CFA100%), fly ash with 40 wt% cement (CFA-C40%), fly ash with 10 wt% flue gas desulfurization (FGD) gypsum (CFA-G10%), and fly ash with 10 wt% water treatment residual (CFA-WTR10%) had better mechanical performance compared to the binders using other mix ratios. Most of the synthesized products were non-crystalline as X-ray diffraction (XRD) analysis showed a broad diffuse halo. Using Fourier transform infrared spectroscopy (IR), asymmetric stretching of Al-O and Si-O bonds and Si-O-Si bending bands appeared as the main peaks. Scanning electron microscope (SEM) pictures of the CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10% specimens also showed amorphous synthesis products were formed around the spherical fly ash particles. Further analysis using energy dispersive X-ray analysis (EDXA) indicated the main products of the CFA100%, CFA-G10%, and CFA-WTR10% specimens were geopolymeric gels. In the CFA100% and CFA-C40% specimens, calcium silicate hydrate (C-S-H) gel and geopolymeric gel were formed simultaneously. The binding properties of the amorphous alkali aluminosilicate geopolymer gel and C-S-H gel contribute to the mechanical strength reaching 80.0 MPa (i.e. 11,600 psi) of the complex binders. In conclusion, utilization of high-Ca fly ash and other Ca-bearing materials in alkali-activated complex binders is feasible. Additionally, compared to Portland cement, producing alkali-activated complex binders can also reduce the use of mined raw materials and energy, and also reduce the release of greenhouse gases. These materials can be widely utilized in various applications such as in building

materials and for solidification/stabilization materials, including other waste materials, thus making them more environmentally benign.

1. INTRODUCTION

Industrialization leads to the generation and release of large quantity of wastes into the environment. Processes that maximize utilization of wastes to create new products, and that minimize pollution in the environment are greatly needed. Alkali-activated materials are a developing field of research for utilizing solid wastes and by-products. Geopolymers, a type of alkali-activated materials, is a term used by Davidovits because of its analogy to organic materials which react at ambient temperature to form solid polymers.¹ The prefix “geo” refers to the inorganic nature of the material. Geopolymerization is a chemical process that provides a rapid transformation of some specific structures to create products that are either partially or totally amorphous and/or meta-stable. In general, two types of cementitious materials can be produced by alkaline activation—first those based on Si and Ca, and second those based on Si and Al.²

Fly ashes are produced by burning pulverized coal and contain 40% - 60% of SiO_2 and 20% - 30% of Al_2O_3 . Fly ashes have a very high fineness with the vast majority of particles having a diameter between less than 1 μm and 100 μm . Fly ash has been classified into two classes, class F fly ash (low-Ca fly ash) and class C fly ash (high-Ca fly ash), based on the chemical compositions of the fly ashes according to ASTM C 618.³ Class F fly ash is produced from burning anthracite and bituminous coals. It has siliceous or siliceous and aluminous material, which itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form cementitious compounds. Class C fly ash is produced normally from lignite and sub-bituminous coals and usually contains significant amounts of calcium hydroxide or lime. Class C fly ash, in addition to having pozzolanic properties, also has some cementitious properties. Coal is a major energy source in the world and large quantities of fly ash are generated and available worldwide. It is estimated that in China alone, by the year 2010, the amount of the fly ash produced will be about 2 billion tones annually with less than half (47.1%) being used.⁴⁻⁶ There is thus a great need to develop new, beneficial uses of fly ash.

Fly ash is one of the important source materials for alkali-activated materials. Class F fly ash is currently most commonly used in geopolymer synthesis. However there seems to be no reason why class C fly ash cannot also be used in a similar way.⁷ Alkali activation of fly ash is a singular procedure by which the grey powder is mixed with certain alkali activators (alkali dissolutions), and the specimens are cured under mild temperature producing hardened materials. The set of reactions taking place during the process can be divided into three consecutive stages: (1) decomposition-coagulation; (2) coagulation-condensation; (3) condensation crystallization.² It has also been suggested, but never definitively proven, that Ca^{2+} is capable of acting as a charge-balancing cation within the geopolymeric binder structures. If this is the case, then there may also be significant implications with respect to Si/Al ordering within the geopolymeric network

structures, as Ca^{2+} is known to greatly reduce the energy penalty associated with Si/Al ordering violation in aluminosilicate networks in aluminosilicate glasses. Ordering violations induced by the presence of Ca^{2+} in charge-balancing sites may therefore be of significant practical interest.⁸⁻¹¹

Compared to Portland cement, alkali-activated complex binders of high-Ca fly ash and other Ca-bearing wastes can save natural resources and energy, and also reduce the release of greenhouse gases. In this paper, different Ca-bearing materials, cement, FGD-gypsum, and water treatment residual, are mixed with Class C high-Ca fly ash to synthesize complex binders using alkali activators such as sodium hydroxide and sodium silicate solution. Questions this work addresses are: (1) What causes alkali activation of high-Ca fly ash and other Ca-bearing materials? (2) What is the role of Ca from different kinds of Ca-bearing materials? (3) Is there coexistence of the calcium silicate hydrate (C-S-H) phase and the geopolymeric gel in this system?

The overall goal of this paper is to conduct research that will provide potential answers to these questions. We will do this by discussing alkali-activated complex binders produced from high-Ca fly ash and other Ca-bearing materials.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

A class C fly ash (CFA) with high-Ca content was obtained from the First Energy Corporation (OH, USA). Type 1 Portland cement (C) was purchased as commercial cement. Flue gas desulfurization (FGD) gypsum (G) was obtained from the Cinergy Corporation (Cincinnati, OH, USA) and water treatment residual (WTR) from a local water treatment plant (Sidney, OH, USA). Alkali activators of sodium silicate solution and sodium hydroxide were commercial products from Fisher Company. Solid content of the original sodium silicate solution is 38.3% while water content is 61.7%. In this experiment, a mixed alkali activator was made from 12.4 wt% sodium hydroxide and 87.6 wt% sodium silicate solution, to obtain a constant molar ratio of 1.5 of $\text{SiO}_2/\text{Na}_2\text{O}$

FGD-gypsum generated from wet-type scrubbing process is often wet and viscous. Fresh water treatment residuals also contain about 90 wt% of water. To dry the raw materials and create activated powders, wet FGD-gypsum and water treatment residual must be thermally treated before use. FGD-gypsum and the water treatment residuals were air-dried first and then baked in a muffle oven for 1 h at 800 °C and 900 °C, respectively. The chemical and mineral compositions of raw materials are summarized in Table 1. Mineral compositions of FGD-gypsum and water treatment residuals were analyzed by X-ray diffraction (XRD) (Fig. 1).

Table 1 Chemical composition of raw materials.

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SO ₃	K ₂ O	Na ₂ O	L.O.I.	Total
High-Ca fly ash (CFA)	38.0	19.0	9.00	5.00	20.0	3.00	0.40	1.00	3.50	98.9
Cement (C)	20.6	5.00	2.80	2.70	63.2	-	1.10	0.50	3.60	99.5
FGD-gypsum (G)	-	0.04	0.03	0.04	40.1	54.7	0.01	0.01	2.11	97.1
Water treatment Residual (WTR)	13.2	2.21	0.90	5.63	40.7	-	0.33	0.27	36.5	99.7

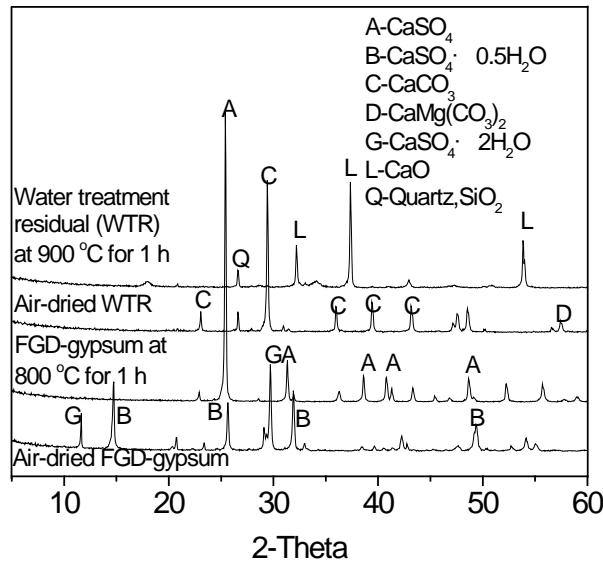


Fig. 1. Mineral compositions of air-dried and thermally treated FGD-gypsum and water treatment residual (WTR).

2.2 Specimen preparation for mechanical test

In this study, high-Ca fly ash was the main reactive Si-Al cementitious resource. In complex solid binders, high-Ca fly ash was replaced, respectively, by cement, FGD-gypsum, and water treatment residual, at ratios of 10 to 50 wt% (Table 2). The addition of this mixed alkali activator was evaluated by maintaining the amount of Na₂O in the

Table 2. Mix ratios of alkali-activated complex binders of high-Ca fly ash and other Ca bearing materials.

Specimen Number	Specimen code ^a	High-Ca fly ash (CFA) (%)	Admixture and its content (%)
1	CFA100%	100	0
2	CFA-C10%	90	Cement (C), 10
3	CFA-C20%	80	Cement (C), 20
4	CFA-C30%	70	Cement (C), 30
5	CFA-C40%	60	Cement (C), 40
6	CFA-C50%	50	Cement (C), 50
7	CFA-G10%	90	FGD-gypsum (G), 10
8	CFA-G20%	80	FGD-gypsum (G), 20
9	CFA-G30%	70	FGD-gypsum (G), 30
10	CFA-G40%	60	FGD-gypsum (G), 40
11	CFA-G50%	50	FGD-gypsum (G), 50
12	CFA-WTR10%	90	Water treatment residual (WTR), 10
13	CFA-WTR20%	80	Water treatment residual (WTR), 20
14	CFA-WTR30%	70	Water treatment residual (WTR), 30
15	CFA-WTR40%	60	Water treatment residual (WTR), 40
16	CFA-WTR50%	50	Water treatment residual (WTR), 50

^aSpecimen codes are defined as follows: CFA is class C fly ash. C is cement, G is FGD gypsum and WTR is water treatment residual. The percentages following C, G, and WTR are the percentages of the fly ash replaced by these materials.

blend equal to 10 wt%. For all the specimens, the water to solid ratio was maintained at 0.4. The water includes the water in the mixed alkali activator and the distilled water added. The paste was poured into molds of 20×20×20 mm to make cubic specimens. One batch of these specimens was cured at 75 °C for 4 h, 8 h, and 24 h and another batch was cured at 23 °C for 3 d, 7 d, and 28 d. The compressive strength of these two batches of specimens was tested at each curing age.

2.3 Activities of the complex raw material blends

To estimate the activities of these complex raw materials blends, leachabilities of Al, Si and Ca were tested as follows:⁸ At temperatures of 23 °C and 75 °C, the ratio of volume (in ml) of 5 mol/l NaOH solution to mass (in grams) of complex raw material blends was 2:1. The suspensions were shaken at 250 rpm for 1 h and 24 h. The suspensions were

then centrifuged and filtered (0.2 μm Minisart membrane filter). The concentration of Al, Si, and Ca in leachates were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Leeman Prodigy high dispersion ICP spectrometer.

2.4 Methods for analysis of synthesized products

The synthesized products of alkali-activated complex binders of high-Ca fly ash and Ca-bearing materials were analyzed using x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope-energy dispersive X-ray analysis (SEM-EDXA). These specimens were cured at 75 °C for 8 h, followed by 23 °C for 28 d. At this time, the specimens were crushed, ground, and passed through a 325 mesh screen. The resultant powder specimens were analyzed directly by the above-mentioned XRD method. For FTIR analysis, the powder specimens were mixed with KBr at a concentration of 0.2 to 1 wt% to make the KBr disks. Then the disks were tested using a Perkin Elmer FT-IR spectrometer. For SEM-EDXA, the crushed specimens were mounted on Al-stubs with double-sided carbon tabs and then coated with a thin layer of platinum in a Hummer 6.2 Sputter Coater. The SEM-EDXA data was collected with the Hitachi S-3500N and Noran EDXA equipment.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

Compressive strength of alkali-activated 100 wt% high-Ca fly ash (CFA100%) specimen was 30.6, 30.2, and 37.7 MPa (note that one MPa is equal to 145 pounds per square inch (psi)) after curing at 75 °C for 4 h, 8 h, and 24 h, respectively. When specimens were cured at 23 °C for 3 d, 7 d, and 28 d, the compressive strength values were 22.6, 34.5, and 59.3 MPa, respectively. When fly ash was partially replaced, respectively, by cement, FGD-gypsum, and water treatment residual, changes of compressive strength were as shown in Fig. 2. Specimens made from cement and fly ash exhibited improved compressive strengths (Fig. 2 (a-1)) after curing for 4-24 h at 75 °C. This improved performance was especially noticeable with the specimen containing 40 wt% cement cured for 8 h at 75 °C (CFA-C40%, Specimen 5 in Table 2) where the compressive strength value reached 80.0 MPa. Specimens made from cement and fly ash and cured at 23 °C for 3-28 d had compressive strengths that were enhanced by increasing the cement content from 10 to 40 wt% (Fig. 2 (a-2)). When fly ash was partially replaced by FGD-gypsum or water treatment residual, compressive strengths were decreased compared to when the replacement was with cement and curing occurred at 75 °C (Fig. 2 (b)) or 23 °C (Fig. 2 (c)).

According to the compressive strength results obtained for each batch of specimens, the proper mix ratios for fly ash and other calcium materials were determined. Specimen specimens containing 100 wt% high-Ca fly ash (CFA100%, Specimen 1 in Table 2), fly

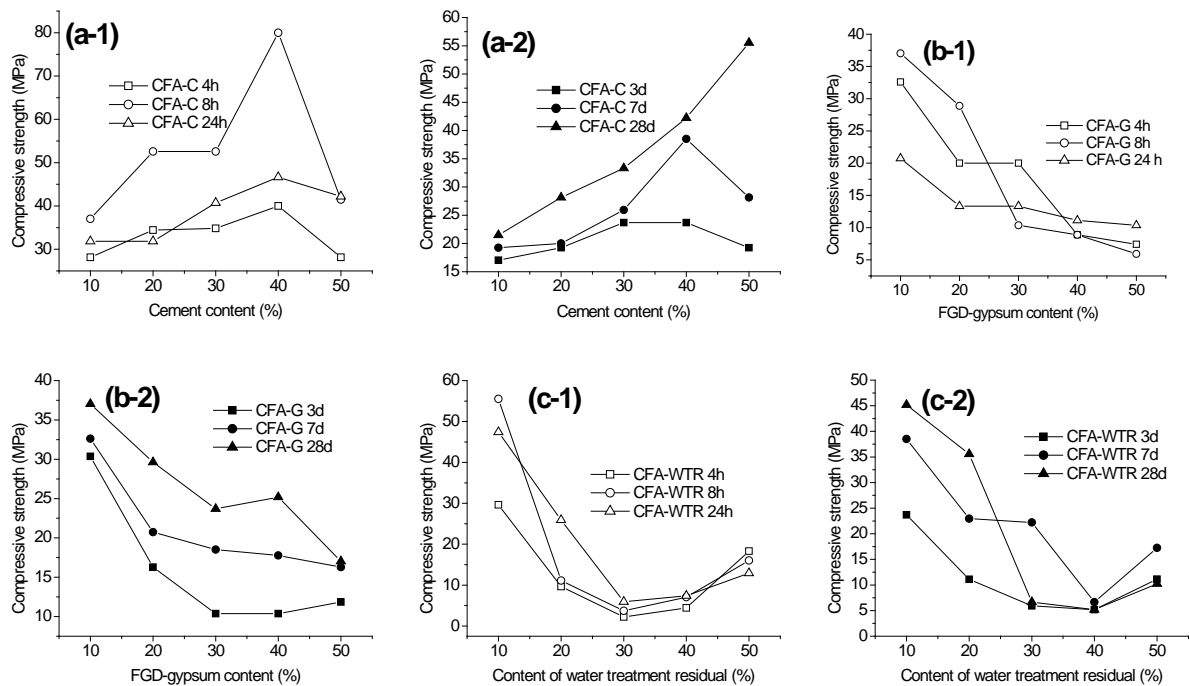


Fig. 2. Compressive strength of alkali activated complex binders: (a-1) high-Ca fly ash with cement (CFA-C) specimens cured at 75 °C for 4-24 h, and (a-2) CFA-C specimens cured at 23 °C for 3-28 d; (b-1) high-Ca fly ash with FGD-gypsum (CFA-G) specimens cured at 75 °C for 4-24 h, and (b-2) CFA-G specimens cured at 23 °C for 3-28 d; (c-1) high-Ca fly ash with water treatment residual (CFA-WTR) specimens cured at 75 °C for 4-24 h, and (c-2) CFA-WTR specimens cured at 23 °C for 3-28 d.

ash with 40 wt% cement (CFA-C40%, Specimen 5 in Table 2), fly ash with 10 wt% of FGD-gypsum (CFA-G10%, Specimen 7 in Table 2), and fly ash with 10 wt% water treatment residual (CFA-WTR10%, Specimen12 in Table 2) had better mechanical performance compared with the hardened binders using other mix ratios. Performance and mechanism of alkali-activated complex binders of CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10% were thus further studied in several additional experiments.

3.2 Activities of complex raw material blends of high-Ca fly ash and Ca-bearing materials

The dissolution of Si, Al, and Ca from the aluminosilicate source (high-Ca fly ash in this case) and Ca-bearing materials (cement, FGD-gypsum, and water treatment residual) governs the initial stage of reactivity.^{7, 12, 13} This initial stage of reactivity involves geopolymerization and hydrate reaction. The formation of a geopolymeric gel depends on the availability of dissociated silicate $[\text{SiO}_n(\text{OH})_{4-n}]^{n-}$ and aluminate $\text{Al}(\text{OH})_4^-$ monomers in the alkaline medium, which is further dependent on the extent of

Table 3. Leaching concentrations of Si, Al, and Ca from complex raw material blends.

Specimen	23 °C		75 °C	
	1h	24h	1h	24h
	Si (mg/l)			
CFA100%	1,230	1,080	2,880	7,540
CFA-C40%	769	494	1,440	2,490
CFA-G10%	1,410	1,690	2,600	5,970
CFA-WTR10%	1,230	1,300	2,590	3,620
	Al (mg/l)			
CFA100%	1,270	2,150	3,180	312
CFA-C40%	181	415	1,350	169
CFA-G10%	1,130	1,910	3,180	67.6
CFA-WTR10%	1,080	1,870	3,070	430
	Ca (mg/l)			
CFA100%	8.89	3.16	1.91	1.86
CFA-C40%	8.71	11.9	7.83	0.03
CFA-G10%	8.42	5.75	4.74	0.03
CFA-WTR10%	8.65	5.46	3.79	1.86

dissolution of these two species from the original aluminosilicate source. In the presence of soluble Ca species, the governing reactions become more complex. Under these circumstances, Ca could either (1) precipitate as $\text{Ca}(\text{OH})_2$, lowering the alkalinity of the medium and thus the driving force or dissolution of Si and Al, or (2) interfere with the formation of the geopolymeric gel by reacting with the dissolved silicate and aluminate species. Thus, the interaction between Ca, Si and Al species in an alkaline medium is expected to have a highly significant impact on the nature of the resultant products

Table 3 presents the leaching concentrations of Si, Al and Ca from each complex raw material blend after 1 h and 24 h contact with NaOH solution at 23 °C, and 75 °C, respectively. The CFA-C40% specimen has less Si and Al concentration in the leaching solution compared to specimens of CFA-100%, CFA-G10%, and CFA-WTR10%. This is not because the leaching rates of Si and Al are slow, but because the initial content of Si and Al in CFA-C40% is less than that in other blends. However, Ca concentration in CFA-C40% leaching solution is more than that in solution obtained from other specimens. At 23 °C, Al leaching contents are increased with leaching time from 1 h to 24 h for all specimens of CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10%.

However Ca leaching content is decreased except for the CFA-C40% specimen. At 75 °C, the concentration of the leached Si is higher at 24 h than that at 1 h, but the concentrations of the leached Al and Ca are lower at 24 h than that at 1 h. Table 3 does not show a clear relationship between the Ca sources and the extent of dissolution of Ca. Also, there is no clear correlation between the concentration of Ca and the concentrations of Si and Al at any given condition. However, the study of dissolution content of Si, Al, and Ca from the aluminosilicate resource and Ca-bearing materials in alkali condition will aid in the estimation of reaction products.

3.3 Synthesized products analysis

3.3.1 X-Ray Diffraction (XRD)

The XRD spectrums of alkali-activated complex binders cured at 75 °C for 8 h, followed by 25 °C for 28 d were obtained. In all XRD spectrums of the alkali-activated complex binders, peaks due to the crystalline components of quartz (SiO_2) from the unactivated fly ash have been determined (Fig. 3). A large part of the structure is attributed to the amorphous content of the specimens. The degree of disorder can be inferred by the way the specimen diffracts the X-rays to form a diffraction pattern. In a non-crystalline

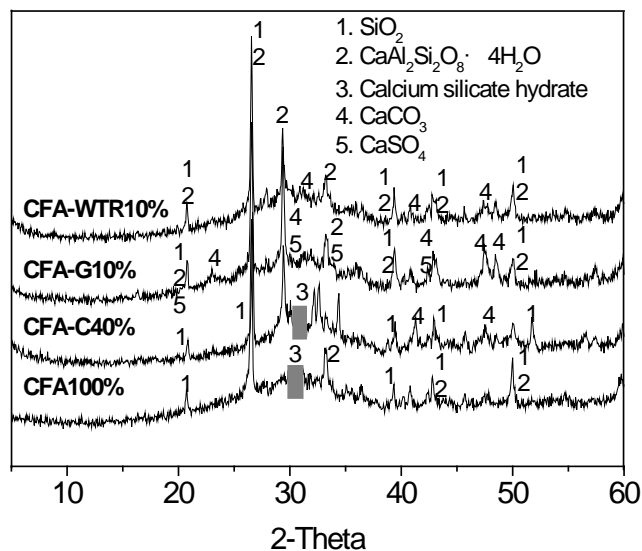


Fig. 3. X-ray diffraction (XRD) of alkali-activated complex binders of high-Ca fly ash and other Ca-bearing materials cured at 75°C for 8 h, followed by 23°C for 28 d. The CFA100% specimen is made only from high-Ca fly ash (Table 2, Specimen 1), the CFA-C40% specimen is produced from 60% fly ash and 40% cement (Table 2, Specimen 5), the CFA-G10% specimen is prepared from 90% fly ash and 10% FGD-gypsum (Table 2, Specimen 7), and the CFA-WTR10% specimen is created from 90% fly ash and 10% water treatment residual (Table 2, Specimen 12).

state, diffraction of X-rays result in a broad, diffuse halo rather than sharp diffraction peaks from 20-40° (2 Theta). In the CFA100% and CFA-C40% specimens, the broad peaks contain amorphous gels of sodium polysilicate zeolite (gismondine, $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) and calcium silicate hydrate (C-S-H) gel. When water treatment residuals are added, the product is mainly amorphous geopolymer of sodium polysilicate zeolite gel. Additionally, unactivated quartz and calcite from the raw materials are also evident in the products.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR absorption spectroscopy seems to be a suitable tool to characterize alkali-activated materials—especially geopolymeric materials.¹⁴⁻²¹ The CFA100% specimen shows main adsorption bands at 747, 1036, 1400, 1648, and 3466 cm^{-1} (Fig. 4). The main peak at 1036 cm^{-1} is attributed to asymmetric stretching of Al-O and/or Si-O bonds originating from individual tetrahedral, and the relative weak peak at 1400 cm^{-1} is also asymmetric stretching of Al-O and Si-O bonds, while the Si-O-Si bending band can be seen at 747 cm^{-1} . All of these bonds indicate the degree of amorphization of the reactive products. The relationship between the Al-O, Si-O, or Si-O-Si asymmetric stretch peak

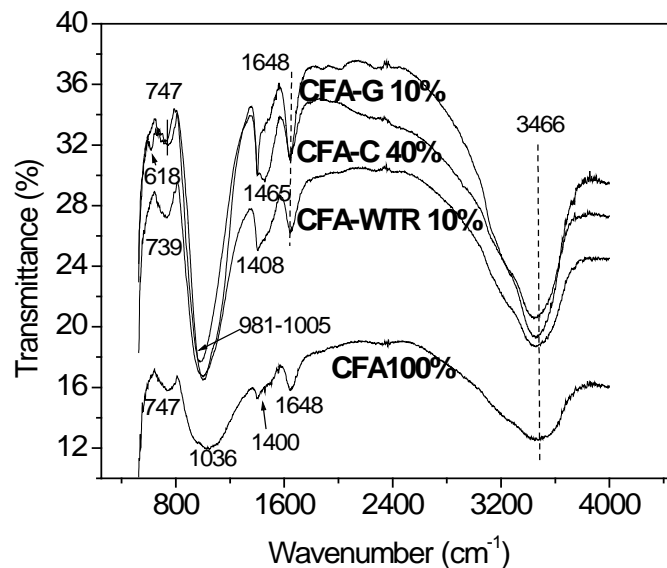


Fig. 4. Fourier transform infrared spectroscopy (FTIR) of alkali-activated complex binders of high-Ca fly ash and other Ca-bearing materials cured at 75°C for 8 h, followed by 23°C for 28 d. The CFA100% specimen is made only from high-Ca fly ash (Table 2, Specimen 1), the CFA-C40% specimen is produced from 60% fly ash and 40% cement (Table 2, Specimen 5), the CFA-G10% specimen is prepared from 90% fly ash and 10% FGD-gypsum (Table 2, Specimen 7), and the CFA-WTR10% specimen is created from 90% fly ash and 10% water treatment residual (Table 2, Specimen 12).

positions and the extent of the geopolymerization process is complex, but very instructive in the study of the mechanism of geopolymerization. Comparing spectra of the CFA-C40%, CFA-G10%, and CFA-WTR10% specimens with that of CFA100%, the Al-O and Si-O bonds asymmetric stretching at 1036 cm^{-1} show there is a movement to lower wave numbers of $981\text{-}1005\text{ cm}^{-1}$. Of course, in all cases, broad bands in the region of $1648\text{-}3500\text{ cm}^{-1}$ characterize the spectrum of stretching and deformation modes of the adsorbed water. Both of these peaks are very prominent of the spectra.

3.3.3 Scanning Electron Microscope-Energy Dispersive X-Ray Analysis (SEM-EDXA)

In SEM pictures of the CFA100%, CFA-G10%, and CFA-WTR10% specimens, amorphous gel was formed around the spherical raw material fly ash particles (Fig. 5.(a, c, and d)). When FGD-gypsum was added, a small quantity of lathy products was observed to be wrapped over the surface of the spherical fly ash particles except for the amorphous gel (Fig. 5.(c)). Additionally, in the CFA100%, CFA-G10%, and CFA-WTR10% specimens, there are spherical fly ash particles that have not entered into any reaction, but for the fly ash in the 40 wt% cement specimen (CFA-C40%) (Fig. 5.(b)), there is almost no raw material existing in the picture.

Further study was conducted by EDXA, The main elements in the alkali-activated products are Si, Al, Ca, Na, and O, with also some Fe, C, and S etc. (Fig. 6). In Table 4, the element and atom weight percentages in the CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10% specimens are summarized.

Ca weight percentage in the CFA - C40% specimen was 1.74-2.56 times that in the CFA100%, CFA-G10%, and CFA-WTR10% specimens, while atom percentage in the CFA-C40% specimen was 1.71-2.78 times compared with that in the CFA100%, CFA-G10%, and CFA-WTR10% specimens. This is attributed to the Ca content in the CFA-C40% specimen being higher because 40 wt% of fly ash was replaced by cement which had a higher Ca content. Ca source is another factor in addition to Ca content that affects the reaction products. Ca in cement, thermally treated FGD-gypsum and water treatment residual, is in the form of dicalcium silicate and tricalcium silicate, calcium sulfate, and calcium oxide, respectively (Fig. 1). Different minerals have different activations and interactivity during alkali activation. Microstructure of alkali-activated fly ash changes with chemical composition. Calcium silicate hydrate (C-S-H) is a gel of hydrated CaO-SiO_2 , which is normally non-stoichiometric. It is generally agreed that C-S-H gel is the main component that contributes to the mechanical strength of cement.²² In contrast, the formation of the three-dimensional amorphous alkali aluminosilicate network with a general formula of $(\text{Na/K})_m\text{-}[\text{-Si-O}_2\text{]}_z\text{-Al-O]}_n\cdot\text{wH}_2\text{O}$ (m is the alkaline element, z is 1, 2, or 3 and n is the degree of polycondensation) is often argued to be the phase that contributes to the binding property of geopolymeric gels.⁹ It is anticipated that if enough Ca is added to a geopolymeric system, some forms of C-S-H gel will be obtained instead. If the products are aluminosilicate network geopolymeric materials, the ratio of Si/Al should be 1, 2 or 3. The Si/Al ratios in the CFA100%, CFA-G10%, and CFA - WTR10% specimens were 3.15, 2.62 and 2.78. Thus, the main products in these specimens are geopolymeric materials, and Ca participates in geopolymerization to

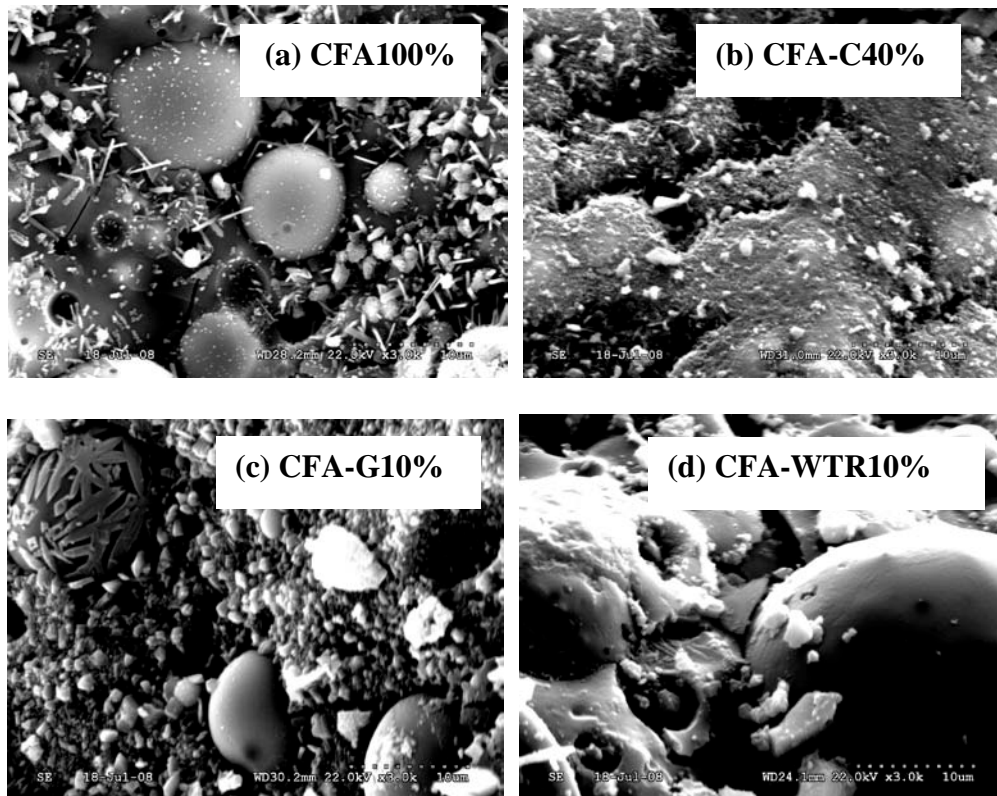


Fig. 5. Scanning electron microscope (SEM) pictures of alkali-activated complex binders of high-Ca fly ash and other Ca-bearing materials cured at 75°C for 8 h, followed by 23°C for 28 d. The CFA100% specimen is made only from high-Ca fly ash (Table 2, Specimen 1), the CFA-C40% specimen is produced from 60% fly ash and 40% cement (Table 2, Specimen 5), the CFA-G10% specimen is prepared from 90% fly ash and 10% FGD-gypsum (Table 2, Specimen 7), and the CFA-WTR10% specimen is created from 90% fly ash and 10% water treatment residual (Table 2, Specimen 12).

obtain charge balance. However, in the CFA-C40% specimen, this Si/Al ratio is 4.27 and indicates that the C-S-H gel and the geopolymeric gel are formed simultaneously within a single system of the CFA-C40% specimen. The Ca, on the one hand, participates in geopolymerization to obtain charge balance while, on the other hand, takes part in hydration reactions to form hydrated products.

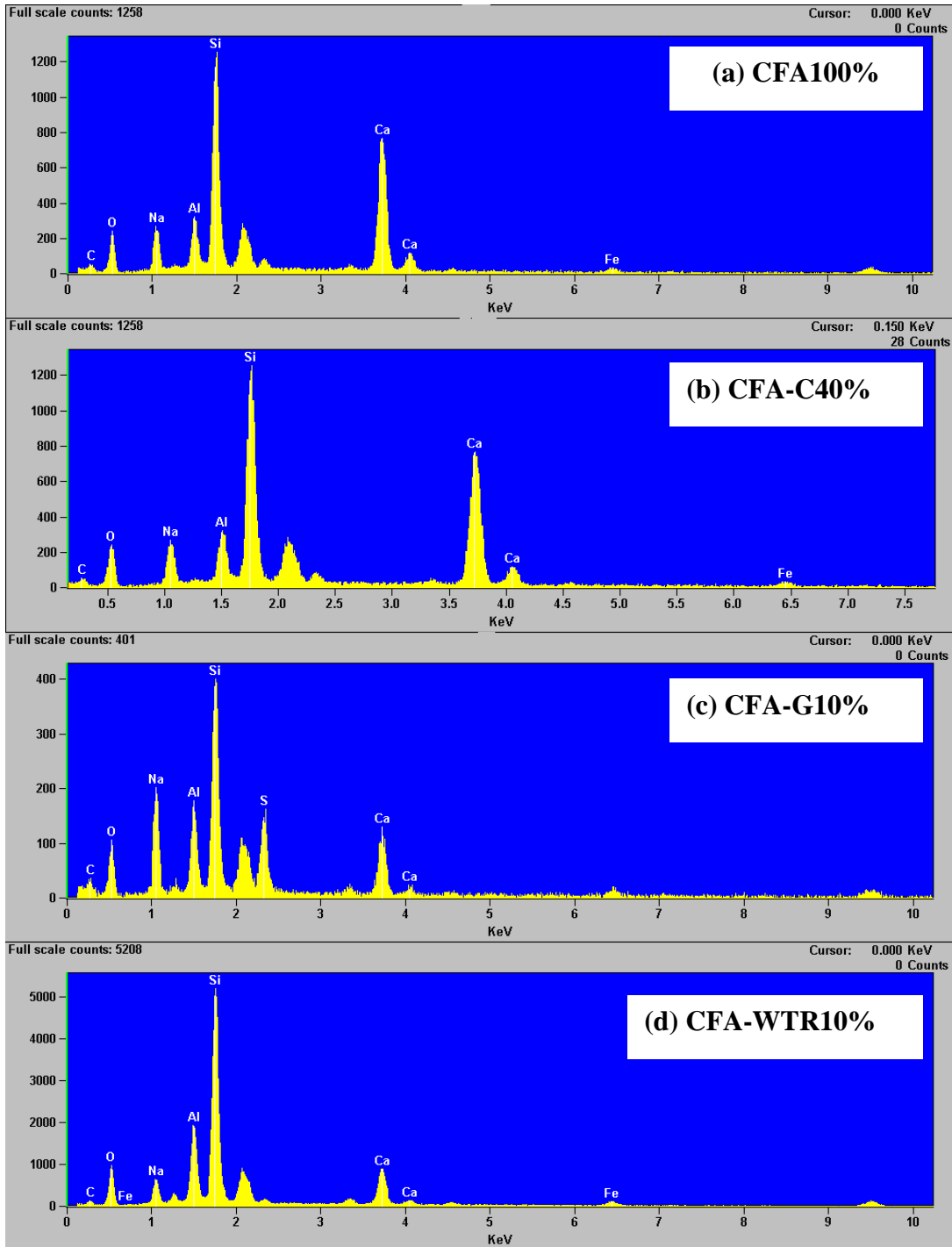


Fig. 6. Energy dispersive X-ray analysis (EDXA) pictures. The CFA100% specimen is made only from high-Ca fly ash (Table 2, Specimen 1), the CFA-C40% specimen is produced from 60% fly ash and 40% cement (Table 2, Specimen 5), the CFA-G10% specimen is prepared from 90% fly ash and 10% FGD-gypsum (Table 2, Specimen 7), and the CFA-WTR10% specimen is created from 90% fly ash and 10% water treatment residual (Table 2, Specimen 12).

Table 4. Element analysis of specimens. The CFA100% specimen is made only from high-Ca fly ash (Table 2, Specimen 1), the CFA-C40% specimen is produced from 60% fly ash and 40% cement (Table 2, Specimen 5), the CFA-G10% specimen is prepared from 90% fly ash and 10% FGD-gypsum (Table 2, Specimen 7), and the CFA-WTR10% specimen is created from 90% fly ash and 10% water treatment residual (Table 2, Specimen 12).

Element	CFA100%		CFA-C40%		CFA-G10%		CAF-WTR10%	
	Wt.%	Atom %	Wt.%	Atom %	Wt.%	Atom %	Wt.%	Atom %
C	5.24	9.50	7.80	13.91	12.83	21.01	6.03	10.59
O	34.25	46.58	35.30	47.26	34.72	42.69	36.33	47.91
Na	6.58	6.23	6.84	6.37	12.01	10.27	4.73	4.35
Mg	1.25	1.11	0.09	0.08	0.39	0.32	0.79	0.69
Al	8.22	6.63	4.67	3.71	7.18	5.24	10.39	8.12
Si	27.00	20.91	20.76	15.83	19.59	13.72	30.06	22.59
S	0.98	0.67	0.35	0.24	3.30	2.02	0.00	0.00
Ca	12.72	6.91	22.07	11.79	8.63	4.24	9.11	4.80
Fe	3.76	1.46	2.11	0.81	1.35	0.48	2.56	0.97
Total	100.00	100.00	99.99	100.00	100.00	99.99	100.00	100.02

4. CONCLUSION

In this paper, alkali-activated complex binders of class C fly ash with high-Ca (CFA), and other Ca-bearing materials including cement (C), FGD-gypsum (G), and water treatment residual (WTR), were studied. Compressive strength, activities of raw materials blends, and synthesized products were studied.

1. Alkali-activated complex binder specimens which are made from 100 wt% high-Ca fly ash (CFA100%), fly ash with 40 wt% cement (CFA-C40%), fly ash with 10 wt% of flue gas desulfurization (FGD) gypsum (CFA-G10%), and fly ash with 10 wt% water treatment residual (CFA-WTR10%) obtained better mechanical performance compared with the specimens using other mix ratios.

2. Comparing the CFA100%, CFA-G10%, and CFA-WTR10% specimens, the raw materials blends of CFA-C40% show less Si and Al content but more Ca content in the NaOH leaching solution. At 23 °C, Al leaching content from all specimens is increased with leaching time from 1 h to 24 h, but Ca leaching content is decreased except for CFA-C40% specimen. At 75 °C, the concentration of the leached Si is higher at 24 h than that at 1 h. However, Al and Ca are lower at 24 h than that at 1 h. There was no clear relationship between the Ca sources and the extent of dissolution of Ca. Also,

there is no clear correlation between the concentration of Ca and the concentrations of Si and Al at any given condition.

3. Most of the activated products of the CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10% specimens were in the non-crystalline state or amorphous as X-ray diffraction analysis showed a broad diffuse halo in $20-40^\circ$ (2-Theta).

4. The main peaks occurring in the Fourier transform infrared spectra of the CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10% specimens are attributed to asymmetric stretching of Al-O/Si-O bonds and to a Si-O-Si bending band. These bonds indicated of the degree of amorphization of the reactive products. The broad bands in the region of $1648-3500\text{ cm}^{-1}$ characterize the spectrum of stretching and deformation modes of the adsorbed water.

5. Synthesis products of the CFA100%, CFA-C40%, CFA-G10%, and CFA-WTR10% specimens were amorphous and found to surround the spherical fly ash particles. There is still unreacted spherical fly ash in the specimens, but for the CFA-C40% specimen, there is almost no raw fly ash observed. The main products of the CFA100%, CFA-G10%, and CFA-WTR10% specimens are geopolymeric materials. However, in the CFA-C40% specimen, calcium silicate hydrate (C-S-H) gel and geopolymeric gel are formed simultaneously within a single system.

Utilization of high-Ca fly ash and other Ca-bearing materials in alkali-activated complex binders is feasible. Additionally, compared to Portland cement, producing alkali-activated complex binders can save natural resources and energy, and also reduce the release of greenhouse gases. These complex binders can be widely utilized in various applications such as in building materials and solidification/stabilization materials.

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REFERENCES

- [1] Buchwald, A., Hilbig, H., and Kaps, C. J. Mater. Sci., 2007, 42, p.3024.
- [2] Fernánde z-Jime ´nez, A. and Palomo, A. Fuel, 2003, 82, p.2259.
- [3] American Society for Testing and Materials (ASTM). www.astm.org, 2005.
- [4] Shi, J.W., Chen, S.H., Wang, S.M., and Xu, G.H. Chin. J. Chem. Ind. Eng. Process., 2008, 27, p.326.

- [5] Wang, J., Ban, H., and Teng, X. Chemosphere, 2006, 64, p.1892.
- [6] Xia, C., He, X., and Li, Y. Technol. Equip. Environ. Pollut. Control., 2000, 2, p.82.
- [7] Van Deventer, J.S.J., Provis, J.L., Duxson, P., and Lukey, G.C. J. Hazard Mater., 2007, 139, p.506.
- [8] Yip, C.K., Lukey, G.C., Provis, J.L., and Van Deventer, J.S.J. Cem. Concr. Res., 2008, 38, p.554.
- [9] Davidovits, J. and Therm, J. Analysis, 1991, 37, p.1633.
- [10] Lee, S.K. and Stebbins, J.F. Am. Mineral, 1999, 84, p.937.
- [11] Provis, J.L., Duxson, P., Lukey, G.C., and Van Deventer, J.S.J. Chem. Mater., 2005, 17, p.2976.
- [12] Xu, H. and Van Deventer, J.S.J. Int. J. Miner. Process., 2000, 59, p.247.
- [13] Provis, J.L. and Van Deventer, J.S.J. Chem. Eng. Sci., 2007, 62, p.2318.
- [14] Khale, D. and Chaudhary, R. J. Mater. Sci., 2007, 42, p.729.
- [15] Phair, J.W. and Van Deventer, J.S.J. Int. J. Miner. Process., 2002, 66, p.121.
- [16] Zhang, Y.S., Sun, W., Chen, Q.L., and Chen, L. J. Hazard Mater., 2007, 143, p.206.
- [17] Palomo, A. and Lo ´pez de la Fuente, J.I. Cem. Concr. Res., 2003, 33, p.281.
- [18] A. Palomo, M. Palacios, Cem. Concr. Res., 2003, 33, p.289.
- [19] Zhang, J.G., Provis, J.L., Feng, D.W., and Van Denventer, J.S.J. J. Hazard Mater., 2008, 157, p.587.
- [20] Palomo, A., Grutzeck, M.W., and Blanco, M.T. Cem. Concr. Res., 1999, 29, p.1323.
- [21] Swanepoel, J.C. and Strydom, C.A. Appl. Geochem., 2002, 17, p.1143.
- [22] Taylor, H.F.W. Cement Chemistry, 2nd edn., Thomas Telford, 1997.