

Research Article

Determination of Gel Products in Alkali-Activated Fly Ash-Based Composites Incorporating Inorganic Calcium Additives

Haoyu Wang ¹, Xianhui Zhao ^{2,3}, Ting Wang ¹, Lei Su ¹, Boyu Zhou ⁴,
and Yonghui Lin ^{4,5}

¹Department of Civil Engineering, Tianjin Ren'ai College, Tianjin 301636, China

²School of Civil Engineering, Hebei University of Engineering, Handan 056038, China

³Provincial Mechanics Experimental Teaching Demonstration Center, Hebei University of Engineering, Handan 056038, China

⁴School of Civil and Transportation Engineering, Hebei University of Technology, Tianjin 300401, China

⁵Department of Development and Domestic Cooperation, Hebei Normal University for Nationalities, Chengde 067000, China

Correspondence should be addressed to Xianhui Zhao; zhaoxianhui@hebeu.edu.cn

Received 1 September 2021; Revised 12 December 2021; Accepted 27 January 2022; Published 15 February 2022

Academic Editor: Sakar Mohan

Copyright © 2022 Haoyu Wang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The introduction of soluble calcium additives contributes to forming calcium-containing geopolymer (N,C)-A-S-H and/or calcium (alumino)silicate hydration C-(A)-S-H in alkali-activated fly ash-based composites (AAFCs). However, the quantitative determination of the final gel product has yet been unclear due to the different chemical components, which influences the prediction of mechanical strength and microstructure. This study aims to propose a method to clarify the gel products in AAFCs by the critical elemental compositions in gel products. Furthermore, the AAFCs were prepared (by casting method) using soda residue (SR) as the calcium additive, fly ash as the aluminosilicate precursor, and sodium silicate solution as the alkaline activator. The compressive strengths of the AAFCs with different SR contents were recorded. The microstructures and gel products of AAFCs were detected through scanning electron microscope (SEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and ²⁹Si nuclear magnetic resonance spectrometer (²⁹Si NMR). Finally, the proposed determination method was verified with the experimental results. The new proposed quantitative method refers to a limit value of 2Ca/Al = 1.00 about the critical chemical elements in gel products, which helps to determine the calcium-containing geopolymer (N,C)-A-S-H or/and calcium (alumino)silicate hydration C-(A)-S-H in stable AAFCs. Results show that the gel products are determined as single (N,C)-A-S-H gels when 2Ca/Al is lower than 1.00; meanwhile, (N,C)-A-S-H and C-(A)-S-H gels coexist when 2Ca/Al is higher than 1.00 by the above proposed quantitative determination method. Furthermore, it works that the industrial solid waste SRs regarded as calcium additive are applied in the AAFCs to verify the gel products by 2Ca/Al = 1.00 as the limit value. The results provide the theoretical and experimental basis for the performance prediction and microstructural determination.

1. Introduction

Geopolymer is detected as a network amorphous polymer gel with three-dimensional structure, and it is usually prepared using alkali-activated aluminosilicate materials. Moreover, the geopolymer possesses a more stable structure and higher mechanical properties than that of Ordinary Portland Cement (OPC) [1]. Nowadays, the aluminosilicate materials include two types of low calcium and high calcium. When low-calcium materials are employed, such as low-

calcium fly ash (CaO, <10%), metakaolin, and so on, the gel products obtained from alkali-activated composites are geopolymer gel N-A-S-H or calcium-containing geopolymer gel (N,C)-A-S-H [2]. And while high-calcium materials are employed, such as high-calcium fly ash (CaO, >10%) and blast furnace slag, and so on, the gel products turn to calcium (alumino) silicate hydration C-(A)-S-H [2]. In general, N-A-S-H and (N,C)-A-S-H gels have higher chemical bond energies and superior mechanical properties than those of C-(A)-S-H gels [3, 4], evenly higher strength [5] and higher

resistance to chemical attack [6]. The main gel product compositions directly affect the macroscopic properties and microstructures of alkali-activated aluminosilicate composites. Therefore, it is of great significance to clarify the gel products of alkali-activated aluminosilicate composites through a fast and convenient method.

Low-calcium fly ash (F class) is one of the more available aluminosilicate sources, and it possesses more referenced experimental results in the application of building materials. Usually, the low-calcium fly ash is gradually eroded and then geopolymerized to form polymeric gels when activated by high concentration of NaOH and/or Na₂SiO₃ solutions [3]. In particular, inorganic calcium additives affect the physical and mechanical properties and chemical products of alkali-activated fly ash-based composites (AAFCs) [7, 8]. The previous study reported that the proper dosage of inorganic calcium additives, such as CaO, Ca(OH)₂, CaCl₂, and so on, contributed to the property enhancement of AAFC [8]. The 0%, 1%, and 3% CaO were, respectively, incorporated as calcium additives to manufacture AAFCs by using F class fly ash and Na₂SiO₃ solution at room temperature. The results demonstrated that the glassy microspheres in fly ash dissolve with the increment of CaO, and the composites possessed more compact structure and higher compressive strength (up to 21.0 MPa) [9]. Moreover, as CaO content increased, the gel products in AAFCs varied from stage one (N-A-S-H) to stage two ((N,C)-A-S-H), and then to stage three (coexistence of (N,C)-A-S-H and C-(A)-S-H)), and finally came to stage four (mixture of C-A-S-H and C-S-H). The compressive strength in stage four (10.0 MPa) was less than that in stage three (40.0 MPa) [10]. Particularly, the apparent phase separation occurred at the coexistence stage of (N,C)-A-S-H and C-(A)-S-H [11], and the resistance to acid attack decreased due to C-A-S-H and/or C-S-H gels [6]. Considering the optimization of the mechanical and durability performances of AAFCs, it is of great theoretical significance to determine the critical calcium content about the phase transition point, where (N,C)-A-S-H changes into the coexistence of C-(A)-S-H and (N,C)-A-S-H. Currently, the gel products (geopolymer or coexistence with C-(A)-S-H) are distinguished by a series of microstructural and compositional characterization techniques (SEM, EDS, XRD, FTIR, etc.)

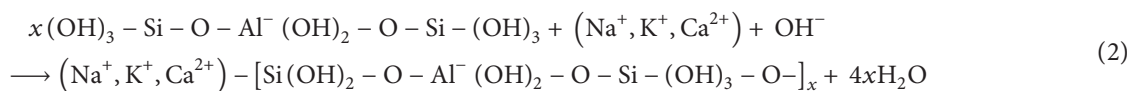
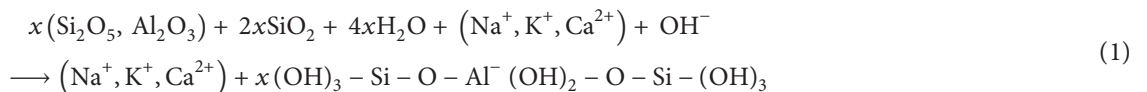
for AAFCs incorporating calcium additives. The current multitechnical characterization brings great inconvenience to product determination. No quantitative determination method is directly proposed based on the chemical components in products.

Furthermore, the soda residue (SR), from the chemically industrial Na₂CO₃ process, is a calcium-containing solid waste composed of Ca(OH)₂, CaCO₃, CaCl₂, and CaSO₄. Previous studies showed that SR improved the physical, mechanical, and microscopic properties of F class fly ash-based geopolymers [5]. The materials have the characteristics of early strength, low shrinkage, high porosity, and better compactness owing to the change of gel products. Therefore, it is of great significance that soda residue as an inorganic calcium additive is used to verify the gel products in AAFCs by chemical components considering the deeper recycling utilization of solid wastes.

The objective of this paper is to propose a determination method for the gel products of AAFCs incorporating inorganic calcium additives. The alkali-activated soda residue fly ash-based composites (pastes) were prepared to investigate the compressive strength. Furthermore, the microstructures and gel products were characterized by a series of advanced techniques (SEM-EDS, XRD, FTIR, and ²⁹Si NMR). The applicability of soda residue as a calcium additive was verified by the proposed determination method based on the ratio of calcium to aluminum. The results provide a theoretical basis for the application of many calcium-containing solid wastes in alkali-activated materials in a larger scale.

2. Determination of Gel Products in Alkali-Activated Fly Ash-Based Composites

2.1. Effect of Calcium Additives on the Geopolymeric Process. The chemical structural composition about the geopolymer gel was proposed as the following empirical expression: $M^+{}_x[-(\text{SiO}_2)_z-\text{AlO}_2]_x$, where M^+ refers to alkali metal cations (e.g., K⁺, Na⁺, Ca²⁺, etc.), x is a reaction parameter, and z is the Si/Al ratio (usually 1, 2, or 3) [9, 12]. The M^+ cations including Na⁺, K⁺, and Ca²⁺ play a role in balancing the negative charges caused by Al-O tetrahedrons in the structure, which keeps the microstructure stable and neutral [13, 14]. The geopolymeric processes are presented as the following formulae (1) and (2) [15–18]. x is a reaction parameter.



All of the above expressions support for the charge balance between Al and M^+ cations. Therefore, the equation

$(\text{Na} + \text{K} + 2\text{Ca})/\text{Al} = 1.00$ (atomic ratio, %) is always satisfied in the geopolymer gel owing to the divalent Ca²⁺. The equation

$(\text{Na} + \text{K} + 2\text{Ca})/\text{Al} = 1.00$ was verified in different AAFCs [15, 16]. Considering the lower calcium of F class fly ash in AAFCs, these results of Na/Al [19, 20], $(\text{Na} + \text{K})/\text{Al}$ [21], $(\text{Na} + \text{K} + \text{Ca})/\text{Al}$ [22], and $(\text{Na} + \text{K} + 2\text{Ca})/\text{Al}$ [15, 16] are very close to 1.00. The equation $(\text{Na} + \text{K} + 2\text{Ca})/\text{Al} = 1.00$ becomes the key elemental feature in the geopolymer gel of AAFCs.

The calcium additives affect the final products of AAFCs. The soluble calcium additives together with CaO in fly ash are dissolved as free Ca^{2+} in the high alkaline environment. It was revealed that the Al monomers (derived from the amorphous phases in fly ash) prefer to occur geopolymerization rather than undergo hydration reaction [16]. The free Ca^{2+} prefers to balance the negative charges in Si-O-Al bonds. However, as a cation of changing structure, the excessive Ca^{2+} makes the gel products form C-A-S-H or C-S-H (both are marked as C-(A)-S-H) that are directly probed by a series of testing techniques. The Al (mainly attributed to C-A-S-H and N-A-S-H gels) plays an essential role in the generation of Si-O-Al network. Furthermore, the free Ca^{2+} cations balance the negative charge prior to Na^+ and K^+ cations due to the smaller diameter [23, 24]. If excessive Ca^{2+} exists, some Ca^{2+} cations will participate in the geopolymerization, and while others will integrate with Si monomers to generate C-S-H gels.

If ensuring that all of Al take part in geopolymerization ($\text{Si}/\text{Al} > 1.00$), the elemental relationship among Na, K, Ca, and Al can be quantified. To determine and form the geopolymer gel, the calcium limits in the gel product satisfy formula (3) [16]:

$$\begin{aligned} \frac{2\text{Ca}}{\text{Al}} &< 1.00, \\ \frac{\text{Si}}{\text{Al}} &> 1.00, \end{aligned} \quad (3)$$

which are established based on the charge-balance equation $(\text{Na} + \text{K} + 2\text{Ca})/\text{Al} = 1.00$, whereas the formula $\text{Si}/\text{Al} > 1.00$ has usually been satisfied for the high-silicon fly ash (mainly Q_4^4 structure unit and $\text{Si}/\text{Al} = 1.00$ [5, 15] in geopolymer gels). Additionally, Somna et al. [25] and Rattanasak et al. [26] detected that the dissolution concentration of Al^{3+} was always less than that of Si^{4+} for different types of fly ash activated by different alkaline solutions. If Na or K-silicate is employed as an alkaline activator, the ions SiO_3^{2-} are added so that Si/Al is still higher than 1.00. Therefore, formula (3) is simplified as formula (4) [16]:

$$\frac{2\text{Ca}}{\text{Al}} < 1.00. \quad (4)$$

Reversely, the excessive cations Ca^{2+} ($2\text{Ca}/\text{Al} \geq 1.00$) are required for geopolymerization, and besides C-A-S-H or C-S-H gels are also formed in the products (here, both are marked as C-(A)-S-H). The theoretical formulae need to be further verified through simulation results and experimental results.

2.2. Verification by Molecular Dynamics Simulation. Molecular dynamics simulation technology can provide the convenient means to verify the above conclusions mentioned in Section 2.1. Wang et al. [27] used the simulation software (Material Studio) to construct the structural models of Na, Ca,

H_2O , OH, and $\text{Si}_2\text{AlO}_{10}$ (Si-Al-Si) in the Material Visualizer module, and the built structural models were geometrically optimized in the DMol³ module. The structural models of C-A-S-H, N-A-S-H, and the mixture were simulated. During simulation, the different Ca/Si and 2Ca/Al ratios of alkali-activated aluminosilicate composites were compared for the gel product compositions, structural features, and XRD patterns. Here, the Ca/Si ratio is 0.00, 0.20, 0.25, 0.33, 0.50, and 1.00 (corresponding to 0.00, 0.80, 1.00, 1.33, 2.00, and 4.00 in 2Ca/Al ratios), respectively (Table 1).

Under the premise of $\text{Si}/\text{Al} = 2.00$ and $(\text{Na} + 2\text{Ca})/\text{Al} \geq 1.00$ in each system, the gel products of low-calcium system ($\text{CaO} < 16.70\%$) are confirmed as N-A-S-H by $2\text{Ca}/\text{Al} < 1.00$. In the medium-calcium system ($\text{CaO} = 16.70\% \sim 21.00\%$), the products are the mixtures of C-A-S-H and N-A-S-H by $2\text{Ca}/\text{Al}$ from 1.00 to 1.33. Evenly, for the high-calcium system ($\text{CaO} \geq 30\%$), the product is the mixtures (N-A-S-H and main C-A-S-H) according to $2\text{Ca}/\text{Al} > 1.33$. Emphatically, $\text{Si}/\text{Al} = 2.00$ ensures that Al is totally involved in the reaction, and $(\text{Na} + 2\text{Ca})/\text{Al} \geq 1.00$ ensures the sufficient sodium alkaline solution [27]. These simulated results provide a theoretical support for the formulae in Section 2.1.

2.3. Proposal of the Quantitative Determination of Gel Products. For the AAFCs incorporating inorganic calcium additives, the quantitative determination of gel products is proposed based on the chemical components in products: $2\text{Ca}/\text{Al} < 1.00$ for a single geopolymer gel (also called “traditional geopolymer”), and but $2\text{Ca}/\text{Al} > 1.00$ for the co-existence of geopolymer gel and C-(A)-S-H gel (also called “modern geopolymer”). $2\text{Ca}/\text{Al} = 1.00$ is regarded as the transition value between the above two cases (Table 2).

The different contents of reagent $\text{Ca}(\text{OH})_2$ as additives were added into the AAFC in the previous research by Zhao et al. [15]. The $2\text{Ca}/\text{Al}$ values for reactants and products are shown in Figure 1(a). It is revealed that the gel products detected by experimental techniques are also completely consistent with the results calculated by the proposed determination method based on $2\text{Ca}/\text{Al}$ ratio in products. Therefore, it is effective to rapidly determine the gel products of the AAFC incorporating inorganic calcium additives by $2\text{Ca}/\text{Al}$ ratio in products. Rakhimova and Rakhimov [2] pointed out that the chemical distinctness and division using Ca and Al contents were made for alkali-activated materials, inorganic polymers, and geopolymers (Figure 1(b)). The geopolymer gel (called “traditional geopolymer”) is just a small fraction of alkali-activated materials according to their definition. Therefore, the boundary value of geopolymer gel is quantified about Ca and Al by using the established determination method (Table 2) for the chemical distinctness and division of gel products in AAFCs.

Rakhimova and Rakhimov [2] pointed out that the chemical distinctness and division using Ca and Al contents were made for alkali-activated materials, inorganic polymers, and geopolymers (Figure 1(b)). Therefore, Al content is a critical limit in geopolymers. Moreover, from Davidovits' point of view, geopolymer definition is first an inorganic gel product; namely, aluminosilicate precursors alkali-activated by strong alkaline solution (including alkali metal

TABLE 1: Elemental composition, structural characteristics, and product identification of alkali-activated aluminosilicate systems based on molecular dynamics simulation.

Name	CaO content ¹ (%)	Ca/Si	Si/Al	(Na + 2Ca)/Al	2Ca/Al	Gel products
No calcium	0.00	0.00	2.00	1.00	0.00	N-A-S-H
Low calcium	<16.70	<0.25	2.00	1.00~1.75	<1.00	N-A-S-H
Medium calcium	16.70~21.00	0.25~0.33	2.00	1.75~2.00	1.00~1.33	Mixture ²
High calcium	>30.00	>0.33	2.00	2.00	>1.33	Mixture ²
High calcium	>30.00	1.00	2.00	4.00	4.00	Mixture ²

¹CaO content refers to the mass percentage of CaO/(CaO + SiO₂ + Al₂O₃), (%). Data are from Wang et al. [27].

²Mixture refers to the coexistence of N-A-S-H and C-A-S-H.

cations Na⁺ or K⁺) generate 3D-network structure product with stable Si-O-Al chemical bonds [28]. After that, the structural alkali metal cations also include Ca²⁺ cation with the development of geopolymer.

In addition, the calcium components are not essential for the form of geopolymeric reaction, but they affect the final product compositions of AAFCS. The soluble calcium additives or CaO from fly ash are dissolved as free Ca²⁺ into the high-alkaline environment. And the amorphous phases in fly ash become Si and Al monomers by alkali activation. The Al monomers prefer to undergo geopolymerization rather than occur hydration [16]. The dissolved cations Ca²⁺ prefer to balance the negative charges in Si-O-Al bonds. But, as one of structure-changing cations, the excessive Ca²⁺ makes the gel products form C-A-S-H or C-S-H that are directly probed. The Al (mainly attributed to C-A-S-H and N-A-S-H gels) plays an essential role in the generation of Si-O-Al network bonds. Furthermore, the Ca²⁺ cations balance the negative charge prior to Na⁺ and K⁺ cations owing to the smaller cation's diameter [23, 24]. If the excessive Ca²⁺ cations exist, some Ca²⁺ cations will participate in the geopolymerization, while the others will combine with Si monomers to generate C-S-H gels.

If ensuring that all of Al take part in geopolymerization (Si/Al > 1.00), the elemental relationship among Na, K, Ca, and Al can be quantified. In order to determine and form the geopolymer gel, the calcium limit in the gel product satisfies the formulae 2Ca/Al < 1.00 based on the charge-balance equation.

3. Materials and Methods

Although the quantitative determination of the gel products is proposed, it still needs to be further verified by industrial solid wastes as inorganic calcium additives at a larger application scale. Here, the AAFCS incorporating industrial solid waste soda residues were manufactured by casting method and the formed gel products were characterized by a series of advanced chemical techniques.

3.1. Materials. The AAFCS were prepared using F class fly ash powder (FFA, aluminosilicate source), soda residue powder (SR, calcium additive), and Na₂SiO₃ solution (NS, alkaline activator).

3.1.1. Solid Powders (SR and FFA). The solid powders utilized to synthesize alkali-activated composites are SR (Sanyou Company, Tangshan, Hebei, China) and FFA (Sanyou Company, Tangshan, Hebei, China). The chemical

components of SR and FFA are tested by X-ray fluorescence (XRF) in Table 3.

After being dried at 40°C, the SR was ground to the amount passing the #325 sieve of 77% (specific gravity 2.35 and pH value 10.78 with 100% water content). The microstructure of the dried SR powder shows the loose structure and low cementation. The SR possesses 83% of inorganic calcium components (including CaCO₃, Ca(OH)₂, CaCl₂, and CaSO₄). Here, the main crystals of SR are calcite, gypsum, and halite according to the previous XRD patterns [5].

The FFA with 6.67% CaO was used without any pretreatment (specific gravity 2.43, specific surface area 509 m²/kg, and pH value 8.50). The FFA also mainly consists of amorphous SiO₂ and Al₂O₃ from glassy microspheres at 19°~29° 2θ in the XRD patterns [15]. And the main crystal phases of FFA are quartz and mullite.

3.1.2. Alkaline Activator (NS). The adopted 2.00 mol/L sodium silicate NS solution (specific gravity of 1.24, modulus ratio SiO₂/Na₂O = 1.00, as well as 9.44% SiO₂, 9.44% Na₂O, and 81.12% H₂O by mass ratio) was prepared by sodium silicate pellets (Kemiou Company, Tianjin, China). The NS was cooled to room temperature before being adopted.

3.2. Preparation of Alkali-Activated Composites. Due to the independence of geopolymeric mechanism on curing condition and preparation method [29, 30], the alkali-activated composites (pastes) were prepared with three different compositions using SR powder, FFA powder, and NS solution under the designed curing conditions (T1, T2, and T3) compared with the controls using FFA powder and NS solution (Table 4). Liquid-to-solid (L/S) refers to the mass ratio of alkaline solution to powders [15]. And all of L/S in the samples were set as 0.75 to obtain the good fluidity. Here, different designed curing conditions were used to fasten the hardening rate and enhance the compressive strength. The better curing conditions were selected to prepare the AAFCS, which helps to clearly distinguish and detect the formed gel products. Regarding the fact that the longer resting period before high temperature contributes to the higher strength of alkali-activated materials [31] and the proper curing temperature positively influences on the mechanical strength [5, 15, 16, 32], the controlled conditions (T1, T2, and T3) were designed as shown in Figure 2. The synthesis was carried out by first blending the powders (SR and FFA) for three minutes. And the NS solution was evenly blended with the powder mixture for another ten minutes. Then, the fresh pastes were cast into prismatic steel moulds (sample size:

TABLE 2: The quantitative determination of the gel products for alkali-activated fly ash-based composites (AAFC) with calcium additives by the chemical components in products.

Stage	Components in products		Type of gel products	Name
	Si/Al	2Ca/Al		
(1)	>1.00	<1.00	Single geopolymer gel	Traditional geopolymer
(2)	>1.00	1.00	Transition value	Limit
(3)	>1.00	>1.00	Mixture of geopolymer and C-(A)-S-H ¹	Modern geopolymer

¹The "C-(A)-S-H" refers to C-A-S-H, C-S-H or mixture of them.

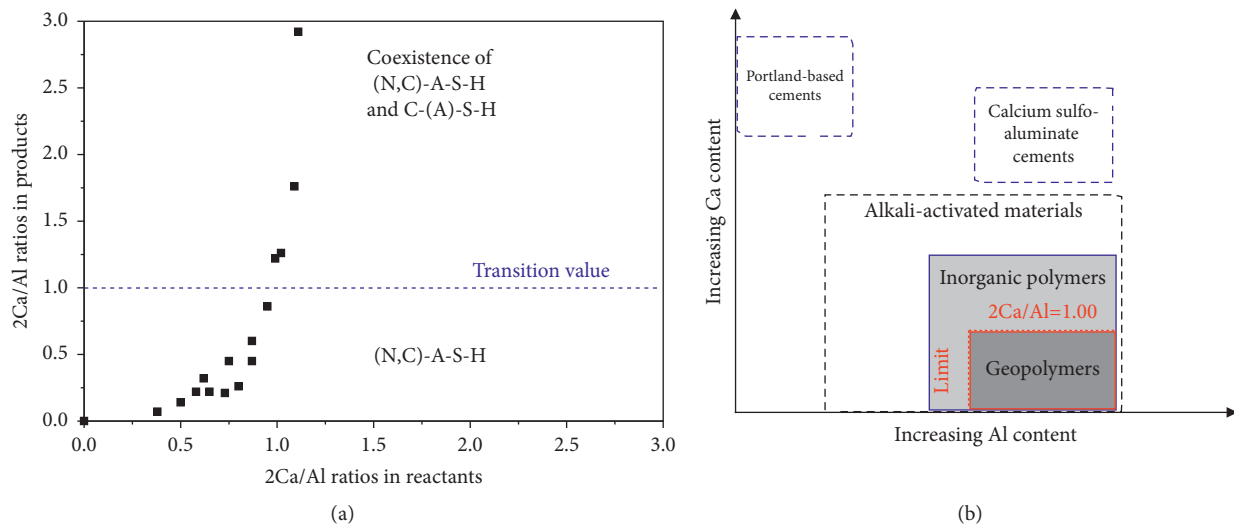


FIGURE 1: (a) Verification of gel products by 2Ca/Al ratios in products and (b) quantitative boundary of geopolymer gel.

40 mm × 40 mm × 160 mm) to get samples according to GB/T 17671-1999 (ISO). Moreover, all samples were initially grouped and then sealed with plastic films for curing under the conditions (T1, T2, and T3) to avoid moisture evaporation. However, the samples under the designed T1 were unsealed from 40 d to 60 d, while the other samples were still sealed during curing (Figure 2). The samples were demoulded at 30 d owing to the slow hardening rate at room temperature. After demould, the designed curing conditions were continued until 60 d.

3.3. Testing Methods

3.3.1. Determination of Compressive Strength. The 60-day compressive strength (UCS) of the samples was measured employing a 200 T auto compressive machine (DYE-2000, Lucheng Yiqi, Cangzhou, Hebei, China) at 2400 N/s in compression rate. The solidifications and failure modes of the samples were observed under compression. The compressive strength and solidification were used to analyse the effect of SR and the influence of curing conditions, which helps to select the better curing condition and SR contents for AAFCs. Here, six identical samples were measured repeatedly to obtain the average compressive strength results.

3.3.2. Characterization of Microstructures and Gel Products. To characterize the final gel products, all samples at 60 d were used to detect the gel products owing to the relatively

stable performance and composition along with the controls in the previous study [5, 15, 16, 33], as shown in Table 5. The specimens for microscopic tests were taken from the compressed samples. The SEM-EDS, XRD, FTIR, and ²⁹Si NMR tests were performed to characterize the microstructures, mineralogy phases, and gel products.

(1) *SEM-EDS Test.* The morphology and elemental components of the gel products were measured by SEM and EDS tests for the samples PNT1, PST1, PST2, and PST3. The micro-area mapping technique was utilized to detect the elemental components of the formed gel products. The elemental results of the gel products were averaged from the mapping area. The scanning electron microscopic coupled with energy-dispersive spectroscopy (Quanta FEG 450, Hillsboro, OR, USA) was adopted.

(2) *XRD Test.* Compared with the controls of raw materials, the XRD patterns of the samples PNT1 and PST3 were measured with the scanning rate of 2°/min from 10° to 70° 2θ. The X-ray diffraction spectroscopy (D/MAX-2500, Rigaku, Japan) was adopted (with CuK radiation) to detect the mineral compositions.

(3) *FTIR Test.* The FTIR spectra were performed for raw materials, PNT3 and PST3, to illustrate the change in chemical bonds before and after alkali activation. After that, the samples were air-dried for 48 h and ground. Then, the samples

TABLE 3: The chemical compositions of soda residue (SR) and F class fly ash (FFA) by XRF test. Loss on ignition refers to the mass loss on ignition at 1000°C (wt.%).

SR	CaCO ₃ 64.00	Ca(OH) ₂ 10.00	CaCl ₂ 6.00	NaCl 4.00	CaSO ₄ 3.00	SiO ₂ 3.00	Al ₂ O ₃ 2.00	Acid insoluble 8.00
FFA	SiO ₂ 48.37	Al ₂ O ₃ 20.90	CaO 6.67	Fe ₂ O ₃ 7.00	FeO 2.31	MgO 3.46	Others 5.34	Loss on ignition 5.95

TABLE 4: The designed mixing proportions and curing conditions for the AAFCs.

No.	FFA (%)	SR (%)	Na ₂ SiO ₃ (mol/L)	2Ca/Al in reactant	Si/Al in reactant	Curing conditions ¹	Curing time (d)
PST1	93.5	6.67	2.00	0.43	2.98	T1	60
PST2	93.5	6.67	2.00	0.43	2.98	T2	60
PST3	93.5	6.67	2.00	0.43	2.98	T3	60
PNT1	100.0	—	2.00	0.38	2.98	T1	60
PNT2	100.0	—	2.00	0.38	2.98	T2	60
PNT3	100.0	—	2.00	0.38	2.98	T3	60

¹The designed curing conditions are presented in Figure 2.

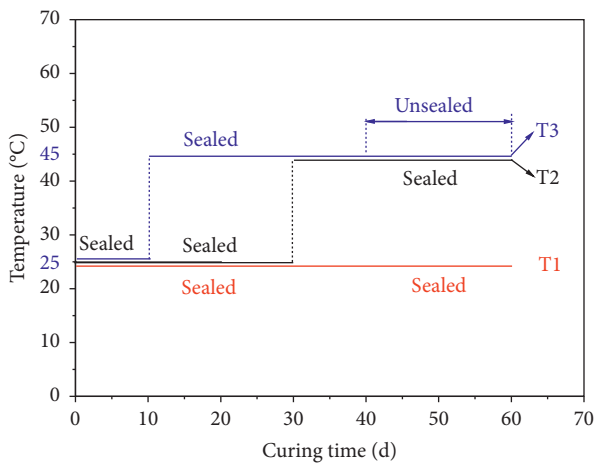


FIGURE 2: The designed curing conditions for AAFC incorporating SR.

(1.3 ± 0.001 mg) were blended with potassium bromide (KBr) pellets (130 mg) to manufacture the tested specimens. The Fourier transform infrared spectroscopy (Nexus 8, Bruker, Karlsruhe, Germany) was adopted to measure FTIR spectra in the wavenumber range from 400 cm⁻¹ to 2000 cm⁻¹.

(4) ²⁹Si NMR Test. The tested specimens were further obtained from PST3 compared with the controls. The nuclear magnetic resonance spectrometer (Varian Infinity Plus 300 MHz, Varian, CA, USA) was adopted to obtain the ²⁹Si NMR spectra. The 6 mm diameter of zirconia rotor (sample tube) and the solid double resonance probe were adopted. The resonance frequencies of ¹H (299.84 MHz) and ²⁹Si (59.57 MHz) were used. The rotation speed of 4000 r/s and the pulse width of 5 μs were set along with the cycle delay time of 10 s and the sampling number of 440.

4. Results and Discussion

4.1. *Compressive Strength and Failure Mode.* The mechanical strength is analysed together with the solidification and failure modes of the samples, as shown in Figure 3.

Figure 3(a) shows that the upper segregation layer of alkali-activated sample PNT1 disappears due to the addition of 6.67% soda residue (SR). The positive improvement effect of SR on the solidification of AAFC is consistent with that (reducing the shrinkage of the casting height) reported in previous references [5, 16]. Moreover, 60-day compressive strengths (UCSs) increase from 9.1 MPa (PNT1) to 11.8 MPa (PST1) by adding 6.67% SR under T1 (Figure 3(b)). The 60-day UCS of PST1 increases by 29.67% over that of PNT1, which shows that the addition of 6.67% SR has a positive effect on the enhancement of UCS at room temperature.

Although PNT2 (44.0 MPa) and PNT3 (53.7 MPa) possess a higher UCS than that of PNT1 (9.1 MPa), PNT2 and PNT3 (similar to PNT1) obtain worse surficial solidification affecting the engineering application of building materials due to the 10-day setting at room temperature. It illustrates that the appropriate higher-temperature curing (e.g., curing at 45°C) greatly contributes to the enhancement of 60-day UCS. Moreover, the 60-day UCSs of well-hardened samples (PST2 and PST3) reach 31.7 MPa and 43.2 MPa under T2 and T3, respectively. After compressed, it can be seen that the sample PST3 presents a mode of brittle failure with 45° angle of diagonal cracks and shows small failure pieces (Figure 3(c)).

The designed curing condition T3 provides the sufficient water environment for a long time of 10 d to dissolve fly ash particles [31]. Furthermore, the curing condition for 20 d at 45°C for unsealed samples guarantees the loss of some water and the formation of gel products owing to the little water environment required for dehydration condensation [5, 32]. Therefore, the designed condition T3 is recommended as the curing method to obtain higher UCS of AAFC incorporating SR.

4.2. *Microstructure and Morphology.* After cured for 60 d at room temperature, PST1 presents the higher dissolution degree in the glassy microspheres of fly ash and the higher compactness in microstructure than that of PNT1 with the morphology (Figures 4(a) and 4(b)). It is also revealed that the surficial solidification of PST1 is better than that of PNT1 (Figure 3). For the designed curing conditions, the formed

TABLE 5: The designed samples and controls for AAFCs detected through characterization tests.

Style	No.	FFA (g)	SR (g)	Ca(OH) ₂ (%)	Na ₂ SiO ₃ (mol/L)	NaOH (mol/L)	L/S	Sand (g)	Curing age (d)
Designs	PST3	420	30	—	2	—	0.75	—	60
	PST1	420	30	—	2	—	0.75	—	60
	PNT3	450	—	—	2	—	0.75	—	60
Controls	P9	360	90	—	—	8	0.75	—	180
	M9	360	90	—	—	8	0.75	1350	180
	P3	450	—	—	—	8	0.75	—	180
	HCP8	450	—	70	—	8	0.75	—	28
	S2F3NS	60	40	—	2	—	1.20	—	180
	GPS3	50	50	—	—	2	0.52	—	90

gel products of PST2 and PST3 exhibit a granular morphology at 60 d (Figures 4(c) and 4(d)), which is similar to the granular morphology of the alkali-activated soda residue fly ash-based geopolymer mortar mentioned in the previous study [5]. Thus, the gel products of PST2 and PST3 are also presumed to be (Na,Ca)-containing geopolymer gels (N,C)-A-S-H. Furthermore, according to the EDS testing, the main elements of O, Na, Al, and Si with less Ca and Cl are detected in the gel products of PST2 and PST3 (Figures 4(e) and 4(f)), which exhibits a verification of the formed (N,C)-A-S-H gels. Here, the average Si/Al, (Na + 2Ca)/Al, and 2Ca/Al in gel products of PST3 with higher strength measure 1.10, 0.88, and 0.34 at spectrum 2, respectively. Therefore, under T3, the sample PST3 with well solidification obtains the higher compactness owing to the formed (N,C)-A-S-H gels.

4.3. Characterization of Mineralogy and Gel Product. The gel products of the samples are inferred by the chemical elements from SEM-EDS tests. Furthermore, the XRD, FTIR, and ²⁹Si NMR spectra are investigated to verify the specific gel products through the mineralogy and chemical bonds about the structure units of ²⁹Si.

The XRD patterns of PST1 and PST3 were investigated to analyse the mineralogy (Figure 5). Compared with 8 mol/L NaOH-activated F class fly ash geopolymer pastes (P3 without SR and P9 with 20.0% SR) from the previous study [5], the PST1 and PST3 include quartz, mullite, and halite crystals and also present amorphous aluminosilicate gels with the broad humps at 17°~38° 2θ. From the intensity of humps, the amorphous product contents in PST3 are more than those in P3 and P9 at room temperature, but no diffraction peaks of zeolites appear in PST3. Therefore, the gel products of PST3 are amorphous after alkali activation under T3.

In addition, the FTIR spectra of sample PST3 and controls were investigated to detect the chemical bonds. The asymmetric stretching vibration absorption peaks (ASVAP) attributed to Si-O-T (Si or Al) bonds are in the range of 1000~1100 cm⁻¹ [14, 17]. Comparing with the raw materials SR and FFA, the corresponding wavenumber of ASVAP on Si-O-T bond in PST3 happens to shift, which displays that the new chemical products form after alkali activation (Figure 6(a)). Moreover, the ASVAP of Si-O-T bond in PST3 shifts to the lower wavenumber compared to that in PNT3. The change in absorption peak from 1033 cm⁻¹ to 1022 cm⁻¹

results from the change of polymeric degree and gel product. It demonstrates that the introduction of SR as calcium additive promotes the polymerization of Si-O-Si and Si-O-Al chains due to the alkalinity and Ca²⁺ cations in the system [5].

Furthermore, the ²⁹Si NMR spectrum of PST3 was performed to clarify the gel products (Figure 6(b)). Compared with NaOH-activated fly ash-based geopolymer incorporating SR (labelled as M9) in [5] and NaOH-activated fly ash-based paste incorporating Ca(OH)₂ (labelled as HCP8) in [15], there are the same strong peaks at close chemical shifts: -84.80 ppm (HCP8), -84.37 ppm (M9), and -84.32 ppm (PST3). All of them correspond to Q⁴(4Al) structural unit in network (N,C)-A-S-H gels. Moreover, the weak peak at -95.76 ppm corresponds to Q²(0Al) from mullite in PST3, and the peak at -106.17 ppm corresponds to Q⁴(0Al) from quartz in PST3. However, no weak peak exists at -65.79 ppm attributed to Q¹(0Al) from C-S-H gel in PST3 [15], which demonstrates that no C-S-H gel forms in PST3. The CaCl₂, Ca(OH)₂, and CaSO₄ from SR dissolve the cations Ca²⁺ into the alkaline environment, and the cations Ca²⁺ along with Na⁺ balance the negative charges from the substitution of Al-O to Si-O tetrahedron [5], forming the amorphous network (N,C)-A-S-H gels with Q⁴(4Al) units.

4.4. Discussion. According to the previous literature [13, 29, 34], the essential mechanism of geopolymerization is independent of the factors about the mixing ratio of reactants, moisture content, alkali-solution type and concentration, as well as curing condition (temperature and age), and so on. Therefore, the 2Ca/Al, Si/Al, and gel products are derived from the data of published research articles [10, 20, 29, 35–49] on Elsevier website, as shown in Figure 7. The average chemical compositions of gel products in micro-areas are measured by EDS (for products). From the data, the 2Ca/Al ratios in gel products from AAFCs were verified by the limit value 1.00. Therefore, 2Ca/Al < 1.00 is used to determine as single geopolymer gel in the gel products according to the detected result in literature, while 2Ca/Al > 1.00 is utilized to determine as the coexistence of (N,C)-A-S-H and C-(A)-S-H gels. The experimental results in the literature are consistent with the theoretical limit value 1.00.

The SR is a solid waste including various inorganic calcium-containing components, and it should be feasible and effective to determine the gel products in the AAFC with

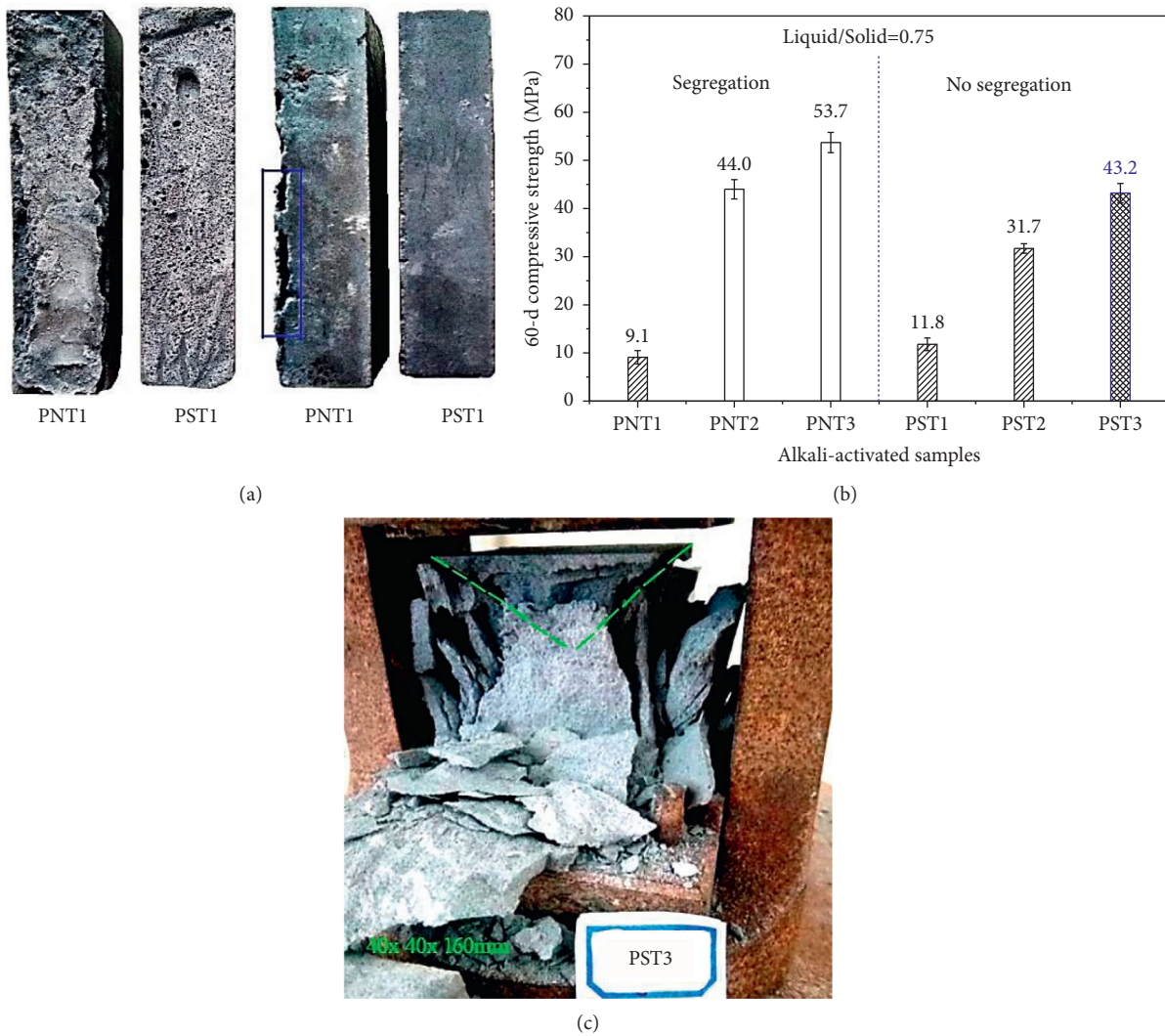


FIGURE 3: (a) Hardening behaviour, (b) compressive strength, and (c) failure mode of the samples cured for 60 d under three designed curing conditions.

SR additive. The solubility of CaSO_4 and CaCO_3 is extremely low (almost 20 ppm) by NaOH activation, which can be ignored about Ca^{2+} dissolution [50–52]. The solubility of CaCO_3 is extremely low, but CaSO_4 is reactive when Na_2SiO_3 solution is an alkaline activator. In addition, CaCl_2 and $\text{Ca}(\text{OH})_2$ from SR can easily dissolve the cations Ca^{2+} in the alkaline environment.

Moreover, for the different AAFCS incorporating SR, $2\text{Ca}/\text{Al}$ and Si/Al in the products were detected by a series of testing technologies to clarify the gel products and verify the proposed quantitative determination method in Section 2.3. The elemental components results were presented in Table 6.

Based on the alkali-activated mechanism and the determination method of gel products, the reaction mechanism for the green composites using F class fly ash ($\text{Si}/\text{Al} > 1.00$) and SR is expressed as follows: the cations Ca^{2+} are released from the soluble inorganic salts CaCl_2 , $\text{Ca}(\text{OH})_2$, and CaSO_4 of SR into the alkaline and water environment. Coupled with the cations Na^+ provided by the activators, Ca^{2+} ($2\text{Ca}/\text{Al} < 1.00$ in products) and Na^+ jointly participate

in balancing the negative charges in the geopolymeric reaction to form a stable structural (N,C)-A-S-H gel. While the $2\text{Ca}/\text{Al}$ ratio exceeds 1.00 in products, the excessive Ca^{2+} reacts with Si monomers to generate some C-S-H gels [5, 15, 16].

From the result of compressive strength and solidification, owing to the relatively coarse particle of SR and the relatively less amount of soluble calcium components, the enhancement effect of compressive strength is not significant for application of the alkali-activated fly ash-based materials. The 6.67% SR only improves the solidification and structure uniformity. If SR was pretreated for the thinner particle, the optimal contents of SR in alkali-activated fly ash-based materials will change. Therefore, in the future, the influence of the SR particle size on compressive strength and solidification need to investigate under different curing temperatures.

In order to prepare the single geopolymer gel without C-(A)-S-H (where C-(A)-S-H refers to C-A-S-H, C-S-H or a mixture of them), the $2\text{Ca}/\text{Al}$ in products must satisfy the

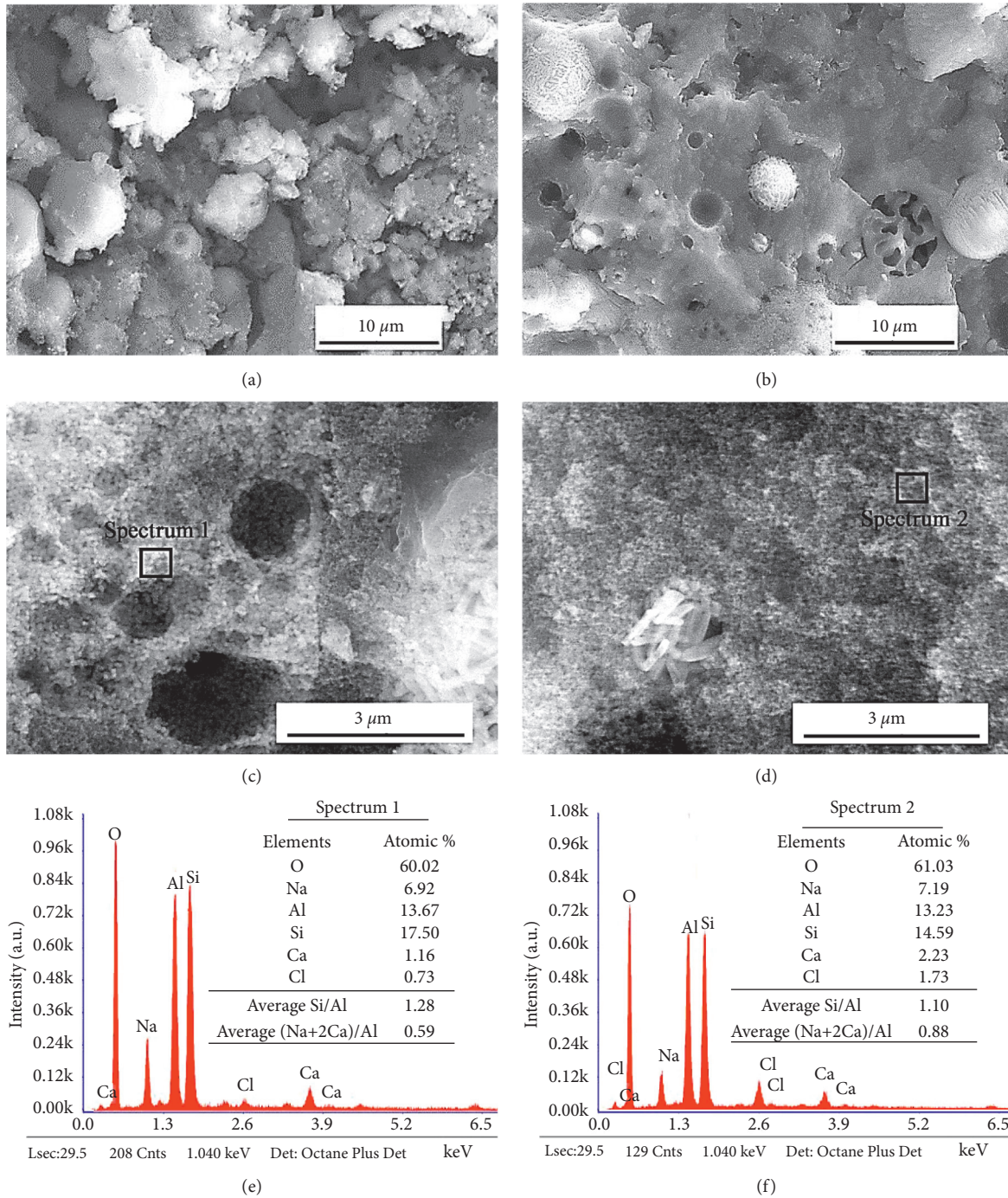


FIGURE 4: The SEM images of (a) PNT1, (b) PST1, (c) PST2, (d) PST3, and the EDS spectra of (e) spectrum 1 and (f) spectrum 2 in gel products of PST2 and PST3 at 60 d.

formula $2Ca/Al < 1.00$ and $Si/Al > 1.00$. That is conducive to predict the gel products in alkali-activated fly ash-based materials and helps in the optimization of mixing ratios responding to early anticipation.

The experimental investigation shows that inorganic calcium sources make significant effect on the properties of alkali-activated fly ash-based materials. It reflects that other soluble inorganic calcium may be used to improve the properties and microstructure of alkali-activated fly ash-

based materials. However, it is difficult to determine the gel product compositions from the blending aluminosilicate precursors of fly ash, blast furnace slag, red mud, and metakaolin which are alkali-activated to prepare the geopolymer materials with calcium sources, owing to the complex chemical components and reaction degrees.

In summary, the SRs are used as calcium additives to prepare the AAFC. The determination of the gel products in the alkali-activated soda residue-fly ash-based

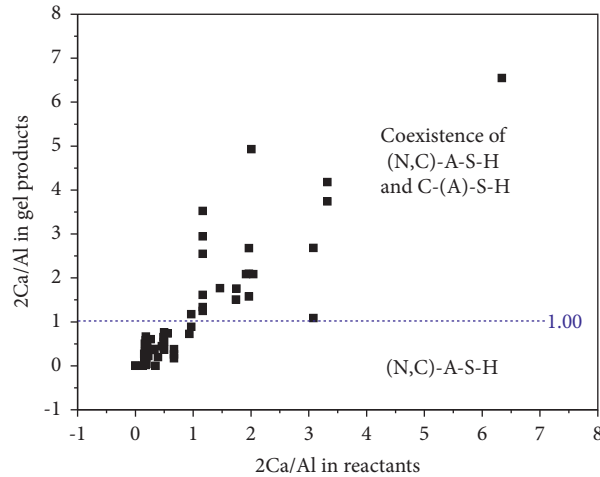


FIGURE 7: The 2Ca/Al data and detected products by testing in gel products and reactants (the premise is Si/Al > 1.00).

TABLE 6: The 2Ca/Al ratios in products and the detected gel products of PST3 and controls.

Samples	SR content	2Ca/Al in product	Si/Al in product	Detected gel products ¹
PST3	6.67%	0.24 (<1.00)	1.28 (>1.00)	S
P3 [5]	—	0.00 (<1.00)	1.75 (>1.00)	S
P9 [5]	20.00%	0.38 (<1.00)	1.83 (>1.00)	S
S2F3NS [16]	40.00%	1.54 (>1.00)	1.69 (>1.00)	C
GPS3 [33]	50.00%	1.52 (>1.00)	1.29 (>1.00)	C

¹The marked "S" refers to the produced single geopolymer gel (N,C)-A-S-H, while the marked "C" refers to the coexistence of geopolymer gel (N,C)-A-S-H and hydration gel C-(A)-S-H.

also critical for the combination of theory analysis and practical application based on chemical components in products.

5. Conclusions

The objective of this paper is to propose a quantitative determination method of gel products based on the chemical components in the products of alkali-activated fly ash-based composites (AAFCs) incorporating inorganic calcium additives, and then the gel products of the AAFC incorporating solid waste soda residue (SR) were detected and characterized. Last, the feasibility of the proposed determination method was verified for SR as calcium additives applied in the AAFCs. The main conclusions are drawn:

- (1) Based on the charge balance in geopolymeric process, the 2Ca/Al ratios in products are proposed as a quantitative method for determining the gel products of the AAFCs incorporating calcium additives. The new proposed quantitative determination method refers to a limit value $2Ca/Al = 1.00$ about the critical chemical elements in gel products, which helps to determine the calcium-containing geopolymer (N,C)-A-S-H or/and calcium (alumino) silicate hydration C-(A)-S-H in stable AAFCs. In the AAFCs system, when the 2Ca/Al ratio is lower than 1.00 in products, the gel products are determined as a single geopolymer gel, and while the geopolymer gel

and C-(A)-S-H gel coexist in the system when the 2Ca/Al ratio is higher than 1.00 in products.

- (2) The designed curing condition T3 provides the proper water environment to dissolve fly ash particles and form the gel products during dehydration condensation. Thus, the condition T3 is recommended to obtain higher compressive strength of the AAFC incorporating SR. Moreover, the well-solidified AAFC incorporating 6.67% SR (labelled as PST3) obtains the better compactness and higher compressive strength when cured under T3.
- (3) It is feasible that the SR as a calcium additive is verified to be applied in the AAFC, and it is effective that the gel products in the AAFC incorporating SR are determined by using $2Ca/Al = 1.00$ in products as a limit value.

In summary, the proposed determination method saves economic and material resources and quantifies the boundary of the geopolymer gel by chemical components. The research result about a limit value $2Ca/Al = 1.00$ in gel products provides a theoretical reference for the mixing ratio design, technique characterization, performance optimization of geopolymer materials, and scientific reutilization of solid waste soda residue. Currently, not enough evidence proves the applicability of other alkali-activated aluminosilicate systems except for the fly ash-based systems, and that needs to be further explored. In the next stage, it is necessary to further theoretically determine the gel products for the alkali-activated

aluminosilicate composites of fly ash, metakaolin and blast furnace slag, and so on.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This work was supported by Tianjin Research Innovation Project for Postgraduate Students (Grant no. 2021KJ078).

References

- [1] T. Bakharev, "Resistance of geopolymer materials to acid attack," *Cement and Concrete Research*, vol. 35, no. 4, pp. 658–670, 2005.
- [2] N. R. Rakhimova and R. Z. Rakhimov, "Reaction products, structure and properties of alkali-activated metakaolin cements incorporated with supplementary materials - a review," *Journal of Materials Research and Technology*, vol. 8, no. 1, pp. 1522–1531, 2019.
- [3] A. Mehta and R. Siddique, "Sulfuric acid resistance of fly ash based geopolymer concrete," *Construction and Building Materials*, vol. 146, pp. 136–143, 2017.
- [4] X. Y. Zhuang, L. Chen, S. Komarneni et al., "Fly ash-based geopolymer: clean production, properties and applications," *Journal of Cleaner Production*, vol. 125, pp. 253–267, 2016.
- [5] X. Zhao, C. Liu, L. Wang, L. Zuo, Q. Zhu, and W. Ma, "Physical and mechanical properties and micro characteristics of fly ash-based geopolymers incorporating soda residue," *Cement and Concrete Composites*, vol. 98, pp. 125–136, 2019.
- [6] X. H. Zhao, H. Y. Wang, B. Y. Zhou, H. Gao, and Y. H. Lin, "Resistance of soda residue-fly ash based geopolymer mortar to acid and sulfate environments," *Materials*, vol. 14, no. 785, 2021.
- [7] D. Khale and R. Chaudhary, "Mechanism of geopolymerization and factors influencing its development: a review," *Journal of Materials Science*, vol. 42, no. 3, pp. 729–746, 2007.
- [8] A. Mehta and R. Siddique, "Properties of low-calcium fly ash based geopolymer concrete incorporating OPC as partial replacement of fly ash," *Construction and Building Materials*, vol. 150, pp. 792–807, 2017.
- [9] J. Temuujin, A. van Riessen, and R. Williams, "Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes," *Journal of Hazardous Materials*, vol. 167, no. 1–3, pp. 82–88, 2009.
- [10] I. Garcia-Lodeiro, E. Aparicio-Rebollo, A. Fernández-Jimenez, and A. Palomo, "Effect of calcium on the alkaline activation of aluminosilicate glass," *Ceramics International*, vol. 42, no. 6, pp. 7697–7707, 2016.
- [11] C. K. Yip, G. C. Lukey, and J. S. J. van Deventer, "The co-existence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation," *Cement and Concrete Research*, vol. 35, no. 9, pp. 1688–1697, 2005.
- [12] M. Zhang, M. Zhao, G. Zhang, D. Mann, K. Lumsden, and M. Tao, "Durability of red mud-fly ash based geopolymer and leaching behavior of heavy metals in sulfuric acid solutions and deionized water," *Construction and Building Materials*, vol. 124, pp. 373–382, 2016.
- [13] A. Fernández-Jiménez, A. Palomo, and M. Criado, "Microstructure development of alkali-activated fly ash cement: a descriptive model," *Cement and Concrete Research*, vol. 35, no. 6, pp. 1204–1209, 2005.
- [14] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, and D. E. Macphee, "Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na₂O-CaO-Al₂O₃-SiO₂-H₂O," *Cement and Concrete Research*, vol. 41, no. 9, pp. 923–931, 2011.
- [15] X. Zhao, C. Liu, L. Zuo, L. Wang, Q. Zhu, and M. Wang, "Investigation into the effect of calcium on the existence form of geopolymerized gel product of fly ash based geopolymers," *Cement and Concrete Composites*, vol. 103, pp. 279–292, 2019.
- [16] X. Zhao, C. Liu, L. Zuo et al., "Synthesis and characterization of fly ash geopolymer paste for goaf backfill: reuse of soda residue," *Journal of Cleaner Production*, vol. 260, Article ID 121045, 2020.
- [17] J. C. Swanepoel and C. A. Strydom, "Utilisation of fly ash in a geopolymeric material," *Applied Geochemistry*, vol. 17, no. 8, pp. 1143–1148, 2002.
- [18] G. Fahim Huseien, J. Mirza, M. Ismail, S. K. Ghoshal, and A. Abdulameer Hussein, "Geopolymer mortars as sustainable repair material: a comprehensive review," *Renewable and Sustainable Energy Reviews*, vol. 80, pp. 54–74, 2017.
- [19] X. Guo, H. Shi, and W. A. Dick, "Compressive strength and microstructural characteristics of class C fly ash geopolymer," *Cement and Concrete Composites*, vol. 32, no. 2, pp. 142–147, 2010.
- [20] X. Guo, H. Shi, L. Chen, and W. A. Dick, "Alkali-activated complex binders from class C fly ash and Ca-containing admixtures," *Journal of Hazardous Materials*, vol. 173, no. 1–3, pp. 480–486, 2010.
- [21] J. E. Oh, P. J. M. Monteiro, S. S. Jun, S. Choi, and S. M. Clark, "The evolution of strength and crystalline phases for alkali-activated ground blast furnace slag and fly ash-based geopolymers," *Cement and Concrete Research*, vol. 40, no. 2, pp. 189–196, 2010.
- [22] T. Bakharev, "Geopolymeric materials prepared using Class F fly ash and elevated temperature curing," *Cement and Concrete Research*, vol. 35, no. 6, pp. 1224–1232, 2005.
- [23] B. A. Fillenwarth and S. M. L. Sastry, "Development of a predictive optimization model for the compressive strength of sodium activated fly ash based geopolymer pastes," *Fuel*, vol. 147, pp. 141–146, 2015.
- [24] H. Rashidian-Dezfouli, P. R. Rangaraju, and V. S. K. Kothala, "Influence of selected parameters on compressive strength of geopolymer produced from ground glass fiber," *Construction and Building Materials*, vol. 162, pp. 393–405, 2018.
- [25] K. Somna, C. Jaturapitakkul, P. Kajitvichyanukul, and P. Chindaprasirt, "NaOH-activated ground fly ash geopolymer cured at ambient temperature," *Fuel*, vol. 90, no. 6, pp. 2118–2124, 2011.
- [26] U. Rattanasak and P. Chindaprasirt, "Influence of NaOH solution on the synthesis of fly ash geopolymer," *Minerals Engineering*, vol. 22, no. 12, pp. 1073–1078, 2009.
- [27] Q. Wang, S. R. Kang, L. M. Wu, Q. Zhang, and Z. Y. Ding, "Structural modeling and molecular dynamics simulation of geopolymer gel," *Materials Reports*, vol. 34, no. 2, pp. 4056–4061, 2020.

- [28] J. Davidovits, "Geopolymers," *Journal of Thermal Analysis*, vol. 37, no. 8, pp. 1633–1656, 1991.
- [29] J. E. Oh, Y. Jun, and Y. Jeong, "Characterization of geopolymers from compositionally and physically different Class F fly ashes," *Cement and Concrete Composites*, vol. 50, pp. 16–26, 2014.
- [30] N. Ranjbar, M. Mehrli, M. R. Maheri, and M. Mehrli, "Hot-pressed geopolymer," *Cement and Concrete Research*, vol. 100, pp. 14–22, 2017.
- [31] A. I. I. Helmy, "Intermittent curing of fly ash geopolymer mortar," *Construction and Building Materials*, vol. 110, pp. 54–64, 2016.
- [32] B. Y. Zhou, L. Wang, G. W. Ma, X. Zhao, and X. H. Zhao, "Preparation and properties of bio-geopolymer composites with waste cotton stalk materials," *Journal of Cleaner Production*, vol. 245, Article ID 118842, 2020.
- [33] X. H. Zhao, C. Y. Liu, L. M. Zuo, Q. Zhu, W. Ma, and Y. C. Liu, "Preparation and characterization of press-formed fly ash cement incorporating soda residue," *Materials Letters*, vol. 259, Article ID 126852, 2020.
- [34] A. Palomo, M. W. Grutzeck, and M. T. Blanco, "Alkali-activated fly ashes," *Cement and Concrete Research*, vol. 29, no. 8, pp. 1323–1329, 1999.
- [35] M. Hu, X. Zhu, and F. Long, "Alkali-activated fly ash-based geopolymers with zeolite or bentonite as additives," *Cement and Concrete Composites*, vol. 31, no. 10, pp. 762–768, 2009.
- [36] I. Garcia-Lodeiro, A. Fernández-Jiménez, P. Pena, and A. Palomo, "Alkaline activation of synthetic aluminosilicate glass," *Ceramics International*, vol. 40, no. 4, pp. 5547–5558, 2014.
- [37] A. G. d. S. Azevedo and K. Strecker, "Brazilian fly ash based inorganic polymers production using different alkali activator solutions," *Ceramics International*, vol. 43, no. 12, pp. 9012–9018, 2017.
- [38] A. Fernández-Jiménez and A. Palomo, "Composition and microstructure of alkali activated fly ash binder: effect of the activator," *Cement and Concrete Research*, vol. 35, no. 10, pp. 1984–1992, 2005.
- [39] P. Duan, C. Yan, and W. Zhou, "Compressive strength and microstructure of fly ash based geopolymer blended with silica fume under thermal cycle," *Cement and Concrete Composites*, vol. 78, pp. 108–119, 2017.
- [40] İ. B. Topçu, M. U. Toprak, and T. Uygunoğlu, "Durability and microstructure characteristics of alkali activated coal bottom ash geopolymer cement," *Journal of Cleaner Production*, vol. 81, pp. 211–217, 2014.
- [41] H. Y. Leong, D. E. L. Ong, J. G. Sanjayan, and A. Nazari, "The effect of different Na₂O and K₂O ratios of alkali activator on compressive strength of fly ash based-geopolymer," *Construction and Building Materials*, vol. 106, pp. 500–511, 2016.
- [42] T. A. Aiken, J. Kwasny, W. Sha, and M. N. Soutsos, "Effect of slag content and activator dosage on the resistance of fly ash geopolymer binders to sulfuric acid attack," *Cement and Concrete Research*, vol. 111, pp. 23–40, 2018.
- [43] P. Timakul, W. Rattanaprasit, and P. Aungkavattana, "Enhancement of compressive strength and thermal shock resistance of fly ash-based geopolymer composites," *Construction and Building Materials*, vol. 121, pp. 653–658, 2016.
- [44] M. Soutsos, A. P. Boyle, R. Vinai, A. Hadjierakleous, and S. J. Barnett, "Factors influencing the compressive strength of fly ash based geopolymers," *Construction and Building Materials*, vol. 110, pp. 355–368, 2016.
- [45] Z. Zheng, X. Ma, Z. Zhang, and Y. Li, "In-situ transition of amorphous gels to Na-P1 zeolite in geopolymer: mechanical and adsorption properties," *Construction and Building Materials*, vol. 202, pp. 851–860, 2019.
- [46] L. N. Assi, E. Deaver, M. K. ElBatanouny, and P. Ziehl, "Investigation of early compressive strength of fly ash-based geopolymer concrete," *Construction and Building Materials*, vol. 112, pp. 807–815, 2016.
- [47] J. E. Oh, J. Moon, S.-G. Oh, S. M. Clark, and P. J. M. Monteiro, "Microstructural and compositional change of NaOH-activated high calcium fly ash by incorporating Na-aluminate and co-existence of geopolymeric gel and C-S-H(I)," *Cement and Concrete Research*, vol. 42, no. 5, pp. 673–685, 2012.
- [48] Y. Huang, M. Han, and R. Yi, "Microstructure and properties of fly ash-based geopolymeric material with 5A zeolite as a filler," *Construction and Building Materials*, vol. 33, pp. 84–89, 2012.
- [49] X. Guo, H. Shi, and X. Wei, "Pore properties, inner chemical environment, and microstructure of nano-modified CFA-WBP (class C fly ash-waste brick powder) based geopolymers," *Cement and Concrete Composites*, vol. 79, pp. 53–61, 2017.
- [50] C. K. Yip, J. L. Provis, G. C. Lukey, and J. S. J. van Deventer, "Carbonate mineral addition to metakaolin-based geopolymers," *Cement and Concrete Composites*, vol. 30, no. 10, pp. 979–985, 2008.
- [51] Y. Liu, M. Gao, X. Zhang, X. Hu, and Q. Guo, "Characteristics of a CaSO₄ composite oxygen carrier supported with an active material for in situ gasification chemical looping combustion of coal," *RSC Advances*, vol. 8, no. 41, Article ID 23372, 2018.
- [52] A. Cwirzen, J. L. Provis, V. Penttala, and K. Habermehl-Cwirzen, "The effect of limestone on sodium hydroxide-activated metakaolin-based geopolymers," *Construction and Building Materials*, vol. 66, pp. 53–62, 2014.