

Article

Effect of Municipal Solid Waste Incineration Ash on Microstructure and Hydration Mechanism of Geopolymer Composites

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Abstract: The geopolymerization process is an appropriate way of disposing of municipal solid waste incineration fly ash (MSWIFA), and possesses the advantages of immobilizing the heavy metals and making full use of its pozzolanic properties in manufacturing green, cementitious materials. In this study, coal fly ash (FA) and metakaolin (MK) were used to prepare a geopolymer composite, with MK partially replaced by different proportions of MSWIFA through the alkali-activation method. The microstructure and hydration mechanism of the geopolymer composites containing MSWIFA were investigated through mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), and Fourier transform-infrared spectroscopy (FT-IR) tests; and the immobilization effect of the geopolymer paste on heavy metal ions was explored through inductively coupled plasma-atomic emission spectrometry (ICP-AES). The MIP analysis showed that the addition of MFARR had an overall degrading effect on the pore structure of the matrix. When the content of MSWIFA reached the maximum of 35%, the porosity and average pore diameter increased by 25% and 16%, respectively, corresponding to the case without MSWIFA. However, the pore size distribution exhibited an improving trend when the MFARR was increased from 15% to 25%. The SEM images revealed that the integrity of the micromorphology of the geopolymer mortar became weaker after adding MSWIFA. When the MSWIFA content was increased to 35%, the microstructural compactness decreased and more pores and microcracks appeared in the matrix. The FT-IR pattern study suggested that all the geopolymer composites had a similar internal structure, consisting of O-H, C-O, Si-O-Si, and Si-O-Al. The main component of the geopolymer paste hydrated at 28 d remained dominated by calcium silica-aluminate (C-A-S-H), when the MSWIFA ranged from 0% to 35%. Finally, the ICP-AES results showed that the leaching concentrations of the geopolymer paste of J-40 at 28 d for Cd, Cr, Cu, Pb, and Zn met the requirements of Chinese standards.

Keywords: municipal solid waste incineration fly ash (MSWIFA); geopolymer; microstructure; hydration mechanism; heavy metal leaching



Citation: Wang, C.; Zhang, P.; Guo, J.; Zhang, H.; Wang, T. Effect of Municipal Solid Waste Incineration Ash on Microstructure and Hydration Mechanism of Geopolymer Composites. *Buildings* **2022**, *12*, 723. <https://doi.org/10.3390/buildings12060723>

Academic Editors: Lei Wang and Shengwen Tang

Received: 28 April 2022

Accepted: 24 May 2022

Published: 26 May 2022

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1. Introduction

Researchers are eager to find a promising alternative to replace cement, due to the growing concern over global climate change. As a promising alternative to cement, geopolymers are attracting widespread attention. Geopolymer composites have much lower carbon emissions than cement, which is beneficial to the environment [1,2]. Therefore, the application of geopolymer binders can help to alleviate a significant amount of the resource consumption and carbon dioxide emissions caused by the production of concrete [3]. Typically, almost all natural minerals rich in silicon and aluminum oxides, as well as industrial wastes, are potential raw materials for geopolymers. The raw materials usually include granulated blast furnace slag (GBFS), fly ash (FA), metakaolin (MK), or rice husk ash (RHA) [4–6]. MK and FA are two generally applied aluminosilicate source materials for

producing geopolymers, because thermal power generation emits a great quantity of FA, and MK is easily available and possesses a satisfactory activity [7–12].

Related research results indicated that MK-based geopolymers usually possess remarkable mechanical properties at normal temperature, but they are vulnerable to cracking and strength degradation at high temperatures [13,14]. An FA-based geopolymer exhibits better high-temperature resistance than MK-based geopolymers. In addition, compared with FA, due to the large specific surface area of MK, the geopolymeric reaction in the early stage is more efficient, and the MK-based geopolymer has a higher early strength [15,16]. Numerous works reported in the literature for the preparation of geopolymers have been carried out using the metakaolin activation method. The inclusion of GBFS in a MK-based geopolymer seems to improve the overall performance, such as the mechanical properties, residual compressive strength, and stability at elevated temperature [13]. Rice husk is quite attractive, because it is an abundant agricultural waste and a large amount is available in some developing countries, such as Thailand and Cameroon [17–19]. RHA is the combustion product of rice husk, and has good pozzolanic reactivity. A great deal of experiments have been conducted to explore the impact of RHA on geopolymer composites. Previous study results showed that the overall performance of MK-based geopolymer can be improved by adding RHA [20–23]. In order to better combine the advantages of MK-based and FA-based geopolymer, MK and FA can be blended to produce a MK–FA-based geopolymer, which will display higher mechanical properties at ambient temperature and elevated temperatures, compared to the condition with only addition of MK or FA [15], which are suitable for applications in bad environments with high temperature.

With the development of the economy and rapid urbanization, a great deal of municipal solid waste is generated, which leads to serious environmental pollution problems [24–26]. Commonly, there are three kinds of treatment methods: compost, incineration, and landfill. For decades, incineration has been considered a good choice for disposing of solid waste, due to its effective mass and volume reduction of waste. The other advantages of incineration include the straightforward treatment process, low cost, and the potential for power generation [27]. After the combustion of waste, a considerable proportion of MSWIFA will be produced. Owing to containing heavy metals and toxic organic substances, MSWIFA is a harmful substance, and it must be properly treated before it is reused [28]. Using zeolites for adsorption of heavy metal cations is a feasible method [29]. Another method for immobilization is preparing geopolymers. Although MSWIFA is a threat to the environment, it contains element such as Si, Al, and Ca, which makes it possible for MSWIFA to serve as a raw material for geopolymers. An alkali-activated method has been proposed for solidification of waste in a variety of works, because alkali-activation can display an excellent solidification effect for heavy metals, which helps relieve MSWIFA deficiency in silicon and aluminum components [30]. Some experiments have been conducted using MK or FA as an additive in the solidification of MSWIFA through the alkali-activated method. A geopolymer was made with MK partially replaced by incinerator fly ash, to assess the effect of immobilization, and the results showed that the leached heavy metals in the test solution fell within the limits [31]. MSWIFA was introduced into an alkali-activated FA-based matrix to analyze its chemical behavior, and an overall decline in the leachability of heavy metals was observed [32]. A stabilization of MSWIFA containing harmful metals using different reagents for alkaline activation was reported, which illustrated that heavy metals such as Pb, Cd, Cr, or Zn could be effectively solidified by using FA-based geopolymerization technology [33]. The study presented the mechanism by which the immobilized heavy metals were thought to be physically or chemically fixed in a geopolymer network, and heavy metal ions may play a role in the charge balance [34].

A comparison of the effects of heavy metal solidification of an MK-based geopolymer and FA-based geopolymer, both containing MSWIFA, was conducted, and the level of immobilization was much higher in the sample of the MK-based geopolymer than that of the FA-based geopolymer [35]. Although many researchers have conducted a great deal of investigations on the fabrication of geopolymer composites and disposal measures

for MSWIFA, there are few research results on the effect of MSWIFA on a MK-FA-based geopolymer. Therefore, in this study, FA and MK were used to prepare a green geopolymer composite, with MK partially replaced by different proportions of MSWIFA through the alkali-activated method. MIP and SEM tests were utilized to reveal the mechanism of MSWIFA in the pore structure of the composite. The hydration mechanism of geopolymer composites containing MSWIFA was analyzed using a FT-IR scanning test, and heavy metal leaching tests were conducted to assess the solidification effect of the geopolymer composite on the heavy metal ions in MSWIFA.

2. Experimental Procedures

2.1. Materials

MK, FA, alkaline activation solution and natural river sand were used as the raw materials for the preparation of geopolymer composites. The chemical compositions of MK, FA, and MSWIFA are listed in Table 1. MK with more than 97% SiO_2 and Al_2O_3 was produced by Chenxing Industrial Co., Ltd., Shijiazhuang, China. The content of silica and alumina of FA was high, 60.98% and 24.47%, respectively, and it was called low-calcium FA because the calcium content was 5.58%. The MSWIFA silica and alumina content in the IFA was low, at 3.37% and 1.69%, respectively. The alkaline activation mainly constituted sodium silicate (Na_2SiO_3 , SiO_2 : Na_2O : H_2O = 25.9: 8.4: 65.7) and sodium hydrate flakes, with 99% NaOH. The modulus ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) of the water glass solution was adjusted from 3.08 to 1.3 using NaOH. In addition, an efficient superplasticizer with 25% water reducing rate was utilized for the experiment. The fine aggregate used in this research was natural river sand, which was supplied by Nanyang sand and gravel plant, Nanyang, China.

Table 1. Chemical compositions of MK, FA, and MSWIFA.

Chemical Compositions (wt.%)	MK	FA	MSWIFA
SiO_2	54.34	60.98	3.2
Al_2O_3	43.52	24.47	2.7
Fe_2O_3	1.17	6.70	0.3
CaO	0.42	5.58	35.9
MgO	0.35	0.68	—
K_2O	0.26	—	9.4
Na_2O	0.18	—	15.4
Cl	—	—	24
LOI *	0.5	0.75	12.8

* Loss on ignition.

2.2. Preparation of Geopolymer Composites

2.2.1. Mix Proportions

Considering the degree of the geopolymerization process, and the lack of research on the mechanism of the microstructure and hydration of MK-FA-based geopolymers, a mixture of FA and MK was proposed to manufacture geopolymer composites in this study. In order to avoid the negative consequences of too rapid gelation of the geopolymer, the mass fraction of FA was fixed at 50% [36–39]. In accordance with related results, the replacement levels of MSWIFA were set as 0%, 5%, 15%, 25%, 35%, and 40% [40–43]. The preparation of geopolymer mortar was based on a paste with a 1:1 binder:sand ratio. The mix proportions of this study are clearly shown in Table 2, in which J stands for paste, and S stands for mortar.

2.2.2. Preparation Process of Geopolymer Composites

In the experiment, it is required that the preparation of alkaline activator with a water glass modulus of 1.3 be completed in advance. To prepare the alkaline activator, NaOH flakes were added to the Na_2SiO_3 solution, which was stirred until the solution changed from cloudy to transparent; and then the solution was sealed and left for 12 h to cool totally,

before the preparation of the geopolymer. The specific preparation process is shown in Figure 1. Specimens with dimensions of 100 mm × 100 mm × 100 mm were cast for the tests in this work. The specimens were demolded after hardening for 24 h in an indoor environment. Then, the specimens were placed in a standard curing room (temperature of 20 ± 2 °C, relative humidity above 95%) for the target curing period. For the MIP and SEM tests, the curing period was 28 d, and the curing periods of the FT-IR tests were 3 d, 7 d, and 28 d.

Table 2. Mix proportions of the geopolymer composites.

Mix ID	FA	MK	MSWIFA	River Sand	Na ₂ SiO ₃	NaOH	Water	Superplasticizer
	kg/m ³	kg/m ³	%	kg/m ³	kg/m ³	kg/m ³	kg/m ³	%
J-00	533.9	533.9	0	–	446.6	71.9	40.6	1.0
J-05	533.9	480.5	5	–	446.6	71.9	40.6	1.0
J-15	533.9	373.7	15	–	446.6	71.9	40.6	1.0
J-25	533.9	267.0	25	–	446.6	71.9	40.6	1.0
J-35	533.9	160.2	35	–	446.6	71.9	40.6	1.0
J-40	533.9	106.8	40	–	446.6	71.9	40.6	1.0
S-00	355.9	355.9	0	712	446.6	71.9	40.6	1.0
S-05	355.9	320.3	5	712	446.6	71.9	40.6	1.0
S-15	355.9	249.1	15	712	446.6	71.9	40.6	1.0
S-25	355.9	178.1	25	712	446.6	71.9	40.6	1.0
S-35	355.9	106.7	35	712	446.6	71.9	40.6	1.0

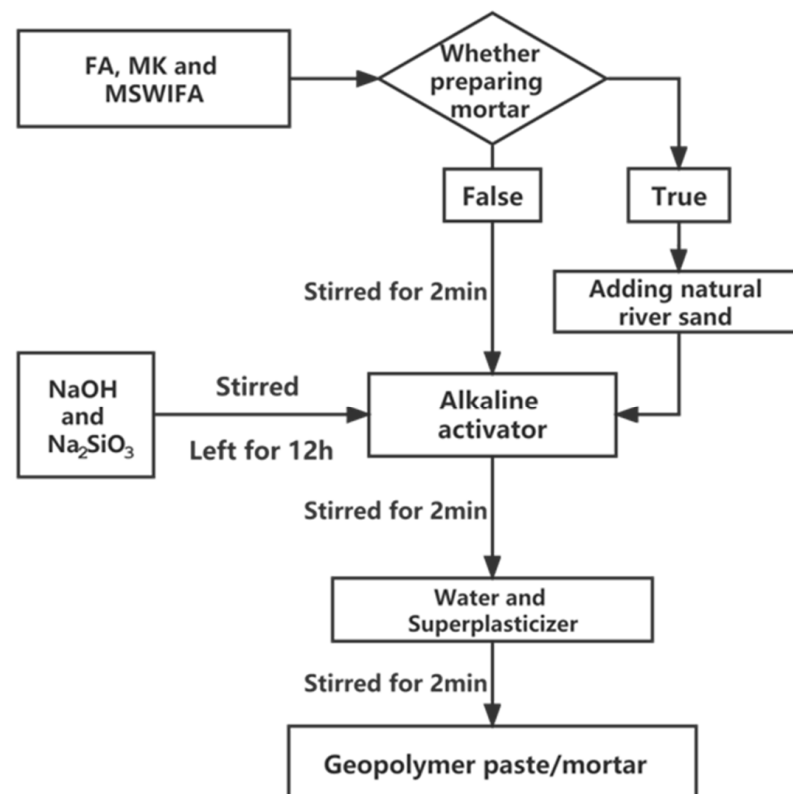


Figure 1. Preparation process of the geopolymer composite.

2.3. Test Methods

2.3.1. Mercury Intrusion Porosimetry (MIP) Test

The mechanical properties and durability of geopolymer composites are associated with the degree of density, which is mainly characterized by the porosity and pore diameter distribution [44–47]. The specimens selected were 2–3 g of irregular particles

with a diameter of about 10 mm, and the pore radius calculation was performed using the Washburn equation [48]. The equipment used in this study was manufactured by Micromeritics Co., Ltd., Norcross, GA, USA, with the type AutoPore IV 9500.

2.3.2. Scanning Electron Microscope (SEM) Test

The variation of raw materials, as well as the mix proportion, makes the microstructure of geopolymer composites very different. In this study, SEM tests were conducted to study the micromorphology and hydration products of the geopolymer mortar, and the results of MIP tests were combined to explore the impact of MSWIFA substitution amount on the micromorphology of the geopolymer mortar. The microtopography of the geopolymer composites was obtained using a ZMS300 type field emission microscope, Carl Zeiss AG, Oberkochen, Germany. Before observation, the formed cube samples were cut into small specimens of 10 mm × 10 mm × 10 mm with a cutting machine. Then, the prepared small samples were put into a vacuum box, and the observation surface was coated with gold. Gold was sprayed, so that the surface emitted secondary electrons for the electron scanning observation.

2.3.3. Fourier Transform-Infrared Spectroscopy (FT-IR) Test

FT-IR tests are often used to study the molecular structure and reaction products of a material. The reaction mechanism of geopolymer composites can be analyzed based on FT-IR scanning tests. In this study, the chemical compositions of the hydration products were examined using an FT-IR spectrometer, of the type Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA. The spectra were collected within a scanning range of 8000–50 cm^{−1}.

2.3.4. Heavy Metal Leaching Concentration Test

In this study, heavy metal leaching concentration tests were carried out according to the following Chinese standards: “Solid Waste-Extraction Procedure for Leaching Toxicity Sulphuric acid and Nitric Acid Method (HJ/T 299-2007)” and “Standard for Pollution Control on the Landfill Site of Municipal Solid Waste (GB 5085.3-2007)” [49,50]. An acid mixture consisting of concentrated sulfuric acid and concentrated nitric acid at 2:1 was put into distilled water to prepare the extractant. After that, another 100 g of MFA specimen was weighed and placed in a dry constant weight container, which was dried at 105 °C; and the water content of MFA was calculated. Then, 200 g of MFA by dry weight was placed in a 2 L extraction bottle. Based on the moisture content of the MFA, the volume of extractant required was calculated according to a liquid-to-solid ratio of 10:1. The extractant was added to the bottle, which was then tightly capped and fixed on an overturning vibration device. Subsequently, the speed of the vibration device was adjusted to 30 r/min and the amplitude was 40 mm; the extraction bottle was removed after 20 h of shaking at room temperature. The extracted solution was collected by a pressure filter, which was digested by microwave digestion. The filtrate was analyzed using ICP-AES, to determine the leaching levels of every heavy metal ion. The limits of leached heavy metal ions Zn, Pb, Cu, Cr, and Cd are respectively 100, 0.25, 40, 4.5, and 0.15 mg/L, according to the Chinese standard, “Standard for Pollution Control on the Landfill Site of Municipal Solid Waste (GB 16889-2008)” [51].

3. Results and Discussion

3.1. Pore Structures of Geopolymer Mortar Containing MSWIFA

Figures 2 and 3 show the influence of the MSWIFA replacement rate (MFARR) on the pore structures of the geopolymer mortar. It should be noted that the porosity and average pore diameter increased from 24.02% and 25.69 mm, to 30.03% and 29.81 mm, respectively, when the MFARR increased from 0% to 35%, which showed the similar trend. While, the growth rate of porosity and average pore diameter decreased significantly when the MFARR was varied from 5% to 25%. According to the results of Bai et al. [52], gel micropores and mesopores have little effect on the properties of a material and its structure.

Similar views also appear in the work of Chen et al. [53]; and this shows that pores have a significant influence on the mechanical properties, shrinkage behavior, and permeability of the matrix when the pore diameter (d) is greater than 200 nm. Therefore, in this research, the pores were divided into three types according to the pore diameter: harmless pores ($d < 50$ nm), harmful pores ($50 \text{ nm} < d < 200$ nm), and multi-harmful pores ($d > 200$ nm). The pore diameter distribution (PDD) of the geopolymer mortar could be calculated based on the results of the MIP tests, which are shown in Table 3. As illustrated in Table 4, the PDD showed a trend of deterioration when the MFARR was varied from 0% to 15%. However, when the MFARR was increased from 15% to 25%, the proportion of harmless pores increased from 57.3% to 60.43%. While, the percentage of multi-harmful pores decreased slightly, and the PDD of the geopolymer mortar was progressively improved. When the MFARR was increased from 25% to 35%, the PDD of the geopolymer mortar deteriorated. From the above analysis, it can be concluded that the increase of MFARR had an overall degrading effect on the pore structures of the matrix.

Table 3. Pore diameter distribution of the geopolymer mortar.

Trial Number	Pore Diameter Distribution (%)		
	<50 nm	50 nm~200 nm	>200 nm
S-00	64.55	5.48	29.97
S-05	64.41	4.12	31.46
S-15	57.3	5.48	37.22
S-25	60.43	6.16	33.4
S-35	57.07	8.41	34.51

Table 4. Heavy metal leaching results and landfill limits.

Heavy Metals	MSWIFA	J-40 mg/L	Landfill Limit
Cd	0.19	0	0.15
Cr	0.06	0.03	4.5
Cu	0.67	0.07	40
Pb	1.48	0.11	0.25
Zn	4.71	0.7	100

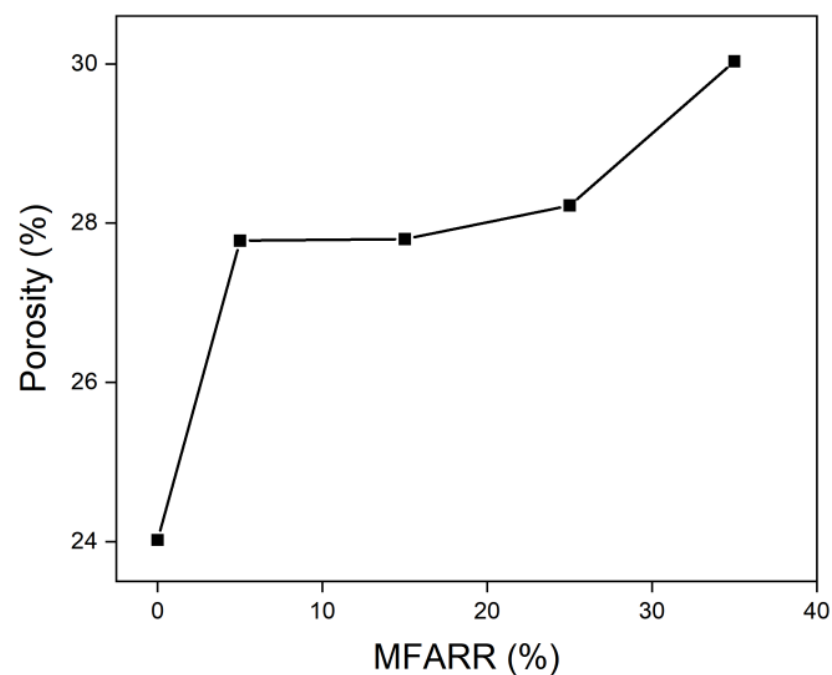


Figure 2. Influence of MFARR on the porosity of the matrix.

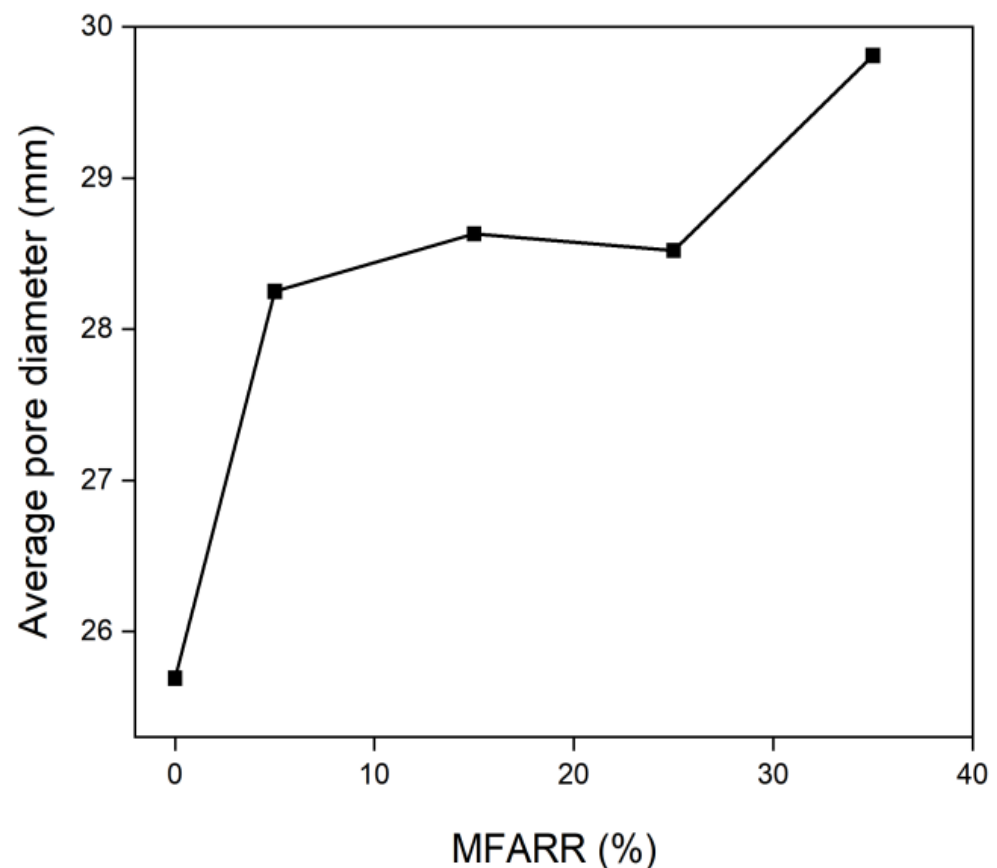


Figure 3. Influence of MFARR on the average pore diameter of the matrix.

The mix proportion of MSWIFA had a significant effect on the pore structure of the matrix. The deterioration impact on the pore structures of the geopolymer mortar was more obvious when the MFARR was increased from 0% to 15% and from 25% to 35%. In contrast, when the MFARR was increased from 15% to 25%, the deterioration impact on the pore structures of the matrix was weaker, with only a small increase in porosity and average pore diameter, and the PDD showed an improving trend. The reason for this may be that CaO was introduced into the original reaction system after adding MSWIFA as raw material, which altered the reaction system of the geopolymer composites. The transformation of reaction system made the reaction mechanism of the matrix and the composition of hydration products more intricate. Related study results showed that CaO existed in the form of Ca^{2+} in alkali solutions [54,55]. During the hydration reaction, silica-alumina oxides formed free $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{4-}$, which easily combined with Ca^{2+} to form calcium silica-aluminate (C-A-S-H). While, Ca^{2+} was able to combine with $[\text{SiO}_4]^{4-}$ to form a C-S-H gel-like structure, which obviously increased the density of the microstructure of the geopolymer composites and improved their pore structure [56,57].

3.2. Microstructure of Geopolymer Mortar Containing MSWIFA

SEM images of the geopolymer mortar and FA particles were obtained, to study the impact of different contents of MSWIFA on the microstructure of the hydration products, which are listed in Figure 4. In accordance with the results of previous experiments, SEM images of the MK-based geopolymer and alkali-activated MSWIFA geopolymer were studied [58,59]. It is notable that the morphology of the MK-based geopolymer possessed a flake-like layer structure, similar to an MK particle; and the morphology of the MSWIFA exhibited an uncharacteristic shape, and its surface was loose, rough, and porous, which was closely linked with the SEM images of the alkali-activated MSWIFA geopolymer. As regards the above analysis and the SEM image of FA (Figure 4f), the holes described as

partially-reacted FA in Figure 4 represent the reaction products of FA, which were not particles resulting from waste or MK. The microstructure of the geopolymer mortar without MSWIFA (Figure 4a) had a denser microscopic morphology and a more complete structure, without obvious cracks and pores, which implied that the cementitious materials fully reacted to form a dense C-A-S-H structure. After adding 5% MSWIFA (Figure 4b), there were no significant changes in the SEM image; however, more obvious microcracks and incompletely reacted round spherical FA particles could be observed within the matrix. It can be seen from Figure 4c,d that there were small differences in the microscopic morphology, but the changes are obvious compared to Figure 4b. With the increase in MFARR, the pores and microcracks within the matrix shown in Figure 4c,d increased, and cracks existed in the area between the fine aggregate and matrix. More incompletely reacted spherical FA particles can also be observed. However, when the MFARR was increased to 35% (Figure 4e), the crack width of the geopolymer mortar increased significantly. The separation of block phenomenon within the matrix was serious, and more microcracks and pores appeared. Figure 4 shows that the microstructural compactness of the geopolymer mortar decreased when the amount of MFARR was increased, which was mainly because the increase of MFARR led to a decrease of silica-alumina oxides in the raw materials and of the geopolymer cementing properties. In addition, the free water absorbed by the MSWIFA evaporated in the curing period, resulting in more cracks and pores in the geopolymer mortar.

3.3. Hydration Mechanism of Geopolymer Paste

The FT-IR spectra show bonds typical for the internal structure of a geopolymer. The infrared spectra of MK, FA, and geopolymer paste of J-00 are presented in Figure 5. The wavenumber corresponding to the absorption peak of the samples of FA and MK is almost the same, and the strongest absorption peaks of the samples of FA and MK appeared at 1048 cm^{-1} and 1097 cm^{-1} in the intermediate frequency region, respectively. While the strongest absorption peak of the geopolymer paste of J-00 appeared at 980 cm^{-1} , which moved in a lower wavenumber direction. Previous studies indicated that the band at 1048 cm^{-1} and 1097 cm^{-1} of samples of FA and MK corresponds to the symmetric stretching vibration peak of Si-O [60,61]. This band is typical in amorphous aluminosilicate glasses. While the band at 980 cm^{-1} of a geopolymer paste of J-00 is related to the asymmetric stretching vibration peak of Si-O [62]. The characteristic peak of the geopolymer paste shifted to a lower wavenumber, revealing that AlO_4 replaced some of the SiO_4 groups on the Si-O-Si symmetric chain structure. Thus, the internal structure of the hydration products of the geopolymer paste is affected [63]. In the spectra of the samples of FA and MK, the absorption peaks near 795 cm^{-1} and 807 cm^{-1} are connected with the six-coordinated Al-O vibrations. In contrast to the geopolymer paste of J-00, the absorption peak weakens and disappears. The absorption peak was replaced by an absorption peak at a wavenumber of about 720 cm^{-1} , which corresponds to four-coordinated Al-O vibrations. The above changes suggest that the six-coordinated Al in FA and MK may have been converted to four-coordinated Al during the reaction of the geopolymer that participated in the hydration reaction [64].

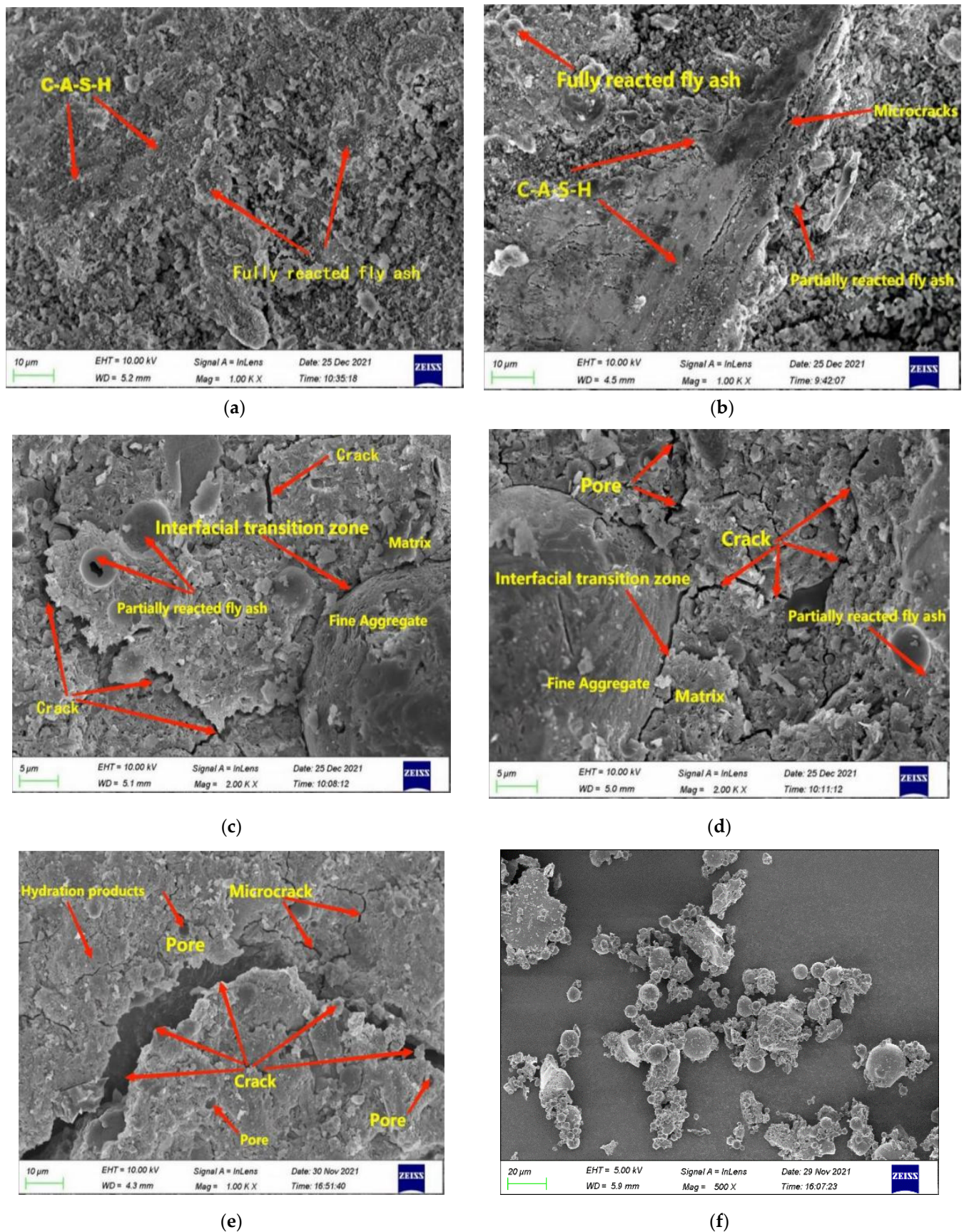


Figure 4. SEM images of geopolymer mortar containing MSWIFA and FA particles. (a) S-00, (b) S-05, (c) S-15, (d) S-25, (e) S-35, (f) FA.

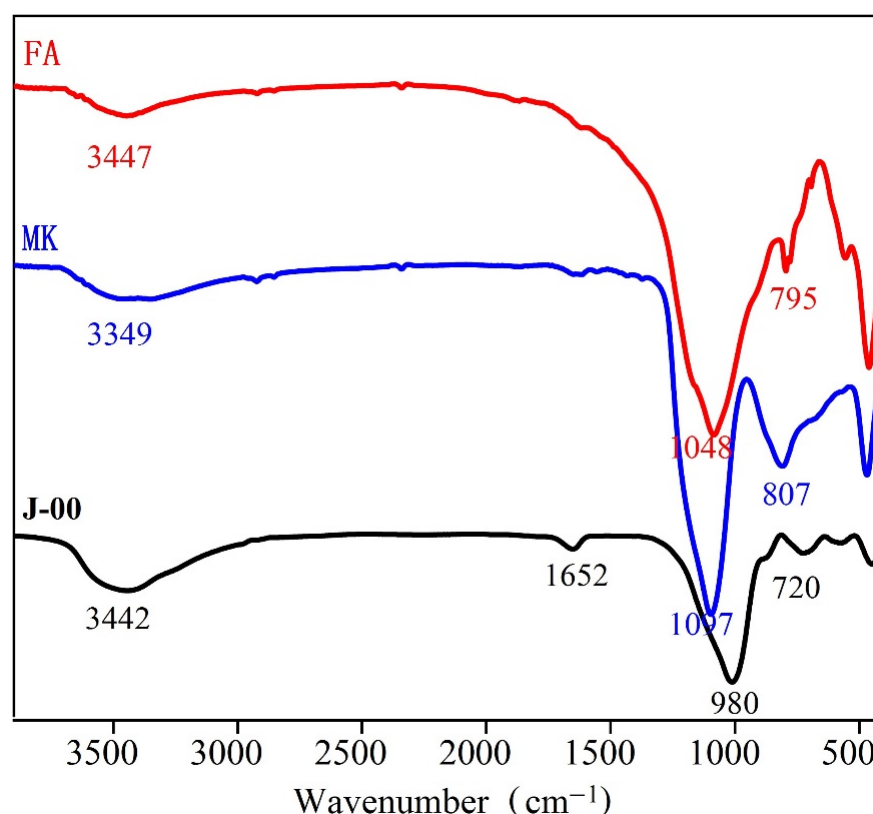


Figure 5. Infrared spectra of FA, MK, and geopolymer paste of J-00.

The infrared spectra of geopolymer pastes with different levels of MFARR are shown in Figure 6. The patterns for all compositions are fairly similar, showing that the content of MSWIFA had a small effect on the reaction products of the geopolymer paste. It is noteworthy that the strongest absorption peak appeared between 970 cm^{-1} and 980 cm^{-1} for every mix proportion of MSWIFA, which as mentioned earlier is link with the stretching vibration of Si-O. The strongest absorption peak was also the main absorption peak of C-A-S-H, which is the main component of the reaction products of the matrices. Compared with the geopolymer paste of J-00, the height and area of the absorption peak of the geopolymer paste at 970 cm^{-1} – 980 cm^{-1} gradually decreased with the addition of MSWIFA. The impact of MSWIFA on the absorption peak of the matrix indicated that the production of the gel substance C-A-S-H decreased as the MFARR was increased, which may have caused a decline in the mechanical properties. The broad band from 3442 to 3467 cm^{-1} was attributed to the Al-OH stretching vibration, and the bands around 1650 cm^{-1} could be due to the vibration of O-H bonds in absorbed water [59,65]. Moreover, the geopolymer showed a small absorption peak at 1433 to 1488 cm^{-1} , which was assigned to the C-O symmetric stretching vibration. However, the small absorption peak did not appear in J-00, revealing that the incorporation of MSWIFA caused the carbonization of the geopolymer paste during the hydration process. The absorption band at 722 – 736 cm^{-1} may represent the Al-OH stretching vibration [52]. Figure 7 depicts the infrared spectra of geopolymer paste hydrated at 3 d, 7 d, and 28 d, when the content of MFARR was 15%. The spectra had similar trends, except for the different absorption rates, which had homogeneous absorption bands. It can be concluded that the peak and area of the main absorption peak of geopolymer composite became higher and larger, respectively, as the curing periods increased, exhibiting an increase in the number of Si-O-Al and Si-O-Si groups. An obvious C-A-S-H absorption peak could already be observed in the infrared spectrum after 3 days of curing. The growth of the absorption peak was larger when the curing period reached 7 days, which may be one of the reasons for the fast growth of the strength of the geopolymer composite in the early stages.

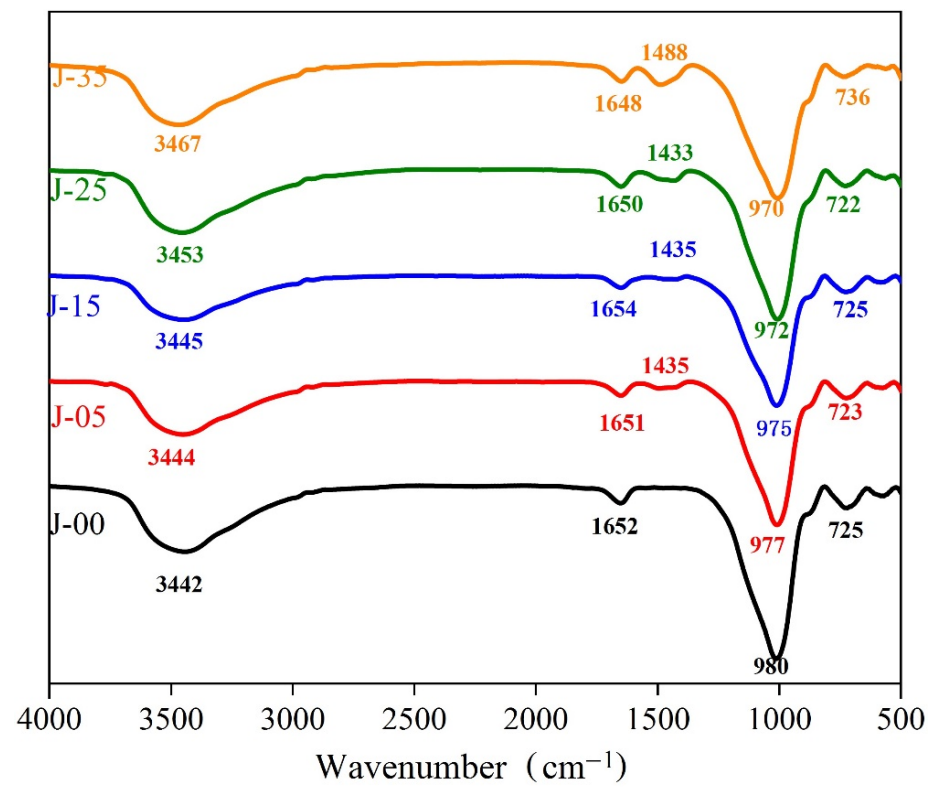


Figure 6. FT-IR of paste with a range of MFARR.

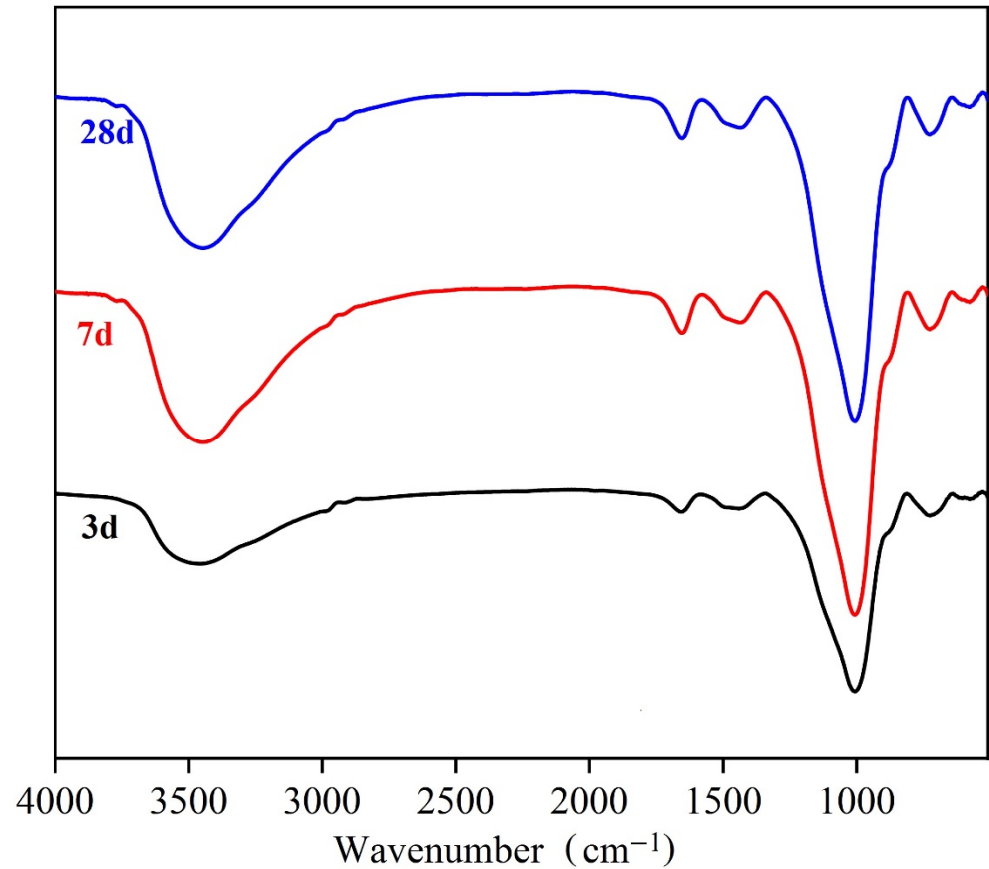


Figure 7. FT-IR of paste with a range of curing periods.

3.4. Heavy Metal Leaching Results

Since a high level of heavy metals affects waste utilization, the heavy metal concentration of the waste was determined, to ensure its safety. The heavy metal leaching results of MSWIFA and the geopolymer paste of J-40 synthesized with a 40% MSWIFA replacement rate are listed in Table 4. When the curing period reached 28 days, the heavy metal leaching concentration of the geopolymer composite was lower than that of MSWIFA. It is noticeable that the concentration of Cd became negligible after the geopolymerization process, declining to 0 mg/L. This behavior can be, to some extent, explained by the formation of cadmium hydroxide within the geopolymer; cadmium hydroxide is responsible for the immobilization of Cd, and may be produced in high concentrations in an alkali-activated environment [30]. The leached level of Pb in MSWIFA was high and even exceeded the limit. Whereas, it was negligible in the MSWIFA-based geopolymer paste, showing that the immobilization of Pb was effective, in accordance with the results obtained in other works [31,66]. Compared to the residues of Cd, Cr, Cu, Pb, and Zn in MSWIFA, the leaching concentrations of the geopolymer paste of J-40 were reduced by 100%, 50%, 89.5%, 92.6%, and 85.1%, respectively. Regarding the standard limit for disposal, the leaching concentrations of heavy metals of the geopolymer paste were far lower, from which it could be confirmed that the geopolymeric reaction had an excellent performance in solidifying heavy metals.

4. Conclusions

In this work, the impact of MSWIFA on the pore structure of a geopolymer mortar was revealed through MIP and SEM tests. The hydration mechanism of the geopolymer paste was also analyzed through FT-IR tests, and the environmental stability of the geopolymer composite was investigated through heavy metal leaching tests. The following conclusions can be drawn from this research:

- (1) With the content of MSWIFA increasing, the integrity of the micromorphology of the geopolymer mortar becomes weaker. Although the porosity and average pore diameter of the matrix gradually increased, there were large differences in the increase rate of the porosity and average pore diameter. In addition, the PDD of the geopolymer mortar tended to deteriorate overall with the increase of MFARR. The appropriate amount of CaO to optimize the pore structure was 25% MFARR, and the improvement of the pore structures for geopolymer composites was more obvious.
- (2) The increase of MFARR had a negative effect on the microstructure of the geopolymer mortar. The microstructural compactness of geopolymer mortar decreased and more pores and cracks appeared in the matrix with the increase of MFARR. The types of geopolymer hydration products did not change, and the hydration products were still dominated by C-A-S-H. The MSWIFA made the geopolymer paste display a minor absorption peak, which indicates that the incorporation of MSWIFA can cause carbonization of the geopolymer paste.
- (3) The leaching levels of Cd and Pb in the raw material MSWIFA exceeded the standard limit. While the leaching levels for every heavy metal ion in the geopolymer paste with 40% MK replaced by MSWIFA were lower than the national standard, which illustrates that the geopolymer composite was beneficial in solidifying the heavy metals in the MSWIFA.

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

Funding: This research was funded by Natural Science Foundation of Henan of China (Grant No. 212300410018), National Natural Science Foundation of China (Grant No. 51979251, U2040224),

Program for Innovative Research Team (in Science and Technology) in University of Henan Province of China (Grant No. 20IRTSTHN009), and National Innovation and Entrepreneurship Training Program for College Students of China (Grant No. 202110459175).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

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

References

1. Yang, K.H.; Song, J.K.; Song, K.I. Assessment of CO₂ reduction of alkali-activated concrete. *J. Clean. Prod.* **2013**, *39*, 265–272. [\[CrossRef\]](#)
2. Zhang, P.; Sha, D.; Li, Q.; Zhao, S.; Ling, Y. Effect of nano silica particles on impact resistance and durability of concrete containing coal fly ash. *Nanomaterials* **2021**, *11*, 1296. [\[CrossRef\]](#)
3. Kastiukas, G.; Zhou, X.; Castro-Gomes, J. Preparation conditions for the synthesis of alkali-activated binders using tungsten mining waste. *J. Mater. Civ. Eng.* **2017**, *29*, 04017181. [\[CrossRef\]](#)
4. Zhang, P.; Gao, Z.; Wang, J.; Guo, J.; Hu, S.; Ling, Y. Properties of fresh and hardened fly ash/slag based geopolymer concrete: A review. *J. Clean. Prod.* **2020**, *270*, 122389. [\[CrossRef\]](#)
5. Davidovits, J. Geopolymers and geopolymeric materials. *J. Therm. Anal.* **1989**, *35*, 429–441. [\[CrossRef\]](#)
6. Wang, L.; Luo, R.Y.; Zhang, W.; Jin, M.M.; Tang, S.W. Effects of fineness and content of phosphorus slag on cement hydration, permeability, pore structure and fractal dimension of concrete. *Fractals* **2021**, *29*, 2140004. [\[CrossRef\]](#)
7. Han, Q.; Zhang, P.; Wu, J.; Jing, Y.; Zhang, D.; Zhang, T. Comprehensive review of the properties of fly ash-based geopolymer with additive of nano-SiO₂. *Nanotechnol. Rev.* **2022**, *11*, 1478–1498. [\[CrossRef\]](#)
8. Kuenzel, C.; Vandeperre, L.J.; Donatello, S.; Boccaccini, A.R.; Cheeseman, C. Ambient temperature drying shrinkage and cracking in metakaolin-based geopolymers. *J. Am. Ceram. Soc.* **2012**, *95*, 3270–3277. [\[CrossRef\]](#)
9. Zhang, P.; Kang, L.; Zheng, Y.; Zhang, T.; Zhang, B. Influence of SiO₂/Na₂O molar ratio on mechanical properties and durability of metakaolin-fly ash blend alkali-activated sustainable mortar incorporating manufactured sand. *J. Mater. Res. Technol.* **2022**, *18*, 3553–3563. [\[CrossRef\]](#)
10. Kong, D.L.; Sanjayan, J.G. Effect of elevated temperatures on geopolymer paste, mortar and concrete. *Cem. Concr. Res.* **2010**, *40*, 334–339. [\[CrossRef\]](#)
11. Wang, L.; Guo, F.X.; Yang, H.M.; Wang, Y. Comparison of fly ash, PVA fiber, MgO and shrinkage-reducing admixture on the frost resistance of face slab concrete via pore structural and fractal analysis. *Fractals* **2021**, *29*, 2140002. [\[CrossRef\]](#)
12. Billong, N.; Kinuthia, J.; Oti, J.; Melo, U.C. Performance of sodium silicate free geopolymers from metakaolin (MK) and Rice Husk Ash (RHA): Effect on tensile strength and microstructure. *Constr. Build. Mater.* **2018**, *189*, 307–313. [\[CrossRef\]](#)
13. Bernal, S.A.; Rodríguez, E.D.; Mejía de Gutiérrez, R.; Gordillo, M.; Provis, J.L. Mechanical and thermal characterisation of geopolymers based on silicate-activated metakaolin/slag blends. *J. Mater. Sci.* **2011**, *46*, 5477–5486. [\[CrossRef\]](#)
14. He, J.; Zhang, G.; Hou, S.; Cai, C.S. Geopolymer-based smart adhesives for infrastructure health monitoring: Concept and feasibility. *J. Mater. Civ. Eng.* **2011**, *23*, 100–109. [\[CrossRef\]](#)
15. Zhang, H.Y.; Kodur, V.; Wu, B.; Cao, L.; Qi, S.L. Comparative thermal and mechanical performance of geopolymers derived from metakaolin and fly ash. *J. Mater. Civ. Eng.* **2016**, *28*, 04015092. [\[CrossRef\]](#)
16. Zhang, X.; Zhang, P.; Wang, T.; Zheng, Y.; Qiu, L.; Sun, S. Compressive strength and anti-chloride ion penetration assessment of geopolymer mortar merging PVA fiber and nano-SiO₂ using RBF-BP composite neural network. *Nanotechnol. Rev.* **2022**, *11*, 1181–1192. [\[CrossRef\]](#)
17. Prasara-A, J.; Gheewala, S.H. Sustainable utilization of rice husk ash from power plants: A review. *J. Clean. Prod.* **2017**, *167*, 1020–1028. [\[CrossRef\]](#)
18. Pode, R. Potential applications of rice husk ash waste from rice husk biomass power plant. *Renew. Sust. Energ. Rev.* **2016**, *53*, 1468–1485. [\[CrossRef\]](#)
19. Nana, A.; Epey, N.; Rodrique, K.C.; Deutou, J.G.N.; Djobo, J.N.Y.; Tome, S.; Alomayri, T.S.; Ngoune, J.; Kamseu, E.; Leonelli, C. Mechanical strength and microstructure of metakaolin/volcanic ash-based geopolymer composites reinforced with reactive silica from rice husk ash (RHA). *Materialia* **2021**, *16*, 101083. [\[CrossRef\]](#)
20. Villaquirán-Cacedo, M.A.; Gutiérrez, R.M.; Sulekar, S.; Davis, C.; Nino, J.C. Thermal properties of novel binary geopolymers based on metakaolin and alternative silica sources. *Appl. Clay Sci.* **2015**, *118*, 276–282. [\[CrossRef\]](#)
21. Tchakouté, H.K.; Rüschler, C.H.; Kong, S.; Kamseu, E.; Leonelli, C. Thermal behavior of metakaolin-based geopolymer cements using sodium waterglass from rice husk ash and waste glass as alternative activators. *Waste Biomass Valorization* **2017**, *8*, 573–584. [\[CrossRef\]](#)
22. Nasruddin, N.R.A.; Mazlan, N.; Basri, M.M.; Ariff, A.M.; Nasir, N.M. Thermogravimetric analysis on rice husk ashes-based geopolymer paste. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *405*, 012014. [\[CrossRef\]](#)

23. Liu, X.; Jiang, J.; Zhang, H.; Li, M.; Wu, Y.; Guo, L.; Wang, W.; Duan, P.; Zhang, W.; Zhang, Z. Thermal stability and microstructure of metakaolin-based geopolymer blended with rice husk ash. *Appl. Clay Sci.* **2020**, *196*, 105769. [\[CrossRef\]](#)
24. Fei, J.C.; Min, X.B.; Wang, Z.X.; Pang, Z.H.; Liang, Y.J.; Ke, Y. Health and ecological risk assessment of heavy metals pollution in an antimony mining region: A case study from South China. *Environ. Sci. Pollut. Res.* **2017**, *24*, 27573–27586. [\[CrossRef\]](#)
25. Liu, D.-G.; Min, X.-B.; Ke, Y.; Chai, L.-Y.; Liang, Y.-J.; Li, Y.-C.; Yao, L.-W.; Wang, Z.-B. Co-treatment of flotation waste, neutralization sludge, and arsenic-containing gypsum sludge from copper smelting: Solidification/stabilization of arsenic and heavy metals with minimal cement clinker. *Environ. Sci. Pollut. Res.* **2018**, *25*, 7600–7607. [\[CrossRef\]](#)
26. Mian, M.M.; Zeng, X.; Nasry, A.A.N.B.; Al-Hamadani, S.M. Municipal solid waste management in China: A comparative analysis. *J. Mater. Cycles Waste Manag.* **2017**, *19*, 1127–1135. [\[CrossRef\]](#)
27. Dong, P.; Liu, J.; Wang, H.; Yuan, H.; Wang, Q. Sustainable municipal solid waste incineration fly ash (MSWIFA) alkali-activated materials in construction: Fabrication and performance. *Nanotechnol. Constr.* **2022**, *14*, 43–52. [\[CrossRef\]](#)
28. Makarichi, L.; Jutidamrongphan, W.; Techato, K.A. The evolution of waste-to-energy incineration: A review. *Renew. Sust. Energ. Rev.* **2018**, *91*, 812–821. [\[CrossRef\]](#)
29. Grela, A.; Łach, M.; Mierzwiński, D.; Bajda, T.; Mikula, J. Obtaining zeolites from slags and ashes from a waste combustion plant in an autoclave process. *E3S Web Conf.* **2017**, *17*, 00026. [\[CrossRef\]](#)
30. Tian, X.; Rao, F.; Li, C.; Ge, W.; Lara, N.O.; Song, S.; Xia, L. Solidification of municipal solid waste incineration fly ash and immobilization of heavy metals using waste glass in alkaline activation system. *Chemosphere* **2021**, *283*, 131240. [\[CrossRef\]](#)
31. Lancellotti, I.; Kamseu, E.; Michelazzi, M.; Barbieri, L.; Corradi, A.; Leonelli, C. Chemical stability of geopolymers containing municipal solid waste incinerator fly ash. *Waste Manag.* **2010**, *30*, 673–679. [\[CrossRef\]](#)
32. Diaz-Loya, E.I.; Allouche, E.N.; Eklund, S.; Joshi, A.R.; Kupwade-Patil, K. Toxicity mitigation and solidification of municipal solid waste incinerator fly ash using alkaline activated coal ash. *Waste Manag.* **2012**, *32*, 1521–1527. [\[CrossRef\]](#)
33. Galiano, Y.L.; Pereira, C.F.; Vale, J. Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers. *J. Hazard. Mater.* **2011**, *185*, 373–381. [\[CrossRef\]](#)
34. Van Jaarsveld, J.G.S.; Van Deventer, J.S.J.; Schwartzman, A. The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics. *Miner. Eng.* **1999**, *12*, 75–91. [\[CrossRef\]](#)
35. Łach, M.; Mierzwiński, D.; Korniejewski, K.; Mikula, J.; Hebda, M. Geopolymers as a material suitable for immobilization of fly ash from municipal waste incineration plants. *J. Air Waste Manag. Assoc.* **2018**, *68*, 1190–1197. [\[CrossRef\]](#)
36. Balczár, I.; Korim, T.; Dobrádi, A. Correlation of strength to apparent porosity of geopolymers—understanding through variations of setting time. *Constr. Build. Mater.* **2015**, *93*, 983–988. [\[CrossRef\]](#)
37. Perná, I.; Hanzlíček, T. The setting time of a clay-slag geopolymer matrix: The influence of blast-furnace-slag addition and the mixing method. *J. Clean. Prod.* **2016**, *112*, 1150–1155. [\[CrossRef\]](#)
38. Wijaya, S.W.; Hardjito, D. Factors affecting the setting time of fly ash-based geopolymer. *Mater. Sci. Forum* **2016**, *841*, 90–97.
39. De Silva, P.; Sagoe-Crenstil, K.; Sirivivatnanon, V. Kinetics of geopolymerization: Role of Al_2O_3 and SiO_2 . *Cem. Concr. Res.* **2007**, *37*, 512–518. [\[CrossRef\]](#)
40. Zhang, P.; Wang, K.; Wang, J.; Guo, J.; Hu, S.; Ling, Y. Mechanical properties and prediction of fracture parameters of geopolymer/alkali-activated mortar modified with PVA fiber and nano- SiO_2 . *Ceram. Int.* **2020**, *46*, 20027–20037. [\[CrossRef\]](#)
41. Gao, Z.; Zhang, P.; Wang, J.; Wang, K.; Zhang, T. Interfacial properties of geopolymer mortar and concrete substrate: Effect of polyvinyl alcohol fiber and nano- SiO_2 contents. *Constr. Build. Mater.* **2022**, *315*, 125735. [\[CrossRef\]](#)
42. Zhang, P.; Wang, K.; Wang, J.; Guo, J.; Ling, Y. Macroscopic and microscopic analyses on mechanical performance of metakaolin/fly ash based geopolymer mortar. *J. Clean. Prod.* **2021**, *294*, 126193. [\[CrossRef\]](#)
43. Wang, K.; Zhang, P.; Guo, J.; Gao, Z. Single and synergistic enhancement on durability of geopolymer mortar by polyvinyl alcohol fiber and nano- SiO_2 . *J. Mater. Res. Technol.* **2021**, *15*, 1801–1814. [\[CrossRef\]](#)
44. Xu, F.; Gu, G.; Zhang, W.; Wang, H.; Huang, X.; Zhu, J. Pore structure analysis and properties evaluations of fly ash-based geopolymer foams by chemical foaming method. *Ceram. Int.* **2018**, *44*, 19989–19997. [\[CrossRef\]](#)
45. Jaya, N.A.; Yun-Ming, L.; Cheng-Yong, H.; Abdullah, M.M.A.B.; Hussin, K. Correlation between pore structure, compressive strength and thermal conductivity of porous metakaolin geopolymer. *Constr. Build. Mater.* **2020**, *247*, 118641. [\[CrossRef\]](#)
46. Gao, Z.; Zhang, P.; Guo, J.; Wang, K. Bonding behavior of concrete matrix and alkali-activated mortar incorporating nano- SiO_2 and polyvinyl alcohol fiber: Theoretical analysis and prediction model. *Ceram. Int.* **2021**, *47*, 31638–31649. [\[CrossRef\]](#)
47. Akono, A.T.; Koric, S.; Kriven, W.M. Influence of pore structure on the strength behavior of particle-and fiber-reinforced metakaolin-based geopolymer composites. *Cem. Concr. Comp.* **2019**, *104*, 103361. [\[CrossRef\]](#)
48. Washburn, E.W. Note on a method of determining the distribution of pore sizes in a porous material. *Proc. Natl. Acad. Sci. USA* **1921**, *7*, 115. [\[CrossRef\]](#)
49. HJ/T 299-2007; Solid Waste-Extraction Procedure for Leaching Toxicity Sulphuric acid & Nitric Acid Method. Ministry of Ecology and Environment of the People's Republic of China: Beijing, China, 2007.
50. GB 50853-2007; Identification Standards for Hazardous Wastes—Identification for Extraction Toxicity. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China: Beijing, China, 2007.
51. GB 16889-2008; Standard for Pollution Control on the Landfill Site of Municipal Solid Waste. Ministry of Ecology and Environment of the People's Republic of China: Beijing, China, 2008.

52. Bai, Y.; Guo, W.; Wang, X.; Pan, H.; Zhao, Q.; Wang, D. Utilization of municipal solid waste incineration fly ash with red mud-carbide slag for eco-friendly geopolymer preparation. *J. Clean. Prod.* **2022**, *340*, 130820. [\[CrossRef\]](#)
53. Chen, S.; Ruan, S.; Zeng, Q.; Liu, Y.; Zhang, M.; Tian, Y.; Yan, D. Pore structure of geopolymer materials and its correlations to engineering properties: A review. *Constr. Build. Mater.* **2022**, *328*, 127064. [\[CrossRef\]](#)
54. Yip, C.K.; Lukey, G.C.; Provis, J.L.; Van Deventer, J.S. Effect of calcium silicate sources on geopolymerisation. *Cem. Concr. Res.* **2008**, *38*, 554–564. [\[CrossRef\]](#)
55. Wang, L.; Lu, X.; Liu, L.; Xiao, J.; Zhang, G.; Guo, F.; Li, L. Influence of MgO on the hydration and shrinkage behavior of low heat Portland cement-based materials via pore structural and fractal analysis. *Fractal Fract.* **2022**, *6*, 40. [\[CrossRef\]](#)
56. Temuujin, J.V.; Van Riessen, A.; Williams, R. Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes. *J. Hazard. Mater.* **2009**, *167*, 82–88. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Guo, X.; Shi, H.; Xia, M. Effect of different calcium resources on reaction mechanism of geopolymer. *Chin. J. Mater. Res.* **2016**, *30*, 348–354.
58. Wang, H.; Li, H.; Yan, F. Synthesis and mechanical properties of metakaolinite-based geopolymer. *Colloids Surf. A Physicochem. Eng. Asp.* **2005**, *268*, 1–6. [\[CrossRef\]](#)
59. Liu, J.; Hu, L.; Tang, L.; Ren, J. Utilisation of municipal solid waste incinerator (MSWI) fly ash with metakaolin for preparation of alkali-activated cementitious material. *J. Hazard. Mater.* **2021**, *402*, 123451. [\[CrossRef\]](#)
60. Akolekar, D.; Chaffee, A.; Howe, R.F. The transformation of kaolin to low-silica X zeolite. *Zeolites* **1997**, *19*, 359–365. [\[CrossRef\]](#)
61. Barbosa, V.F.; MacKenzie, K.J.; Thaumaturgo, C. Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: Sodium polysialate polymers. *Int. J. Inorg. Mater.* **2000**, *2*, 309–317. [\[CrossRef\]](#)
62. Aredes, F.G.M.; Campos, T.M.B.; Machado, J.P.B.; Sakane, K.K.; Thim, G.P.; Brunelli, D.D. Effect of cure temperature on the formation of metakaolinite-based geopolymer. *Ceram. Int.* **2015**, *41*, 7302–7311. [\[CrossRef\]](#)
63. Van Jaarsveld, J.G.S.; Van Deventer, J.S.J. The effect of metal contaminants on the formation and properties of waste-based geopolymers. *Cem. Concr. Res.* **1999**, *29*, 1189–1200. [\[CrossRef\]](#)
64. Zhang, Y.S.; Sun, W.; Jia, Y.T.; Jin, Z.Q. Composition and structure of hardened geopolymer products using infrared ray analysis methods. *J. Wuhan Univ. Technol.* **2005**, *27*, 27–30.
65. Korniejenko, K.; Kejzlar, P.; Louda, P. The Influence of the Material Structure on the Mechanical Properties of Geopolymer Composites Reinforced with Short Fibers Obtained with Additive Technologies. *Int. J. Mol. Sci.* **2022**, *23*, 2023. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Wang, Y.; Han, F.; Mu, J. Solidification/stabilization mechanism of Pb (II), Cd (II), Mn (II) and Cr (III) in fly ash based geopolymers. *Constr. Build. Mater.* **2018**, *160*, 818–827. [\[CrossRef\]](#)