

Alkali-activated complex binders from class C fly ash and Ca-containing admixtures

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ABSTRACT

Processes that maximize utilization of industrial solid wastes are greatly needed. Sodium hydroxide and sodium silicate solution were used to create alkali-activated complex binders (AACBs) from class C fly ash (CFA) and other Ca-containing admixtures including Portland cement (PC), flue gas desulfurization gypsum (FGDG), and water treatment residual (WTR). Specimens made only from CFA (CFA100), or the same fly ash mixed with 40 wt% PC (CFA60–PC40), with 10 wt% FGDG (CFA90–FGDG10), or with 10 wt% WTR (CFA90–WTR10) had better mechanical performance compared to binders using other mix ratios. The maximum compressive strength of specimens reached 80.0 MPa. Geopolymeric gel, sodium polysilicate zeolite, and hydrated products coexist when AACB reactions occur. Ca from CFA, PC, and WTR precipitated as $\text{Ca}(\text{OH})_2$, bonded in geopolymers to obtain charge balance, or reacted with dissolved silicate and aluminate species to form calcium silicate hydrate (C–S–H) gel. However, Ca from FGDG probably reacted with dissolved silicate and aluminate species to form ettringite. Utilization of CFA and Ca-containing admixtures in AACB is feasible. These binders may be widely utilized in various applications such as in building materials and for solidification/stabilization of other wastes, thus making the wastes more environmentally benign.

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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. 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, the amount of fly ash produced is about 2 billion mt annually with less than half (47.1%) being used [1–3]. Approximately 65.0 million t of fly ash were produced in the United States in 2007 with a utilization rate of approximately 44% [4]. There is thus a great need to develop new and beneficial uses of fly ash.

Alkali-activated complex binders (AACBs) are a developing field of research for utilizing solid wastes and by-products. Geopolymers, a type of AACB, are materials analogous to organic materials

that react at ambient temperature to form solid polymers [5]. The prefix “geo” refers to the inorganic nature of the material. Geopolymerization is a chemical process that provides a rapid transformation of some geopolymeric structures to create products that are either partially or totally amorphous and/or meta-stable. In general, two types of cementitious raw materials can be used for geopolymerization—those based on Si and Ca or those based on Si and Al [6].

Fly ash is produced by burning pulverized coal and is classified into two classes according to ASTM C618 [7]—class F fly ash (FFA) and class C fly ash (CFA). Class F fly ash is produced from burning anthracite and bituminous coals. It contains siliceous or siliceous and aluminous materials, which possess 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 [8,9].

Fly ash is one of the important source materials for AACB and both FFA and CFA contain a reasonable amount of silica and alumina. Currently, FFA is most commonly used in the synthesis of these binders. From a compositional viewpoint, the only significant difference between these two fly ashes is that CFA contains higher

Abbreviations: AACB, alkali-activated complex binders; CFA, class C fly ash; FFA, class F fly ash; PC, portland cement; FGDG, flue gas desulfurization gypsum; WTR, Water treatment residual; C–S–H, calcium silicate hydrate; XRD, X-ray diffraction; FTIR, Fourier transform infrared spectroscopy; SEM-EDXA, scanning electron microscope-energy dispersive X-ray analysis.

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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
Class C fly ash (CFA)	38.0	19.0	9.00	5.00	20.0	3.00	0.40	1.00	3.50	98.9
Portland cement (PC)	20.6	5.00	2.80	2.70	63.2	–	1.10	0.50	3.60	99.5
Flue gas desulfurization gypsum (FGDG)	–	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

amounts of Ca than FFA. Indeed, CFA could be viewed as compositionally in between FFA and ground granulated blast furnace slag. The fact that the mixes of the blast furnace slag and FFA are often preferred in the production of AACB also suggests an indication of the potential of using CFA to create geopolymers [10,11]. Alkali activation of fly ash can be divided into three consecutive stages [6]: (1) decomposition–coagulation; (2) coagulation–condensation; (3) condensation–crystallization. When CFA is the main material for preparing AACB, the role of Ca during this process is of significant practical interest [12].

There have been few published papers on using CFA to create AACB [8,13]. We have also conducted work in our laboratory showing that creation of AACB from CFA and WTR is feasible and could result in savings of natural resources and energy, and reduce the release of greenhouse gases [14]. In this paper, additional Ca-containing admixtures (Portland cement–PC, flue gas desulfurization gypsum–FGDG, and water treatment residuals–WTR) were replaced with CFA to synthesize AACB using a mixed alkali activator of sodium hydroxide and sodium silicate solution.

2. Experimental procedures

2.1. Materials

Class C fly ash was obtained from the First Energy Corporation (OH, USA). Type 1 Portland cement was purchased as commercial cement. Flue gas desulfurization gypsum was obtained from the Cinergy Corporation (Cincinnati, OH, USA) and WTR from a local water treatment plant (Sidney, OH, USA). Two different alkali activators, sodium silicate solution and sodium hydroxide, were commercial products from Fisher Company. The amount of the original sodium silicate in solution was 38.3% (w/w) while water content was 61.7% (w/w). 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 SiO₂/Na₂O.

Flue gas desulfurization gypsum generated from wet-type scrubbing process is often wet and viscous. The air-dried WTR also contain about 35 wt% of water. To dry these raw materials and create activated powders, they must be dried and thermally treated before use. The FGDG and WTR were air-dried first and then baked in a muffle furnace for 1 h at 800 and 900 °C, respectively. The chemical and mineral compositions of raw materials are summarized in Table 1. Mineral compositions of FGDG and WTR were analyzed by X-ray diffraction (XRD) (Fig. 1).

2.2. 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 [12]. At temperatures of 23 or 75 °C, the ratio of volume (in mL) of 5 mol/L NaOH solution to mass (in g) of complex raw material blends was 4:1. The suspensions were shaken at 250 rpm for 1 or 24 h. The suspensions were then centrifuged and filtered (0.2 μm Minisart membrane filter). The concentrations of Al, Si, and Ca in leachates were analyzed by inductively coupled plasma atomic emission spectrometry.

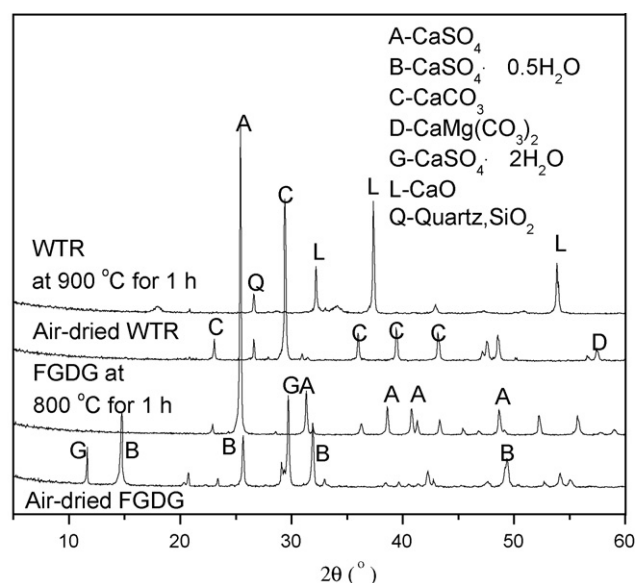


Fig. 1. Mineral compositions of air-dried and thermally treated flue gas desulfurization gypsum (FGDG) (800 °C for 1 h) and water treatment residual (WTR) (900 °C for 1 h).

2.3. Specimen preparation for mechanical test

Class C fly ash was the main aluminosilicate resource in this study and it was systematically replaced in specimen samples by different amounts of PC, FGDG, and WTR at ratios of 10–50 wt% (Table 2). The amount of the mixed alkali activator was evaluated

Table 2

Mix ratios of alkali-activated complex binders (AACB) of class C fly ash (CFA) and Ca-bearing admixtures.

Specimen number	Specimen code ^a	Class C fly ash (CFA) (%)	Admixture and its content ^b (%)
1	CFA100	100	0
2	CFA90–PC10	90	PC, 10
3	CFA80–PC20	80	PC, 20
4	CFA70–PC30	70	PC, 30
5	CFA60–PC40	60	PC, 40
6	CFA50–PC50	50	PC, 50
7	CFA90–FGDG10	90	FGDG, 10
8	CFA80–FGDG20	80	FGDG, 20
9	CFA70–FGDG30	70	FGDG, 30
10	CFA60–FGDG40	60	FGDG, 40
11	CFA50–FGDG50	50	FGDG, 50
12	CFA90–WTR10	90	WTR, 10
13	CFA80–WTR20	80	WTR, 20
14	CFA70–WTR30	70	WTR, 30
15	CFA60–WTR40	60	WTR, 40
16	CFA50–WTR50	50	WTR, 50

^a Specimen codes are defined as follows: CFA is class C fly ash, PC is the type I Portland cement, FGDG is flue gas desulfurization gypsum, and WTR is water treatment residual. The numbers following CFA are the percentages of the fly ash in the specimen and the numbers following PC, FGDG, and WTR are the percentages of the fly ash in the specimen replaced by these materials.

^b The abbreviations in this column are the same as in the specimen code column.

by maintaining the amount of Na_2O in the blend equal to 10 wt%. For all the specimens, the water to solid ratio was maintained at 0.4. The water included both the water in the mixed alkali activator and the distilled water added. The paste was poured into molds of 20 mm × 20 mm × 20 mm to make cubic specimens. One batch of these specimens was cured at 75 °C for 4, 8, and 24 h and another batch was cured at 23 °C for 3, 7, and 28 d. The compressive strength of these two batches of specimens was tested at each curing age. All the values are the averages of four separate tests. Data that deviated from the mean by more than 10% were eliminated, but this occurred only rarely.

2.4. Methods for analysis of synthesized products

The synthesized products of CFA and Ca-containing admixtures were analyzed using XRD, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope-energy dispersive X-ray analysis (SEM-EDXA). The specimens used in this part of the study 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 XRD. For FTIR analysis, the powder specimens were mixed with KBr at a concentration of 0.2–1 wt% to make the KBr disks. Then the disks were tested using a Perkin Elmer FTIR spectrometer. For SEM-EDXA, the crushed specimens were mounted on Al-stubs with double-sided carbon tabs and coated with a thin layer of platinum in a Hummer 6.2 Sputter Coater. Magnification for the SEM-EDXA analysis was 3000 times and working voltage was 20 kV. The SEM-EDXA data were collected using Hitachi S-3500N and Noran EDXA equipment.

3. Results and discussion

3.1. Activities of complex raw material blends of class C fly ash (CFA) and Ca-containing admixtures

Measuring the dissolution content of Si, Al, and Ca from the aluminosilicate resource (CFA in this case) and Ca-containing admixtures (PC, FG DG, and WTR) under alkali condition will aid in the estimation of reaction products. Table 3 presents the leaching concentrations of Si, Al and Ca from each blend of raw materials after 1 or 24 h contact with NaOH solution at 23 or 75 °C. The dissolution of Si, Al, and Ca governs the initial stage of reactivity [15–17]. This initial stage of reactivity involves geopolymerization and hydration reactions.

Table 3
Concentrations of Si, Al, and Ca from each blend of raw materials after leaching for 1 or 24 h at either 23 or 75 °C.

Specimen	23 °C		75 °C	
	1 h	24 h	1 h	24 h
Si (mg/L)				
CFA100	1230	1080	2880	7540
CFA60–PC40	769	494	1440	2490
CFA90–FGDG10	1410	1690	2600	5970
CFA90–WTR10	1230	1300	2590	3620
Al (mg/L)				
CFA100	1270	2150	3180	312
CFA60–PC40	181	415	1350	169
CFA90–FGDG10	1130	1910	3180	67.6
CFA90–WTR10	1080	1870	3070	430
Ca (mg/L)				
CFA100	8.89	3.16	1.91	1.86
CFA60–PC40	8.71	11.9	7.83	0.03
CFA90–FGDG10	8.42	5.75	4.74	0.03
CFA90–WTR10	8.65	5.46	3.79	1.86

The formation of a geopolymeric gel depends on the availability of dissociated Si monomer $[\text{SiO}_n(\text{OH})_{4-n}]^{n-}$ and Al monomer $\text{Al}(\text{OH})_4^-$ in the alkaline medium, which is further dependent on the extent of dissolution of these two species from the original aluminosilicate source. At 23 °C, the Si and Al concentration in specimens of CFA100, CFA90–FGDG10, and CFA90–WTR10 were high and their contents were increased with leaching time from 1 to 24 h. This indicates that the main product of these specimens is probably a geopolymeric gel. At 75 °C, the concentrations of the leached Si and Al are 1.8–2.8 times higher than at 23 °C. This suggests that elevated curing temperatures can increase the geopolymeric reactions. In contrast, the CFA60–PC40 specimen had less Si and Al concentrations in the leaching solution compared to other specimens of CFA100, CFA90–FGDG10, and CFA90–WTR10. This is because in the CFA60–PC40 specimen, the leached Si and Al are quickly consumed when Ca species from cement are hydrated. Thus, it is possible that the geopolymeric gel and hydrated product of calcium silicate hydrate (C–S–H) can coexist.

In the presence of soluble Ca species, the governing reactions become more complex. Table 3 also indicates a relationship between the Ca sources and its extent of dissolution. Ca species in CFA, PC, WTR were mainly calcium oxide, dicalcium silicate and tricalcium silicate while Ca in FG DG was in the form of calcium sulfate. All of these Ca species are soluble. Therefore, the initial leaching concentrations of Ca from the complex raw material blends (CFA100, CFA60–PC40, CFA90–FGDG10, and CFA90–WTR10) were similar and ranged from 8.42–8.89 mg/L. However, the trends changed with increased leaching time. Ca leaching content was decreased except for the CFA60–PC40 specimen. Ca species of oxides and silicate minerals from CFA, PC, and WTR could either (1) precipitate as $\text{Ca}(\text{OH})_2$, (2) be bonded in geopolymeric gel by replacing cations within the geopolymer or (3) react with dissolved silicate and aluminate species to form C–S–H gel. Additionally, Ca in the form of sulfate from FG DG may also react with dissolved silicate and aluminate species to form the hydrated product, ettringite. At 75 °C compared to 23 °C, the concentrations of the leached Ca in all specimens were lower at both 1 and 24 h. It is because Ca solubility is decreased at higher temperatures.

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.

3.2. Synthesized products analysis

3.2.1. Compressive strength

Compressive strengths of alkali-activated 100 wt% CFA (CFA100) specimens were 30.6, 35.6, and 38.8 MPa after curing at 75 °C for 4, 8, and 24 h, respectively. When specimens were cured at 23 °C for 3, 7, and 28 d, the compressive strength values were 22.6, 34.5, and 59.3 MPa, respectively. When fly ash was partially replaced by PC, FG DG, and WTR, changes of compressive strength were as shown in Fig. 2. Specimens made from PC and CFA exhibited improved compressive strengths (Fig. 2A) after curing for 4–24 h at 75 °C. This improved performance was especially noticeable with the specimen containing 40 wt% PC cured for 8 h at 75 °C (CFA60–PC40, Specimen 5 in Table 2) where the compressive strength value reached 80.0 MPa. Specimens made from PC and CFA and cured at 23 °C for 3–28 d had compressive strengths that were enhanced by increasing the PC content from 10 to 40 wt% (Fig. 2B). When fly ash was partially replaced by FG DG or WTR, and curing occurred at 75 and 23 °C, compressive strengths were decreased (Fig. 2C–F).

According to the compressive strength results obtained for each batch of specimens, the proper mix ratios for CFA and Ca-containing admixtures were determined. Specimens containing 100 wt% CFA (CFA100, Specimen 1 in Table 2), CFA with 40 wt% PC (CFA60–PC40, Specimen 5 in Table 2), CFA with 10 wt% of FG DG (CFA90–FGDG10,

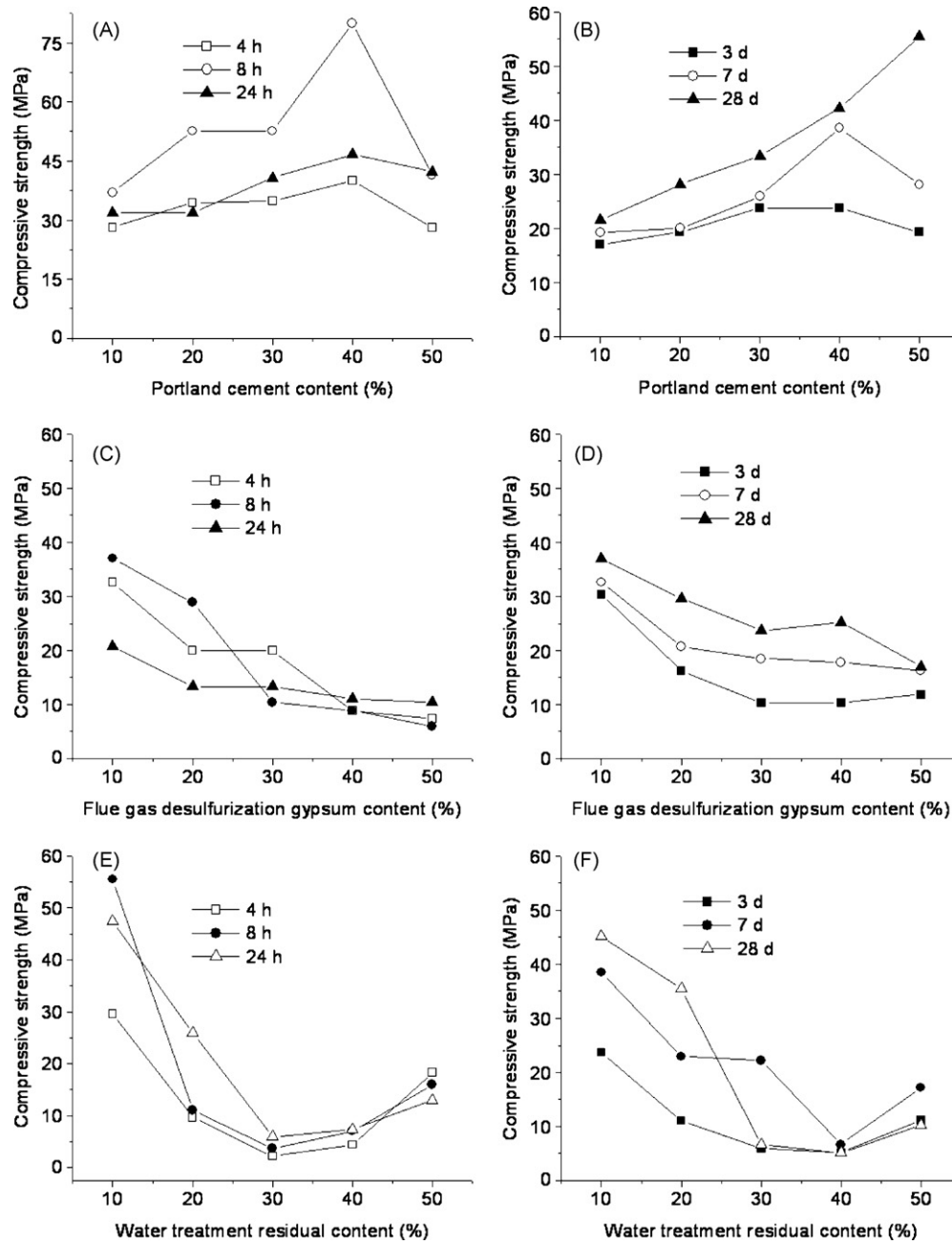


Fig. 2. Compressive strengths of alkali-activated complex binders made from class C fly ash mixed with different amounts of (A) Portland cement and the specimens cured at 75 °C for 4–24 h; (B) Portland cement and the specimens cured at 23 °C for 3–28 d; (C) flue gas desulfurization gypsum and the specimens cured at 75 °C for 4–24 h; (D) flue gas desulfurization gypsum and the specimens cured at 23 °C for 3–28 d; (E) water treatment residual and the specimens cured at 75 °C for 4–24 h; (F) water treatment residual and the specimens cured at 23 °C for 3–28 d.

Specimen 7 in Table 2), and CFA with 10 wt% WTR (CFA90–WTR10, Specimen 12 in Table 2) had better mechanical performance compared with the specimens using other mix ratios. Microstructures and performance of CFA100, CFA60–PC40, CFA90–FGDG10, and CFA90–WTR10 were thus further studied in these specimens in several additional experiments.

3.2.2. X-ray diffraction (XRD)

The XRD patterns of AACB cured at 75 °C for 8 h, followed by 23 °C for 28 d were obtained. In all XRD patterns of AACB, peaks due to the crystalline components of quartz (SiO_2) from the fly ash were evident (Fig. 3). A type of sodium polysilicate zeolite ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) was also observed in the XRD pattern. The degree of disorder can be inferred by the way the specimen diffracts

the X-rays to form a diffraction pattern. For all specimens, diffraction of X-rays resulted in a broad, diffuse halo rather than sharp diffraction peaks from 20° to 40° (2θ). This indicates that a large part of the structure in these specimens was attributed to the amorphous or non-crystalline state. In the CFA100 and CFA60–PC40 specimens, the broad halo represents geopolymeric and C–S–H gels. When WTR and FGDS were added, the products were mainly geopolymeric gel. CaSO_4 and CaCO_3 were also evident in the specimens of CFA90–FGDG10 and CFA90–WTR10, respectively.

3.2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR absorption spectroscopy is well known for its sensitivity in characterizing materials with short-range structural order, and has been useful for characterizing alkali-activated materials.

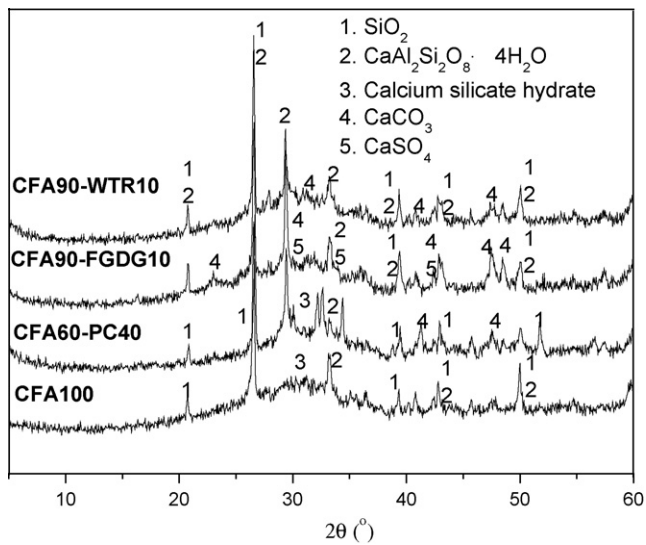


Fig. 3. X-ray diffraction (XRD) of alkali-activated complex binders of class C fly ash (CFA) and Ca-bearing admixtures cured at 75 °C for 8 h, followed by 23 °C for 28 d. The CFA100 specimen is made only from CFA (Table 2, Specimen 1), the CFA60–PC40 specimen is produced from 60% CFA and 40% cement (Table 2, Specimen 5), the CFA90–FGDG10 specimen is prepared from 90% CFA and 10% flue gas desulfurization gypsum (Table 2, Specimen 7), and the CFA90–WTR10 specimen is created from 90% CFA and 10% water treatment residual (Table 2, Specimen 12).

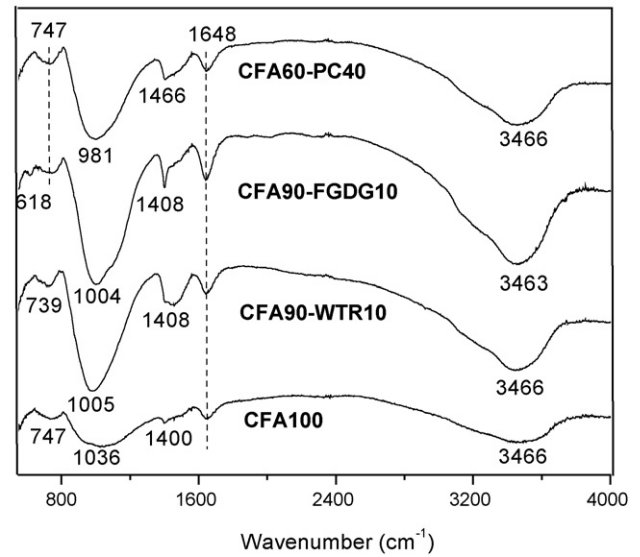


Fig. 4. Fourier transform infrared spectroscopy (FTIR) of alkali-activated complex binders of class C fly ash (CFA) and Ca-bearing admixtures cured at 75 °C for 8 h, followed by 23 °C for 28 d. The CFA100 specimen is made only from CFA (Table 2, Specimen 1), the CFA60–PC40 specimen is produced from 60% CFA and 40% cement (Table 2, Specimen 5), the CFA90–FGDG10 specimen is prepared from 90% CFA and 10% flue gas desulfurization gypsum (Table 2, Specimen 7), and the CFA90–WTR10 specimen is created from 90% CFA and 10% water treatment residual (Table 2, Specimen 12).

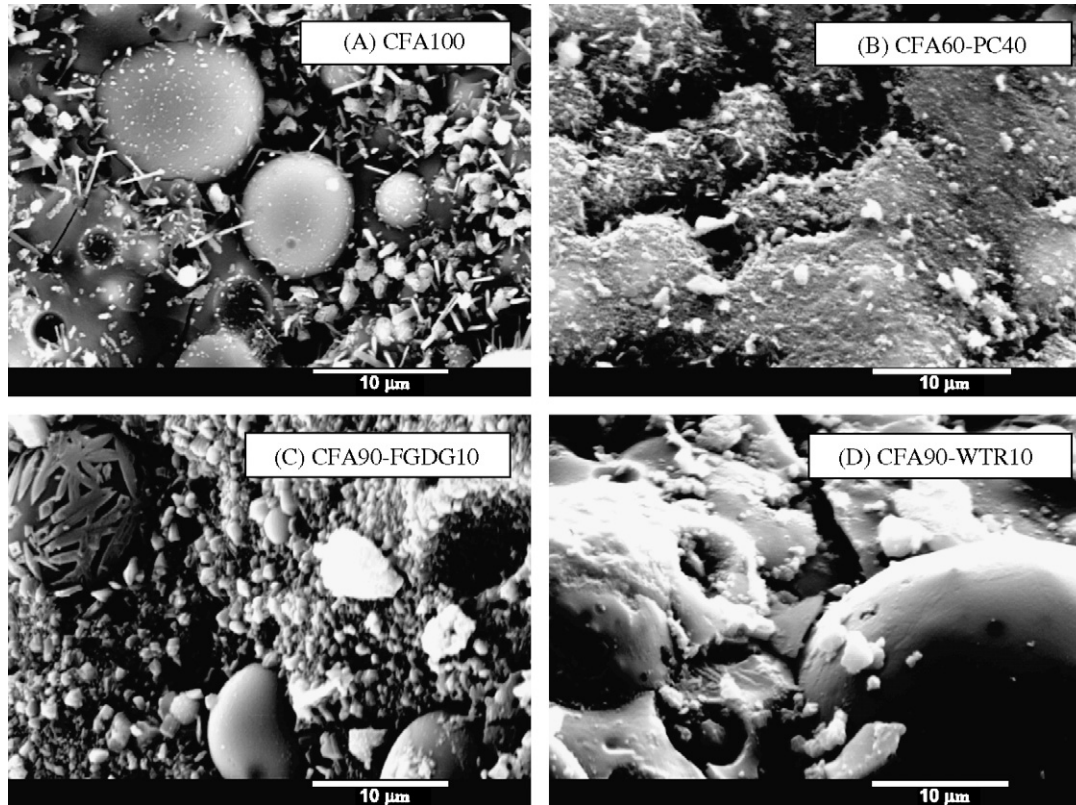


Fig. 5. Scanning electron microscope (SEM) images of alkali-activated complex binders of class C fly ash (CFA) and Ca-bearing admixtures cured at 75 °C for 8 h, followed by 23 °C for 28 d. Magnification = 3000× and working voltage was 20 kV. The CFA100 specimen (A) is made only from CFA (Table 2, Specimen 1), the CFA60–PC40 specimen (B) is produced from 60% CFA and 40% cement (Table 2, Specimen 5), the CFA90–FGDG10 specimen (C) is prepared from 90% CFA and 10% flue gas desulfurization gypsum (Table 2, Specimen 7), and the CFA90–WTR10 specimen (D) is created from 90% CFA and 10% water treatment residual (Table 2, Specimen 12).

Table 4

Element analysis of specimens with concentrations given in weight % and atom %. The CFA100 specimen is made only from class C fly ash (CFA) (Table 2, Specimen 1), the CFA60–PC40 specimen is produced from 60% CFA and 40% Portland cement (Table 2, Specimen 5), the CFA90–FGDG10 specimen is prepared from 90% CFA and 10% flue gas desulfurization gypsum (Table 2, Specimen 7), and the CFA90–WTR10 specimen is created from 90% CFA and 10% water treatment residual (Table 2, Specimen 12).

Element	CFA100		CFA60–PC40		CFA90–FGDG10		CFA90–WTR10	
	Weight %	Atom %	Weight %	Atom %	Weight %	Atom %	Weight %	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

The main peaks in the region 981–1466 cm^{-1} were attributed to asymmetric stretching vibrations of Al–O/Si–O bonds, while the Si–O–Si/Si–O–Al bending band can be seen between 618 and 747 cm^{-1} (Fig. 4). These bands are common in ring silicates and provide an indication of the degree of amorphisation of the material, since its intensity does not depend on the degree of crystallization [18]. The Al–O/Si–O bonds at 1036 cm^{-1} of the CFA100 specimen became sharper and shifted towards the lower frequencies of 981–1005 cm^{-1} in the specimens of CFA60–PC40, CFA90–FGDG10, and CFA90–WTR10. All these shifts indicate that the addition of admixtures improved the reaction of the vitreous components of CFA with the mixed alkali activator to form the geopolymer [19]. The relationship between the Al–O, Si–O, Si–O–Si, or Si–O–Al peak positions and the extent of the geopolymerization process is complex, but very instructive in the study of the process of geopolymerization.

In all specimens, broad bands in the region of 1648–3500 cm^{-1} characterized the spectrum of stretching and deformation vibrations of OH and H–O–H group from the weakly bound water molecules which were adsorbed on the surface or trapped in the large cavities between the rings of geopolymeric products [20].

3.2.4. Scanning electron microscope-energy dispersive X-ray analysis (SEM-EDXA)

In SEM images of the CFA100, CFA90–FGDG10, and CFA90–WTR10 specimens, the spherical fly ash particles were located around the geopolymeric and hydrated products (Fig. 5A, C and D). When FGDG was added, a small quantity of lathy products on the surface of the spherical fly ash particle was observed. This is probably ettringite that formed from the reaction of Ca and the desolated Al and Si (Fig. 5C). Additionally, in the CFA100, CFA90–FGDG10, and CFA90–WTR10 specimens, there were spherical fly ash particles that have not entered into any reaction. However, for the CFA60–PC40 (Fig. 5B) specimen, there was almost no raw material existing in the image.

Further study was conducted by EDXA. The main elements in the products were Si, Al, Ca, Na, and O, with also some Fe, C, and S. In Table 4, the element and atom weight percentages in each specimen were summarized. Ca weight percentage in the CFA60–PC40 specimen was 1.74–2.56 times that in the CFA100, CFA90–FGDG10, and CFA90–WTR10 specimens, while atom percentage in the CFA60–PC40 specimen was 1.71–2.78 times that in the CFA100, CFA90–FGDG10, and CFA90–WTR10 specimens. This is attributed to the Ca content in the CFA60–PC40 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. As mentioned above, Ca in CFA, PC, FGDG and WTR was in the forms of calcium oxide, dicalcium silicate and

tricalcium silicate, and calcium sulfate. Different minerals have different activations and interactivity during alkali activation. Microstructures of AACB from CFA and Ca-containing admixtures changed with chemical compositions. C–S–H is a gel of hydrated CaO–SiO₂, which is normally non-stoichiometric [21]. In contrast, the formation of the three-dimensional amorphous geopolymeric gel with a general formula of (Na/K)_m–[–Si–O₂]_z–Al–O]_n·wH₂O (*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 [22]. 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, CFA90–FGDG10, and CFA90–WTR10 specimens were 3.15, 2.62 and 2.78. Thus, the products in these specimens could be mainly geopolymeric gel. On the other hand, there were also hydrated products. Ca from CFA and WTR precipitated as Ca(OH)₂, bonded in geopolymers to obtain charge balance, or reacted with dissolved silicate and aluminate species to form C–S–H gel. However, Ca from FGDG probably reacted with dissolved silicate and aluminate species to form the hydrated product, ettringite. In the CFA60–PC40 specimen, this Si/Al ratio is 4.27 and indicated that the C–S–H gel and the geopolymeric gel may be coexisting within this single system. In this case, the Ca both participated in geopolymerization and took part in hydration reactions.

4. Conclusion

Alkali-activated complex binders (AACB) from class C fly ash (CFA) and Ca-containing admixtures including Portland cement (PC), flue gas desulfurization gypsum (FGDG), and water treatment residual (WTR), were created. The maximum compressive strength of specimens reached 80.0 MPa. Geopolymeric gel, sodium polysilicate zeolite, and hydrated products (probably including calcium hydroxide, calcium silicate hydrate (C–S–H), or ettringite) coexist in this AACB reaction system. Ca from CFA, PC, and WTR precipitated as Ca(OH)₂, bonded in geopolymers to obtain charge balance, or reacted with dissolved silicate and aluminate species to form C–S–H gel. However, Ca from FGDG probably reacted with dissolved silicate and aluminate species to form a hydrated product, ettringite.

Utilization of CFA and Ca-containing admixtures to make AACB is feasible. These complex binders can be widely utilized in various applications such as in building materials and solidification/stabilization materials. Compared to Portland cement, producing AACB from industrial wastes can save natural resources.

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