



# Article Silica Fume Enhances the Mechanical Strength of Alkali-Activated Slag/Fly Ash Pastes Subjected to Elevated Temperatures

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**Abstract:** The fireproof design of geopolymers through adjusting multi-component metallurgical solid wastes has attracted increasing attention, due to their potential low carbon emission, cost effectiveness, and role in environmental conservation. Herein, the effects of silica fume (SF) on the microstructure and mechanical properties of alkali-activated slag/FA (fly ash) pastes subjected to elevated temperatures (150, 500, 850, and 1200 °C) are investigated to clarify whether or not SF has a positive role in the mechanical strength of the slag/FA (slag/FA = 30:70, wt.%) geopolymer during building fires. The results show that the replacement of FA with 10 wt.% SF (silica fume) promotes the increasing pore volume with a diameter of 0.2~3  $\mu$ m, leading to an increase in the compressive or flexural strength below 850 °C, "right shifts" of the endothermic peak, and uniform and compact fracture surfaces. Meanwhile, gehlenite and labradorite are generated after exposure above 850 °C. The bloating effect of the SF-containing sample occurs at 1200 °C, leading to a greater deformation due to the further restructuring of the amorphous geopolymer chain N–A–S–H or N–(Ca)–A–S–H composed of [SiO<sub>4</sub>]<sup>4–</sup> and [AlO<sub>4</sub>]<sup>5–</sup>. This paper explores an effective approach to improving geopolymers' fireproof performance by adjusting the formulation of solid waste.

Keywords: alkali activated; silica fume; elevated temperatures; slag; fly ash

## 1. Introduction

Alkali-activated geopolymer binders, aluminosilicate inorganic polymers produced through the "depolymerization-restructuring" of activate aluminosilicate under chemical modification, have the advantages of high strength, good corrosion resistance, low carbon emission during production, and amorphous network structures, holding unique properties compared with Portland cement, such as reduced  $CO_2$  emission, a simple technological process, excellent durability, and reduced cost [1,2]. Recently, building fires have been increasingly threatening human settlements and, as an alternative to cement, geopolymers should be able to withstand fire up to about 1000 °C. Therefore, the fireproof design of geopolymers through adjusting multi-component metallurgical solid wastes [3], such as by altering the formulations, curing regime, and doping crosslinking agent to improve their fire resistance, has attracted increasing attention.

Currently, the global perspective on sustainability promotes the conversion of the industrial by-product slag, derived from blast furnace iron making and fly ash (FA) from coal-fired power plants, into Al 7075 composites or cementitious materials [4,5]. The active calcium contained in slag is prone to transforming into a Ca-containing binder, while the spherical FA also improves the mobility of slurry and the cost effectiveness. Therefore, binary slag/FA geopolymers are very promising for developing solid-waste-based pastes without heat curing at about 60  $^{\circ}$ C [6] due to the as-formed sodium alumino-silicate hydrate (N–A–S–H) networks from reactive calcium involved in slag. Investigations and



Citation: Dai, W.; Wang, Y. Silica Fume Enhances the Mechanical Strength of Alkali-Activated Slag/Fly Ash Pastes Subjected to Elevated Temperatures. *Fire* **2023**, *6*, 252. https://doi.org/10.3390/fire6070252

Academic Editor: Tiago Miguel Ferreira

Received: 30 May 2023 Revised: 21 June 2023 Accepted: 22 June 2023 Published: 27 June 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). wide applications of binary slag/FA geopolymers [7–9] have been hotspots for achieving a recycling economy and environmental protection. Meanwhile, silica fume (SF), as an industrial by-product, also possesses an amorphous aluminosilicate nature due to the greater N–A–S–H networks resulting in increased compressive strength [10,11]. Theoretically, SF could trigger and enhance geopolymerization [12], presenting improved fire resistance, due to thermally stable N–A–S–H, compared with the C–S–H in cement. Because C–S–H is vulnerable to thermal stress or shocks under approximately 800 °C, it is prone to decomposing into calcium oxide and silica with a number of cracks.

Meanwhile, the excellent heat resistance of binary slag/FA geopolymers has been demonstrated in comparison to traditional Portland cement [13]. Pavel et al. [14] describe the behavior and structural changes in the slag matrix during and after exposure to temperatures as high as 1200 °C. The effect of elevated temperatures on the chemical stability and residual compressive strength of neat sodium-sulfate-activated slag pastes is also reported [15]. However, the relative strength of the neat slag paste is superior to the incorporated counterpart SF, which exerts an adverse impact on thermal shock resistance [16]. Therefore, whether or not SF plays a positive role in binary slag/FA geopolymers needs to be clarified to develop multi-component SF/slag/FA binders with fireproof properties, especially for performance under elevated temperatures corresponding to building fires of about 1000 °C. It is necessary to explore an effective and low-cost approach for designing geopolymers with good thermal shock resistance based on multi-component metallurgical solid waste.

Consequently, the previous research or literature has indicated that few publications have reported the performance of SF involved in binary slag/FA pastes after exposure to elevated temperatures of about 1000 °C, corresponding to fires in buildings and urban spaces. The optimization of multi-component metallurgical solid wastes as low-carbon construction materials is worth exploring to seek efficient and intrinsically safe fireproof buildings. The primary purpose of this paper is to investigate the effects of SF on the microstructure of slag/FA binders after exposure to elevated temperatures, which are activated by sodium silicate solution with an SF/slag/FA ratio of 10:30:60 (wt.%) [17]. The characterizations contain the residual stresses, mass loss, shrinkage, mineral phase, heat flow, and morphology, with an alkali-activated slag/FA (slag: FA = 30:70, wt.%) binder without SF as a control. It explores the effect of SF on the mechanical strength of alkali-activated slag/fly ash pastes subjected to elevated temperatures corresponding to building fires, prompting an effective recycling approach for improving geopolymers' fireproof performance by adjusting the formulation of solid waste.

## 2. Material and Methods

## 2.1. Raw Materials

FA was obtained from the Hancheng power plant (Xi'an city of Shaan'Xi province in China) with a Blaine specific surface area of  $500 \text{ m}^2/\text{kg}$  and a mean particle size of  $11.2 \text{ }\mu\text{m}$  after oven-drying at 105 °C and ball-milling for 1 h. Granulated, ground, blast furnace slag was obtained from Delong powder company with a Blaine specific surface area of  $420 \text{ m}^2/\text{kg}$  and a mean particle size of  $15.5 \text{ }\mu\text{m}$ . SF was collected from Linyuan company with a Blaine specific surface area of  $25 \text{ m}^2/\text{g}$  and a mean particle size of  $2.6 \text{ }\mu\text{m}$ . The chemical compositions of raw materials are shown in Table 1. Alkali-activator Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O (A.R.) was purchased from Tianjin Yaohua chemical reagent company.

Mass Percent (wt.%) Raw Materials CaO SiO<sub>2</sub>  $Al_2O_3$ Fe<sub>2</sub>O<sub>3</sub> MgO Na<sub>2</sub>O K<sub>2</sub>O SO<sub>3</sub> TiO<sub>2</sub> Loss FA 55.18 31.19 5.07 0.29 1.99 0.28 1.05 0.53 3.82 0.60 31.29 14.31 0.61 8.51 0.58 2.94 0.83 0.54Slag 39.65 0.63 SF 1.81 86.21 3.49 1.85 1.93 1.18 0.38 0.841.660.65

Table 1. Chemical composition of raw materials.

## 2.2. Preparation of Specimens

The alkali-activated ternary SF/slag/FA pastes were synthesized by adding sodium silicate (15 wt.% Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O) solution into the uniform mixture of FA, slag, and SF with a water/(SF + salg + FA) ratio of 0.3 to form the slurry in a cement mortar machine. The weight ratio of FA/slag/SF was 6:3:1 [17] and the binary specimen with a slag/FA ratio of 7:3 was used as a reference. Nevertheless, the specimens were heat-cured in a standard cement mortar curing box, which is cost-effective and promising for application in reality. The slurry was poured into a stainless triplet mold of  $160 \times 40 \times 40$  mm<sup>3</sup> and vibrated up and down for 60 s, and then was demolded after curing for 1 day and cured in a standard cement mortar curing box with a relative humidity of 90% at room temperature (RT) for 28 days.

#### 2.3. Characterizations

The mechanical strength of specimens was systematically tested, including compressive and flexural strength, according to the standard of GB/T17671-2021 corresponding to the ISO 679:2009 test method for strength of cement mortar. The specimens after curing 28 d were exposed to elevated temperatures with increments of 350 °C over 150–1200 °C and a heating rate of 5 °C/min, maintaining for 2 h various elevated temperatures of 150, 500, 850, and 1200 °C, and then air-cooled to RT for evaluation. A temperature of 1200 °C was selected to correspond to a real building fire, and the duration of 2 h corresponds to the fire endurance of ordinary cement.

Compressive strength was tested by a fully automatic cement mortar compressive testing machine of YAW-300 type with a pressurization rate of 2.4 kN/s; the error was 0.1 MPa. Flexural strength was measured by a motorized bending tester of DKZ-5000 type with an error of 0.03 MPa. The mechanical strength of specimens was tested with 3 replicates, using the average value as the final result with a standard deviation of <5%. Micro-morphology analysis of samples was conducted on a Quanta 200 scanning electron microscope (SEM) with a working condition of 20 kV voltage. The X-ray diffractometer (XRD, D/MAX-2200, Nippon Scientific Co., Ltd., Tokyo, China) was used to record XRD patterns of specimens using Cu K $\alpha$  radiation.

Thermogravimetric analysis (TG) with Mettler was used to measure the mass loss and heat flow of specimens during the heating process from 50 to 950 °C under a nitrogen atmosphere at a heating rate of 30 °C/min. Differential scanning calorimetry (DSC) was performed by recording the real-time heat flow curves to measure the heat release by the Mettler during continuous heating. The differential thermogravimetric (DTG) results were calculated using the differential weight of specimens during heating, and the peak was assigned to the temperature of maximum weight loss rate. Digital photos were shot on a Fujifilm AV100 camera. Fourier transform infrared spectroscopy (FTIR) spectrum was measured using a spectrometer (FTIR-650) in absorption mode, the transmission of the IR beam was recorded in real time, it was conducted in the range of 3000~500 cm<sup>-1</sup> with a spectral resolution of 2 cm<sup>-1</sup>, and samples were mixed with KBr with a sample/KBr weight ratio of 1/100. Pore size distributions of samples after 28 days of curing were tested by AUTOPORE 9500 mercury porosimetry under a nitrogen pressure of 0.3 MPa.

## 3. Results

## 3.1. XRD

The XRD patterns of specimens after exposure to elevated temperatures are shown in Figure 1, it is noted that the patterns of SF-containing specimens are similar to that of specimens without SF, indicating that no new mineral formed after incorporating SF at 150~500 °C. Because the SF inherently belongs to amorphous silica without any crystallines, the triggered reactions only extend or crosslink the amorphous N–A–S–H chains. However, gehlenite as Ca<sub>2</sub>Al(AlSiO<sub>7</sub>) (No. of JCPDS:98-000-0226) and labradorite as (Ca, Na) (Si, Al)<sub>4</sub>O<sub>8</sub>, (No. of JCPDS:98-000-0272) form a predominant mineral phase after treatment at 850 °C and 1200 °C; this demonstrates that exposure to 850 °C induces a transformation of gehlenite and labradorite, which is further enhanced by the heating treatment of 1200 °C, and the molar ratio of  $CaO/SiO_2$  and  $Al_2O_3/SiO_2$  decreases from gehlenite to labradorite due to the activated silica participates in the reactions.



**Figure 1.** XRD of sample including (**a**) slag/FA binders and (**b**) SF/slag/FA binders.

Meanwhile, there are diffraction peaks of quartz (SiO<sub>2</sub>, No. of JCPDS: 98-000-0369) and mullite (Al<sub>4+2x</sub>Si<sub>2-2x</sub>O<sub>10-x</sub> (x~0.4), No. of JCPDS:98-000-0319) in the XRD patterns of specimens after exposure to 850 °C and 1200 °C, but the diffraction intensity of the peaks significantly weakens. Bernardo et al. [18,19] demonstrated that the mixture of water glass/soda–lime–silica/clay, as well as a mixture of red mud/fly ash/porcelain stoneware tiles, could transform into labradorite with good mechanical strength after calcination. Segui et al. [20] suggest that labradorite grows into a binder composed of pozzolan, lime, and gypsum. Because kaolin clay promotes the formation of labradorite in glass ceramics [21], Fang et al. [22] suggest that the released CaO, together with unreacted portlandite and gypsum, interacts with N–A–S–H to form labradorite after calcination at 1050 °C. Therefore, it is proposed that activated CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> could transform into labradorite reatment.

Because the content of quartz in C-type fly ash decreases on sintering above 850 °C and transforms into new crystallite structures [23], the findings of our research are in agreement with the report that gehlenite is drastically reduced as it starts to react with quartz towards wollastonite and anorthite at 1050 °C in Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> clay [24]. Ding et al. [25] also as-

sert that mullite and corundum from FA could dissolve and transform into calcium sodium hydrate silicate (NaCaHSiO<sub>4</sub>). This confirms that quartz and mullite could transform into feldspar above 850  $^{\circ}$ C in an alkali-activated binary slag/FA binder system.

# 3.2. *Mechanical Strength of Specimens Subjected to High Temperatures* 3.2.1. Residual Stress of Specimens

The residual stress of specimens exposed to elevated temperatures is shown in Figure 2. The SF-containing specimen displays higher mechanical performance than the specimen without SF, indicating that SF imparts a strengthening effect on the slag/FA binder, as well as after exposure to various elevated temperatures. The residual compressive strengths are improved after heat treatments of 150 and 500 °C compared with the specimen at RT, corresponding to 105.6 MPa (increased by 8.8%, 150 °C) and 108.6 MPa (increased by 14.1%, 500 °C) for the specimen-incorporated SF. Ordinary cement is prone to disintegrate and collapse at about 600 °C [26] due to the dehydration or decomposition of calcium silicate hydrate, while the slag/FA geopolymer exhibits improved mechanical strength, corresponding to enhanced fire resistance. It is speculated that the as-formed N–A–S–H or N–(Ca)–A–S–H chains hold higher flexibility for tackling the thermal shock of firing, compared to the vulnerable C–S–H.



**Figure 2.** Mechanical strength of specimens subjected to high temperatures including (**a**) compressive strength and (**b**) flexural strength.

Given the decomposition [26] of N–A–S–H or N–(Ca)–A–S–H after 850 °C treatment, a rapid decline in residual stress for the two specimens appears. However, the flexural strength of the SF-containing specimen after 1200 °C treatment climbs to 5.6 MPa sharply, while that of the specimen without SF is only 1.1 MPa, which might be attributed to the transformation of labradorite combined with the XRD results.

# 3.2.2. Deformation

The mass loss of specimens and volume shrinkage of specimens are displayed in Figure 3. Regarding the SF-containing specimen, higher stability is present under sub-high temperatures, while greater mass loss and shrinkage are observed under high temperatures. The shrinkage approaches 6.9% at 500 °C, 8.6% at 850 °C, and 9.4% at 1200 °C, implying that the replacement with 10 wt.% SF triggers more volume deformation under higher temperatures, compared with the control without SF. Because the as-formed N–A–S–H derived from the incorporated SF and the unreacted SF hold high reactivity, they are prone to melt and trigger silicate reactions.



**Figure 3.** Deformation of specimens after exposure to elevated temperatures, including (**a**) mass loss and (**b**) volume shrinkage.

# 3.3. Morphology and Microstructure

# 3.3.1. Macromorphologies

The color change in specimens is shown in Figure 4; the gray surface gradually transforms into yellow with increasing cracks, and the volume of specimens exhibits a slight and continuous shrinkage in their dimensions with the increasing heat treatment temperatures. The higher temperature causes bigger cracks as shown in Figure 4, due to the thermal stress from the various swelling coefficients within the geopolymer. However, the SF-containing specimens display fewer and shallower cracks in comparison to specimens without SF, especially after treatment at 850 °C, corresponding to the higher strength. Generally, the incorporated SF enhances the mechanical strength of the slag/FA binder from RT to 850 °C, evidenced by the improved strength, which is also favorable for withstanding building fires.



Figure 4. The surface appearance of specimens after heat treatment.

However, obvious melting is observed for the SF-containing specimen subjected to 1200 °C, which is disadvantageous to withstanding a building fire effectively. Therefore, the bloating effect on the dimension for SF-containing specimens occurs after exposure to 1200 °C, while specimens without SF keep their initial shape, revealing the reduced melting point of slag/FA binders incorporating SF.

### 3.3.2. Micromorphologies

The micromorphologies of specimens subjected to elevated temperatures are presented as a series of electron micrographs with an amplification of  $5000 \times$  in Figures 5 and 6. The coexistence of amorphous silicate gels and crystals is observed, but unreacted spherical FA particles disappear and the rod-like or needle-like feldspar increases with the increasing treatment temperatures gradually, due to further geopolymerization. Generally, uniform and smooth fracture surfaces with smaller holes are observed for the ternary SF/slag/FA binder (Figure 6a–c) after sub-high temperature (500 °C) exposure in comparison to the binary specimen with the rugged and non-uniform surface (Figure 5a–c). Interestingly, more and larger pores or holes appear on the fracture surface of specimens after 850 °C heating as shown in Figure 5d, which shrink for SF-containing specimens as shown in Figure 6d. Compared with the needle-like feldspars in Figure 5e, the SF-containing sample exhibits a compact and dense structure after exposure to 1200 °C and the needle-like feldspars are covered or embedded with uniform and amorphous silicates as shown in Figure 6e, revealing that doping with SF effectively inhibits cracking and facilitates densification to some extent.



**Figure 5.** SEM photos of binary slag/FA binders after heat treatment: (a) RT, (b) 150  $^{\circ}$ C, (c) 500  $^{\circ}$ C, (d) 850  $^{\circ}$ C, (e) 1200  $^{\circ}$ C.



**Figure 6.** SEM photos of ternary SF/slag/FA binders after heat treatment: (**a**) RT, (**b**) 150 °C, (**c**) 500 °C, (**d**) 850 °C, (**e**) 1200 °C.

## 3.3.3. Pore Size Distributions

The replacement with 10 wt.% SF favors improvements in the compactness of binary slag/FA pastes; the pore volume of  $0.2 \sim 3 \mu m$  demonstrates an obvious increase as shown in Table 2, as it climbs from 11.39% to 35.81%. Because the incorporated SF could trigger the formation of N–A–S–H or N–(Ca)–A–S–H, prompting the chain propagation of the geopolymer, the Ca mainly derives from the slag to balance the charge of aluminosilicate inorganic polymers. Also, the unreacted SF enters or fills the interstices of N–A–S–H, making the porosity drop from 20.93% to 13.47% and the median pore diameter decrease from 6.4 to 5.6 nm. Combined with the SEM images in Figures 5a and 6a, it is confirmed again that the incorporated SF plays an effective and crucial role in reinforcing the microstructure of slag/FA pastes, leading to the compact and dense structure.

Table 2. Pore size distributions of specimens at RT.

Specimens	<20 nm	20–200 nm	0.2~3 μm	>3 µm	Median Pore	Porosity
	(%)	(%)	(%)	(%)	Diameter (nm)	(%)
Slag/FA paste	40.02	9.17	11.39	38.43	6.4	20.93
SF/slag/FA paste	41.16	3.14	35.81	19.88	5.6	13.47

## 3.4. TG/DTG and DSC

The TG/DTG and heat flow curves of specimens are shown in Figure 7, and the peak shifts from 128 °C to 135 °C after the replacement of FA with 10 wt.% SF from the DTG curve, corresponding to the higher thermal stability. Meanwhile, the end temperature of mass loss rises from 166 to 185 °C from the TG in Figure 7a,b, indicating higher thermal stability. Because of the pozzolan and the filling effects of SF, which could react with N–A–S–H or N–(Ca)–A–S–H to form more gels and also enter or fill the space left by geopolymerization [8,9], there is an increase in the DTG peak.

The heat flow (DSC) of the specimen reveals that the SF postpones the thermal exchange between the matrix and surrounding area in the sub-high temperature, the endothermic peak shifts from 139 to 148 °C, and the tiny exothermic peak shifts from 280 to 301 °C as shown in Figure 7c. It is reported that the dehydration of specimens occurs below 300 °C, dehydroxylation derived from SiO<sub>4</sub> or AlO<sub>4</sub> tetrahedron occurs at about 500 °C, and 900 °C is required for the complete decomposition of N–(C)–A–S–H [27]. It is appropriate to emphasize that no endothermic peak at around 450 °C caused by the dehydration of Ca(OH)<sub>2</sub> is detected, revealing that no Ca(OH)<sub>2</sub> is formed [28]. There is no endothermic peak at around 500 °C, presenting few SiO<sub>4</sub> or AlO<sub>4</sub> tetrahedrons. Interestingly, the tiny exothermic peak at 832 °C might be attributed to the melting of amorphous silicates involved in the geopolymer.



Figure 7. Cont.



Figure 7. TG/DTG and DSC of samples including (a) slag/FA paste, (b) SF/slag/FA paste, and (c) DSC.

## 3.5. FTIR Analysis

The peak at 1005 cm<sup>-1</sup> is assigned to the oligomeric Si-O vibration [29], which shifts to a lower wavenumber after the incorporation of SF due to the increasing content of monomeric Si(OH)<sub>4</sub> as shown in Figure 8c,d. The absorption peak at 2360 cm<sup>-1</sup> is attributed to the C=O in CO<sub>2</sub> from the environment, which is inevitable in the testing condition. However, the new peak at 1348 cm<sup>-1</sup> is assigned to the vibration of  $[SiO_4]^{4-}$  and  $[AIO_4]^{5-}$  [30], corresponding to the combination of activated aluminosilicates, evidenced by the XRD results. The peak at 672 cm<sup>-1</sup> is associated with Si-O-Al stretching vibrations [31]. The reactive Si-OH in the N–A–S–H or N–(Ca)–A–S–H chains dehydrates and transforms into silicates. Similarly, the combination reactions between  $[SiO_4]^{4-}$  and  $[AIO_4]^{5-}$  occur during the heat treatment of 1200 °C, corresponding to the formation of gehlenite and labradorite, corresponding with the results of XRD and SEM.



**Figure 8.** FTIR spectra of samples including (**a**) SF/slag/FA binder after 1200 °C exposure, (**b**) slag/FA binder after 1200 °C exposure, (**c**) slag/FA binder after 150 °C exposure, and (**d**) SF/slag/FA binder after 150 °C exposure.

## 4. Discussions

#### 4.1. Mechanical Strength and Elevated Temperatures

During the sub-high temperature, the pozzolan and the filling effects of SF promote the formation and transformation of amorphous silicates within the binary slag/FA binder, which is beneficial for improved strength. The amorphous SiO<sub>2</sub> involved in the SF is a typical forming agent of the network, and the enrichment of Si(OH)<sub>4</sub> accelerates the forming of a silicate network by extending  $\equiv$ Si–O–Si $\equiv$  chains (serving as the precursor from the hydrolysis of Na<sub>2</sub>SiO<sub>3</sub>) and creating bridging oxygen groups, which can trap the Ca<sup>2+</sup> for charge equilibrium and grow into N–A–S–H or N–(Ca)–A–S–H. Actually, a moderate temperature treatment ( $\leq$ 100 °C) may enhance the tensile properties of the FA/cement binder due to the formation of more micro-cracks [32].

When the temperature is above 800 °C, the mechanical strength of the specimens suffers a dramatic drop. This is in agreement with Su et al. [33], implying that the heat treatment at about 800 °C is fatal for geopolymers. On the other hand, replacement with 10 wt.% SF lowers the CaO/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> molar ratios, which drop from 0.325 and 0.638 to 0.297 and 0.528 (SF-containing sample) according to the chemical composition, respectively. The SF-containing sample exerts a lower melting point and a higher volume deformation at 1200 °C. Wu et al. [34] suggest that lower CaO/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> could enhance the viscosity in the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–CaO–MgO–Na<sub>2</sub>O–K<sub>2</sub>O system. A lower melting point induced by substitution with 10 wt.% SF promotes the increasing content of silicate melts, which could "seal" the cracks, improving the temperature-induced dehydration, dehydroxylation, and thermal incompatibility [35], as well as the stress induced by varying degrees of shrinkage within the matrix during the cooling process [36].

## 4.2. Microstructure and Elevated Temperatures

Because the dehydration of calcium silicate hydrate (C–S–H) occurs at 135–150 °C [37], the doped SF can react with binary slag/FA binder and transform into N–A–S–H or N–(Ca)–A–S–H, leading to a denser and compact microstructure, presenting a right shift of the endothermic peak form the result of DTG, as well as increases in the mechanical properties. Meanwhile, an empirical relationship between the flexural strength and porosity (*p*) is shown in Equation (1), where  $\sigma_0$  and n are two constants determined experimentally [38]. It follows that the flexural strength decreases exponentially with porosity. The replacement of FA with SF favors a lower porosity and an increase in the pore volume of 0.2~3 µm, as well as the retardance of water evaporation due to denser structures [39].

$$FS = \sigma_0 \bullet \exp(-np) \tag{1}$$

During heat treatment at a sub-high temperature, the mechanical strength is improved due to the further geopolymerization within the slag/FA paste, with "right shifts" of the mass loss peak and the endothermic peak of heat flow, leading to a denser and smooth fracture surface in the microscopic morphology.

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The SF begins to fuse at 1100 °C and forms a viscous liquid phase [40]. However, when the specimen is exposed to 1200 °C heat treatment for 2 h, melting of the amorphous silicates at 1000~1100 °C occurs, which boosts the bloating effect within the matrix. The specimen without SF appears to melt little because of the tension induced by the escaping O<sub>2</sub>, which promotes more cracks and accelerates a fast deterioration of the matrix, corresponding to the lower flexural strength. Tsai et al. [41] find that the bloating effect occurs in municipal solid waste, and our finding is that the amorphous SF diminishes the melting point, boosting the reactions between  $[SiO_4]^{4-}$  and  $[AlO_4]^{5-}$  and the formation of labradorite. As a kind of phase change material, the bloating SF holds beneficial effects for crack blunting and twisting [42] in the liquid phase.

On the whole, SF plays a strengthening role in the slag/FA paste due to the filling effect and pozzolan reactivity at the sub-high temperature. The filling effect could insert the gap or holes and form micro-cracks, and pozzolan reactivity promotes more amorphous gels through further geopolymerization, which favors the increasing pore volume of 0.2~3  $\mu$ m. This results in a continuous increase in the mechanical strength, favoring "right shifts" of the endothermic peak and the initial and final temperature of mass loss, presenting a uniform and smooth fracture surface. Meanwhile, during the heat treatment above 850 °C, the substitution of FA with 10 wt.% SF diminishes the melting point of the binary slag/FA binder, and the unreacted SF is prone to melting and transforms into a liquid phase, which could generate crack blunting and twisting, leading to the occurrence of a bloating effect with a greater volume deformation, promoting the formation of labradorite between  $[SiO_4]^{4-}$  and  $[AlO_4]^{5-}$  involved in the geopolymer chains, as evidenced by the results of XRD.

#### 5. Conclusions

The effect of silica fume on the microstructure of alkali-activated slag/FA (slag/FA = 30:70, wt.%) pastes after exposure to elevated temperatures (150, 500, 850, and 1200 °C) is investigated by XRD, SEM, TG, MIP, and FTIR spectroscopy. It is determined that adjusting the formulation of solid waste could improve geopolymers' fireproof performance, and the following conclusions are drawn:

- (1) The replacement of FA with 10 wt.% SF triggers an increasing pore volume of 0.2~3 µm during sub-high temperatures below 850 °C, leading to a continuous increase in the mechanical strength, "right shifts" of the endothermic peak, and a uniform and compact fracture surface due to its filling and pozzolan effects through the propagation of N–A–S–H or N–(Ca)–A–S–H.
- (2) The transformation of gehlenite and labradorite is determined for the samples after exposure to an elevated temperature above 850 °C. The bloating effect is proposed to be involved in unreacted SF together with the amorphous N–A–S–H or N–(Ca)–A–S– H at 1200 °C, leading to a greater deformation due to the further restructuring of the geopolymer chain composed of the [SiO<sub>4</sub>]<sup>4–</sup> and [AlO<sub>4</sub>]<sup>5–</sup> tetrahedra.
- (3) However, this study's limitations lie in accurately testing the bonding structure of N–A–S–H or N–(Ca)–A–S–HN, which is full of challenges because of the shortage of relative techniques and theories. Meanwhile, future improvements in the application of these geopolymers as cementitious materials with multi-component metallurgical solid waste require the development of relative standards and rules, especially policies to subsidize enterprises.

**Author Contributions:** Conceptualization, Y.W.; methodology, Y.W. and W.D.; software, W.D.; validation, W.D. and Y.W.; formal analysis, W.D.; investigation, W.D. resources, Y.W.; data curation, W.D.; writing—original draft preparation, W.D.; writing—review and editing, Y.W.; visualization, Y.W.; supervision, Y.W.; project administration, Y.W.; funding acquisition, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

## References

- Wang, S.; Liu, B.; Zhang, Q.; Wen, Q.; Lu, X.; Xiao, K.; Ekberg, C.; Zhang, S. Application of geopolymers for treatment of industrial solid waste containing heavy metals: State-of-the-art review. J. Clean. Prod. 2023, 390, 136053. [CrossRef]
- Harmal, A.; Khouchani, O.; El-Korchi, T.; Tao, M.; Walker, H.W. Bioinspired brick-and-mortar geopolymer composites with ultra-high toughness. *Cem. Concr. Compos.* 2023, 137, 104944. [CrossRef]
- Peng, X.; Li, H.; Hu, Y. Preparation of metakaolin-fly ash cenosphere based geopolymer matrices for passive fire protection. J. Mater. Res. Technol. 2023, 23, 604–610. [CrossRef]
- Kaliyannan, G.V.; Kumar, P.S.; Kumar, S.M.; Deivasigamani, R.; Rajasekar, R. Mechanical and tribological behavior of SiC and fly ash reinforced AI 7075 composites compared to SAE 65 bronze. *Mater. Test.* 2018, 60, 1225–1231. [CrossRef]
- 5. Roy, R.; Chakraborty, S.; Bisai, R.; Palaniappan, S.K.; Pal, S.K. Suitability of Bottom Ash for Stowing in Underground Coal Mines with and Without Addition of Settling Agent. *J. Inst. Eng. India Ser. D* 2021, *102*, 505–520. [CrossRef]
- 6. Raut, A.; Murmu, A.; Alomayri, T. Physico-Mechanical and thermal behavior of prolong heat Cured geopolymer blocks. *Constr. Build. Mater.* **2023**, *370*, 130309. [CrossRef]
- 7. Oh, J.; Monteiro, P.; Jun, S.; Choi, S.; Clark, S.M. The evolution of strength and crystalline phases for alkali-activated ground blast furnace slag and fly ash-based geopolymers. *Cem. Concr. Res.* 2010, 40, 189–196. [CrossRef]
- 8. Luo, X.; Xu, J.; Bai, E.; Li, W. Systematic study on the basic characteristics of alkali-activated slag-fly ash cementitious material system. *Constr. Build. Mater.* **2012**, *29*, 482–486. [CrossRef]
- 9. Chithiraputhiran, S.; Neithalath, N. Isothermal reaction kinetics and temperature dependence of alkali activation of slag, fly ash and their blends. *Constr. Build. Mater.* **2013**, *45*, 233–242. [CrossRef]
- Danish, A.; Öz, A.; Bayrak, B.; Kaplan, G.; Aydın, A.C.; Ozbakkaloglu, T. Performance evaluation and cost analysis of prepacked geopolymers containing waste marble powder under different curing temperatures for sustainable built environment. *Resour. Conserv. Recycl.* 2023, 192, 106910. [CrossRef]
- Sothornchaiwit, K.; Dokduea, W.; Tangchirapat, W.; Keawsawasvong, S.; Thongchom, C.; Jaturapitakkul, C. Influences of Silica Fume on Compressive Strength and Chemical Resistances of High Calcium Fly Ash-Based AlkaliActivated Mortar. *Sustainability* 2022, 14, 2652. [CrossRef]
- Hossein, H.A.; Hamzawy, E.M.; El-Bassyouni, G.T.; Nabawy, B.S. Mechanical and physical properties of synthetic sustainable geopolymer binders manufactured using rockwool, granulated slag, and silica fume. *Constr. Build. Mater.* 2023, 367, 130143. [CrossRef]
- 13. Zhang, B.; Ma, Y.; Yang, Y.; Zheng, D.; Wang, Y.; Ji, T. Improving the high temperature resistance of alkali-activated slag paste using municipal solid waste incineration bottom ash. *J. Build. Eng.* **2023**, *72*, 106664. [CrossRef]
- 14. Rovnaník, P.; Bayer, P.; Rovnaníková, P. Characterization of alkali activated slag paste after exposure to high temperatures. *Constr. Build. Mater.* **2013**, *47*, 1479–1487. [CrossRef]
- Rashad, A.; Bai, Y.; Basheer, P.; Collier, N.; Milestone, N. Chemical and mechanical stability of sodium sulfate activated slag after exposure to elevated temperature. *Cem. Concr. Res.* 2012, *42*, 333–343. [CrossRef]
- 16. Rashada, A.; Khalil, M. A preliminary study of alkali-activated slag blended with silica fume under the effect of thermal loads and thermal shock cycles. *Constr. Build. Mater.* **2013**, *40*, 522–532. [CrossRef]
- 17. Shilar, F.; Ganachari, S.; Patil, V.; Reddy, I.N.; Shim, J. Preparation and validation of sustainable metakaolin based geopolymer concrete for structural application. *Constr. Build. Mater.* **2023**, *371*, 130688. [CrossRef]
- Bernardo, E.; Dal Maschio, R. Glass–ceramics from vitrified sewage sludge pyrolysis residues and recycled glasses. *Waste Manag.* 2011, *31*, 2245–2252. [CrossRef]
- 19. Bernardo, E.; Esposito, L.; Rambaldi, E.; Tucci, A.; Pontikes, Y.; Angelopoulos, G.N. Sintered esseneite–wollastonite–plagioclase glass–ceramics from vitrified waste. *J. Eur. Ceram. Soc.* 2009, *29*, 2921–2927. [CrossRef]
- Segui, P.; Aubert, J.E.; Husson, B.; Measson, M. Utilization of a natural pozzolan as the main component of hydraulic road binder. Constr. Build. Mater. 2013, 40, 217–223. [CrossRef]
- 21. Bernardo, E.; Bonomo, E.; Dattoli, A. Optimisation of sintered glass–ceramics from an industrial waste glass. *Ceram. Int.* **2010**, *36*, 1675–1680. [CrossRef]

- 22. Fang, Y.; Kayali, O. The fate of water in fly ash-based geopolymers. Constr. Build. Mater. 2013, 39, 89–94. [CrossRef]
- 23. Yilmaz, G. Structural characterization of glass–ceramics made from fly ash containing SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub>–CaO and analysis by FT-IR–XRD–SEM methods. *J. Mol. Struct.* **2012**, *1019*, 37–42. [CrossRef]
- 24. Rathossi, C.; Pontikes, Y. Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments. Part I: Reaction paths, crystalline phases, microstructure and colour. *J. Eur. Ceram. Soc.* **2010**, *30*, 1841–1851. [CrossRef]
- Ding, J.; Ma, S.; Zheng, S.; Zhang, Y.; Xie, Z.; Shen, S.; Liu, Z. Study of extracting alumina from high-alumina PC fly ash by a hydro-chemical process. *Hydrometallurgy* 2016, 161, 58–64. [CrossRef]
- Sarıdemir, M.; Çelikten, S. Effects of Ms modulus, Na concentration and fly ash content on properties of vapour-cured geopolymer mortars exposed to high temperatures. *Constr. Build. Mater.* 2023, 363, 129868. [CrossRef]
- Guerrieri, M.; Sanjayan, J. Behavior of combined fly ash/slag-based geopolymers when exposed to high temperatures. *Fire Mater.* 2010, 34, 163–175. [CrossRef]
- Rashad, A.; Sadek, D.; Hassan, H. An investigation on blast-furnace slag as fine aggregate in alkali-activated slag mortars subjected to elevated temperatures. J. Clean. Prod. 2016, 112, 1086–1096. [CrossRef]
- Hua, S.; Yan, W.; Duan, J. Polymerization of silicate on TiO<sub>2</sub> and its influence on arsenate adsorption: An ATR-FTIR study. *Colloids Surf. A Physicochem. Eng. Asp.* 2015, 469, 180–186. [CrossRef]
- Penilla, R.; Bustos, A.; Elizalde, S. Zeolite synthesized by alkaline hydrothermal treatment of bottom ash from combustion of municipal solid wastes. J. Am. Ceram. Soc. 2003, 86, 1527–1533. [CrossRef]
- 31. Bai, Y.; Guo, W.; Zhao, Q.; Zhang, N.; Xue, C.; Wang, S.; Song, Y. Performance deterioration of municipal solid waste incineration fly ash-based geopolymer under sulfuric acid attack. *Constr. Build. Mater.* **2023**, *391*, 131847. [CrossRef]
- 32. Yu, J.; Lin, J.; Zhang, Z.; Li, V.C. Mechanical performance of ECC with high-volume fly ash after sub-elevated temperatures. *Constr. Build. Mater.* **2015**, *99*, 82–89. [CrossRef]
- Su, H.; Xu, J.; Ren, W. Mechanical properties of geopolymer concrete exposed to dynamic compression under elevated temperatures. *Ceram. Int.* 2016, 42, 3888–3898. [CrossRef]
- Wu, G.; Yazhenskikh, E.; Hack, K.; Wosch, E.; Müller, M. Viscosity model for oxide melts relevant to fuel slags. Part 1: Pure oxides and binary systems in the system SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–CaO–MgO–Na<sub>2</sub>O–K<sub>2</sub>O. *Fuel Process. Technol.* 2015, 137, 93–103. [CrossRef]
- 35. Zhang, H.Y.; Kodur, V.; Wu, B.; Cao, L.; Wang, F. Thermal behavior and mechanical properties of geopolymer mortar after exposure to elevated temperatures. *Constr. Build. Mater.* **2016**, *109*, 17–24. [CrossRef]
- Ren, X.; Zhang, W.; Zhang, Y.; Zhang, P.-X.; Liu, J.-H. Effects of Fe<sub>2</sub>O<sub>3</sub> content on microstructure and mechanical properties of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. *Trans. Nonferr. Met. Soc. China* 2015, 25, 137–145. [CrossRef]
- Rong, Z.; Sun, W.; Xiao, H.; Jiang, G. Effects of nano-SiO<sub>2</sub> particles on the mechanical and microstructural properties of ultra-high performance cementitious composites. *Cem. Concr. Compos.* 2015, *56*, 25–31. [CrossRef]
- Zhao, X.; Zhang, N.; Ru, H.; Liang, B.; Chen, D. Mechanical properties and toughening mechanisms of silicon carbide nanoparticulate reinforced Alon composites. *Mater. Sci. Eng. A* 2012, 538, 118–124. [CrossRef]
- Zhang, Y.J.; Wang, Y.C.; Xu, D.L.; Li, S. Mechanical performance and hydration mechanism of geopolymer composite reinforced by resin. *Mater. Sci. Eng. A* 2010, 527, 6574–6580. [CrossRef]
- 40. Xu, J.; Zhao, F.; Guo, Q.; Yu, G.; Liu, X.; Wang, F. Characterization of the melting behavior of high-temperature and low-temperature ashes. *Fuel Process. Technol.* **2015**, *134*, 441–448. [CrossRef]
- 41. Tsai, C.; Wang, K.; Chiou, I. Effect of SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–flux ratio change on the bloating characteristics of lightweight aggregate material produced from recycled sewage sludge. *J. Hazard. Mater. B* **2006**, *134*, 87–93. [CrossRef] [PubMed]
- 42. Fernandes, F.; Manari, S.; Aguayo, M.; Santos, K.; Oey, T.; Wei, Z.; Falzone, G.; Neithalath, N.; Sant, G. On the feasibility of using phase change materials (PCMs) to mitigate thermal cracking in cementitious materials. *Cem. Concr. Compos.* **2014**, *51*, 14–26. [CrossRef]

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