



## Review Article

# Thermal and Mechanical Properties of Geopolymers Exposed to High Temperature: A Literature Review

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Geopolymers are prepared by alkali solution-activated natural minerals or industrial waste materials, which have been widely used as new sustainable building and construction materials for their excellent thermal and mechanical properties. The thermal and mechanical properties of geopolymers at high temperature have attracted great attention from many researchers. However, there are few systematic works concerning these two issues. Therefore, this work reviewed the thermal and mechanical behaviors of geopolymers at high temperature. Firstly, the thermal properties of geopolymers in terms of mass loss, thermal expansion, and thermal conductivity after high temperature were explained. Secondly, the mechanical properties of residual compressive strength and stress-strain relationship of fly ash geopolymers and metakaolin geopolymers after high temperature were analyzed. Finally, the microstructure and mineralogical characteristics of geopolymers upon heating were interpreted according to the changes of microstructures and compositions. The results show that the thermal properties of geopolymers are superior to cement concrete. The geopolymers possess few mass loss and a low expansion ratio and thermal conductivity at high temperature. The thermal and mechanical properties of the geopolymers are usually closely related to the raw materials and the constituents of the geopolymers. Preparation and testing conditions can affect the mechanical properties of the geopolymers. The stress-strain curves of geopolymer are changed by the composition of geopolymers and the high temperature. The silicon-type fillers not only improve the thermal expansion of the geopolymers but also enhance mechanical properties of the geopolymers. But, they do not contribute to reducing the thermal conductivity. The different raw materials, aluminosilicate precursor and reinforcement materials, result in different geopolymer damage during the heating. However, phase transitions can occur during the process of heating regardless of the raw materials. The additional performance enhancements can be achieved by optimizing the paste formulation, adjusting the inner structure, changing the alkali type, and incorporating reinforcements.

## 1. Introduction

Geopolymers, known as a synthetic inorganic polymer, are produced by the alkali activation of a variety of aluminosilicates, such as metakaolin (MK), fly ash (FA), rice husk ash (RHA), red mud (RM), and so on [1, 2]. Due to its high mechanical properties, corrosion resistance, durability, especially desirable performance under high temperature, wide source of raw materials, and low energy consumption, geopolymers has become an increasingly popular research area in recent years [3–5]. It is considered to be potential substitutes for Portland cement. Consequently, geopolymers have wide applications in fields such as toxic chemical wastes

absorption, ultraviolet radiation resistance, and drug delivery [6–11]. They are also widely used in lightweight concrete and foam concrete for the superior insulation properties [12, 13]. For example, Arellano Aguilar et al. [12] prepared lightweight concrete with 50% lower density compared with the conventional cement concrete by using MK and FA geopolymers. Zhang et al. [14] prepared heat reflective and thermal insulation coating by using the MK geopolymers and found that the heat reflectivity of the prepared coating exceeded 90% and the thermal insulation temperature difference was 24°C.

When cement concrete is subjected to fire, the calcium hydroxide groups begin to decompose at a lower

temperature.  $\text{Ca}(\text{OH})_2$  in ordinary cement concrete decomposes at 300~400°C;  $\text{CaCO}_3$  decomposes at 700°C and melts at 800°C [15]. Apparently, it is urgent to improve the stability performance of ordinary cement concrete under high temperature. Geopolymer coating on building surfaces, however, is reported as a novel and effective approach for this issue. For example, FA and MK geopolymer coatings developed by Temuujin et al. [16, 17] have been proven to be excellent in good flame resistance at 800°C. Furthermore, Cheng and Chiu [18] proved that the MK geopolymer panel had low heat transfer efficiency. The geopolymer coating had been proven to be fire resistant. Therefore, it is necessary to further study its thermal properties, including mass loss after high temperature, thermal expansion, and thermal conductivity changes. These properties are believed to be closely related to the flame retardants of geopolymers.

The strength of ordinary cement concrete begins to decrease when the temperature is beyond 400°C. The strength of concrete at 800°C is only 20% of the strength of concrete at room temperature [19]. But, the residual strength of FA geopolymers at 800°C is 36.13% of that at room temperature [20], and the residual strength varies with activator concentration and heating period. Sarker et al. [21] reported that the residual strength of FA geopolymer/aggregate composite was about 70% at 650°C while the residual strength of ordinary Portland concrete was only 52%. However, previous studies have heated FA geopolymers and geopolymer/aggregate samples to 800°C to assess the loss of compressive strength due to thermal damage. The results showed that the strength of geopolymers increased by 53% after high temperature treatment. However, under the same conditions, the compressive strength of geopolymer/aggregate composites with the same ratio decreased by 65% [22]. On the other hand, Kong et al. [23] reported that the compressive strength of MK geopolymers decreased by 27~51% for  $\text{Si}/\text{Al} \leq 1.54$  after it was exposed to 800°C for 60 minutes. In summary, the mechanical properties of geopolymers at high temperature are better than those of ordinary concrete. However, the high-temperature residual strength of the geopolymers is affected by many factors.

Many researchers have conducted studies on the thermal properties of geopolymers and the mechanical properties at high temperatures. Therefore, based on previous research, this work summarizes the changes in the thermal and mechanical properties of geopolymers at elevated temperatures. In this work, the thermal properties and mechanical behaviors of geopolymers at high temperatures are reviewed for the purpose of better understanding and improving the properties of geopolymers at high temperatures. The objectives of this work can be summarized as follows:

- (1) To analyze thermal properties in terms of mass loss, thermal deformation, and thermal conductivity of geopolymers exposed to high temperature.
- (2) To analyze mechanical properties in terms of residual compressive strength and stress-strain relationship of geopolymers exposed to high temperature.

- (3) To illustrate the microstructure and composition changes of geopolymers after being heated.

## 2. Thermal Properties of Geopolymers Exposed to High Temperature

### 2.1. Thermal Stability Analyses of Geopolymers

*2.1.1. Mass Loss of Geopolymers.* Thermal stability of materials can be evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), as shown in Figure 1 [24–28]. It can be seen that different types of geopolymers have good thermal stability at high temperature. For instance, mass loss of MK geopolymer is about 13% at 600°C as shown in Figure 1 [25]. But, the mass loss is more than 25% when the cement paste is heated to 600°C [24]. Incorporation of boiler slag admixture contributes to the enhancement of thermal stability of geopolymer. The mass loss of the geopolymer made from a mixture of 30% boiler slag (BS) and 70% MK is 9.43% when it is heated to 1250°C [26].

FA geopolymers also have similar stability. When FA geopolymer mortar was heated to 600°C, the mass loss was only about 6%. However, the replacement of FA by palm oil fuel ash (POFA) causes significant difference to the mass loss of geopolymer mortar [27]. And the mass loss of FA/POFA geopolymer mortar is highly related to the ratio of POFA in the composite geopolymer mortar. The higher the content of POFA, the lower the temperature required to achieve the same mass loss. Although incorporating 20% soda residue makes the alkali-activated FA-based geopolymer mortar possess higher compressive strength, the 86.5% mass loss at 900°C is 4.0% lower than that without soda residue [28]. For geopolymer paste that incorporates FA as only source material, the mass loss of FA geopolymer paste is 19.8% and 20.2% when it is heated to 600°C and 800°C, respectively [29].

As shown in Figure 1(b), all curves demonstrate a small endothermic peak at 50~150°C, corresponding to the evaporation of free water. After that, a stronger exothermic peak appears at the range of 300~500°C, which is attributed to the phase transition of mineral compositions [28]. In general, the difference between the width and height of peak can reflect the change of chemical constituent and proportion of geopolymer formulation.

It can be concluded from the above analysis that the thermal stability of the geopolymers is excellent. The sources of geopolymer materials are believed to have an important influence on the composition and pore structure of the hydration products, causing different vapor effects and chemical decomposition upon heating. Therefore, the mass loss at high temperature is closely related to the raw material and composition of the geopolymers.

*2.1.2. Mechanism Analyses.* Generally, two effects are believed to be responsible for the mass loss of geopolymers at high temperature, which are water evaporation and dihydroxylation. Hardened geopolymer

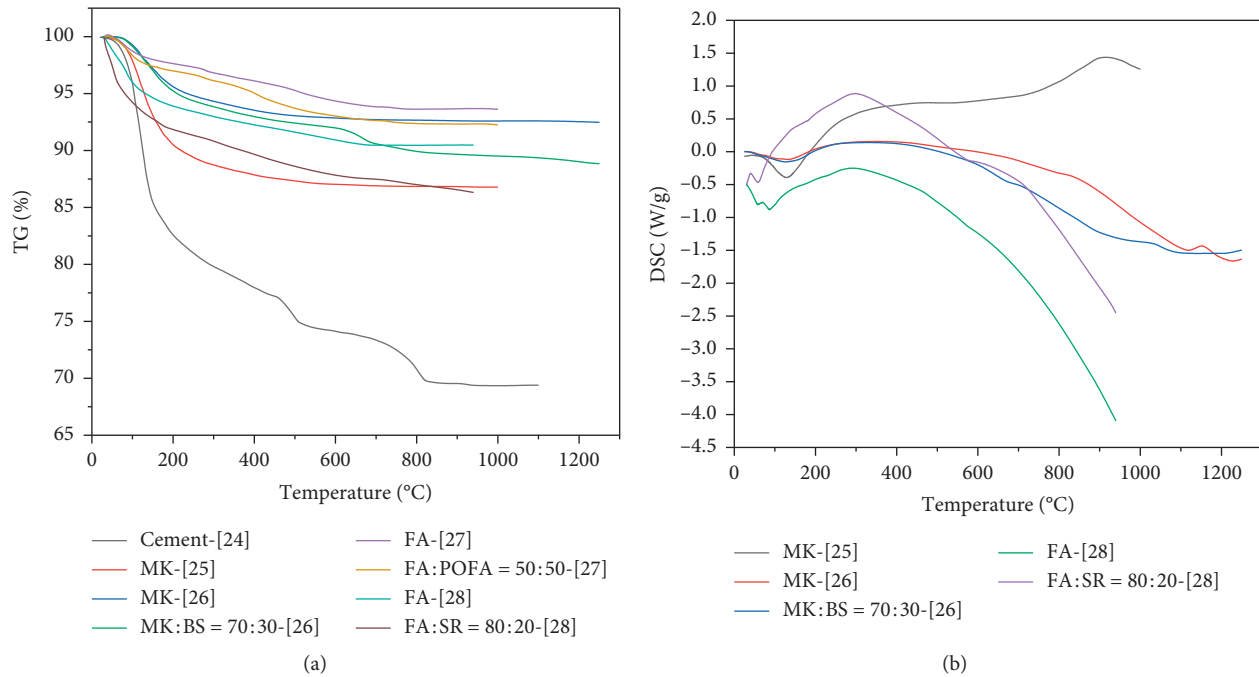


FIGURE 1: The TG/DSC curves of geopolymers. (a) TG curves. (b) DSC curves.

materials contain physical water, chemical water, and hydroxyl. Each type of water evaporates at different temperature range; physical water and chemical water evaporate at 20~100°C and 100~300°C, respectively, while hydroxyl groups evaporate at temperatures above 300°C [30]. In addition, some researchers have observed that the nepheline phase is formed when the geopolymers are heated to 1000°C [31–34]. So, they think the mass loss at high temperatures is related to the formation of nepheline phases. For example, nepheline contained in FA geopolymer mortar is blamed for the mass loss when geopolymers heated to 750°C [35].

In addition to the above analysis, components in geopolymers are critical to the thermal mass loss since some components are unstable under the high temperature. Similarly, the unburned carbon present in the raw materials (e.g., boiler slag) of geopolymers often fully burned at the range of 600°C to 800°C resulting in the weight variation of geopolymers [36]. It is reported that the mass loss of FA/cotton fiber geopolymers above 300°C is due to the dehydroxylation of chemically bonded water and the decomposition of cotton fibers [36]. After adding slag, the crystallinity of calcium carbonate contained in geopolymers differs with the ambient temperatures (from 590°C to 690°C). However, the crystallinity is related to the mass variation of geopolymers [37]. The substitution of MK by quartz and limestone powder, respectively, in MK-based geopolymer pastes causes significant mass loss after heating [31, 38]. The endothermic peak of DTG curves below 200°C for quartz powder sample is greater in comparison with that of neat MK sample, while the endothermic peak for limestone powder sample is smaller than that of reference sample. This means that more geopolymerization has occurred with the inclusion of quartz powder.

The mechanism analysis shows that pore pressure effects, also called vapor effects, and phase transformation are the most important mechanisms that affect the strength of geopolymers at elevated temperatures [39, 40]. During the heating, the mass loss caused by escaping of moisture accounts for more than half of the total mass loss. Under 100°C, the physically bonded water or free water located in the pores evaporates, which contributes about 55~60% of the total water content in the geopolymer structure [29]. Then, further heating above 100°C leads to evaporation of the chemically bonded water and the hydroxyl group OH inside the gel pores [41]. Consequently, pore pressure grows gradually in the pore structures as a result of heat transfer and moisture evaporation. When the vapor pressure comes to the maximum limit of the matrix, intensive thermal cracking and spalling occur. That is to say that low permeability, which is harmful for the release of internal vapor pressure, is more prone to heating damage. Therefore, the water content and interconnected pores have essential effect on the mass loss and strength retention of geopolymers. Moreover, the mass loss and residual strength are also affected by the change of composition of geopolymers and the phase transition process of geopolymers during high temperature heating.

In general, for all the geopolymers, the most significant mass loss occurs between room temperature and 200°C, which is mainly attributed to the evaporation of both the free water and part of the chemically bonded water from the geopolymer. The second major weight loss, observed at 300~650°C, corresponds to the dehydroxylation of Si-OH, Al-OH, and Ca-OH groups. The last mass loss usually appears at over 750°C and is due to the decomposition of carbonate species [41, 42].

In summary, the mass loss and strength retention of the geopolymers is closely related to the composition and pore structure of the geopolymers. Although geopolymers have been reported to be intrinsically thermally resistant, not all geopolymer formulations exhibit good thermal resistance. Further research could be carried out via optimizing the paste formulation to be less susceptible to dehydration damage, improving the permeability, changing the alkali type to increase the critical temperature, and reducing water consumption during the preparation for the additional thermal performance improvements.

## 2.2. Thermal Deformation Analyses of Geopolymers

### 2.2.1. Thermal Expansion/Shrinkage of Geopolymers.

Thermal deformation, expansion or shrinkage, is the tendency of matter to change in shape, area, and volume in response to a change in temperature. It can not only characterize the thermal properties of materials but also be closely related to other properties such as thermal stability, thermal capacity, and melting temperature. The thermal incompatibility between geopolymer matrix and its aggregate components is the most likely reason for strength loss in geopolymer concrete at high temperature. Therefore, the study of thermal deformation or strain of geopolymers is of great significance to the mechanical properties of cementitious materials [27].

The thermal deformation characteristics of ordinary Portland cement (OPC) paste and geopolymer samples are shown in Figure 2 [39, 43, 44]. In contrast to OPC paste, the changes of thermal shrinkage of geopolymers are much smaller. For example, as the temperature increases to 1000°C, the shrinkage of cement paste shows a linear increase up to 2.6%, while FA/MK geopolymer exhibits a polynomial trend and the peak shrinkage value is only 1.0% [43]. Besides, the increasing rate of thermal shrinkage of geopolymers is very small. It is found that the thermal expansion of the geopolymers prepared with Collie FA (CLFA) is more than 8.1% at the temperature of 300°C with the increase of silica content [41]. However, when other kinds of FAs are used, Port Augusta (PAFA), Eraring (ERFA), Bayswater (BWFA), and Tarong (TRFA), the geopolymers show a tendency of shrinkage. With the increase of Si/Al ratio, there is no obvious rule of shrinkage. The thermal shrinkage of various geopolymers has no fixed range. For instance, the expansion curves of FA geopolymers and MK geopolymers on metal substrate are measured, respectively. With the increase of Si/Al ratio, the shrinkage rate of FA geopolymers is about 5% at the temperature of 800°C [18], while the MK geopolymers exhibit a thermal shrinkage tendency when Si/Al ratio is relatively low, but they show an expansion tendency when Si/Al ratio is relatively high [19].

It should be noted that the aforementioned research studies are all aimed at pastes. As for geopolymer concretes, the paste phase shrinks when it is exposed to high temperature, whilst the aggregates expand, as shown in Figure 2. That is to say that the thermal properties of geopolymer

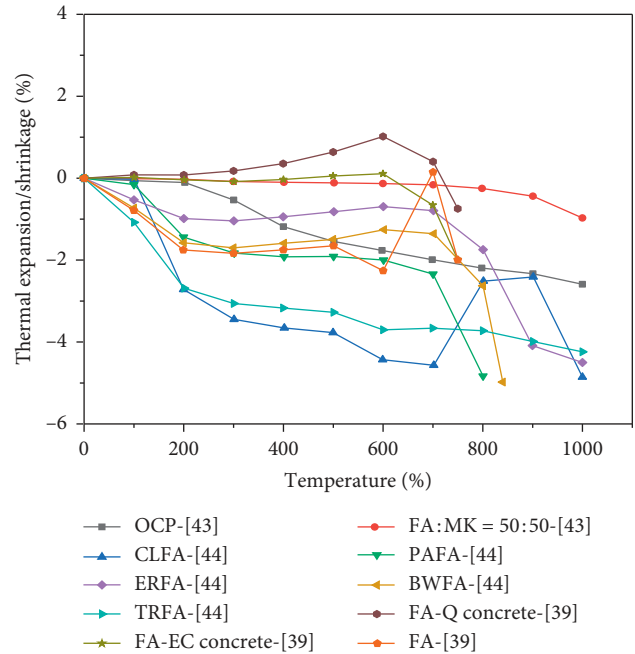


FIGURE 2: Changes in thermal deformation of geopolymers pastes and concretes at elevated temperatures. Note: Q represents quartz aggregate and EC represents expanded clay aggregates.

concretes are a summation of the effects of both pastes and aggregates. In order to evaluate the influence of aggregates type on the thermal properties of geopolymer concretes, the samples with either quartz aggregate or expanded clay aggregate were exposed to heating up to 750°C. Under the same conditions, the expansion deformation of concrete incorporating quartz aggregate (FA-Q) is much larger than that of concrete using expanded clay aggregate (FA-E). The main reason is the higher permeability and porous internal structure of FA-E, which facilitates the escaping of water and also leads to the reduction of dehydration damage during heating. It can be concluded that the thermal expansion and shrinkage of the geopolymers concretes are closely related to the paste composition and permeability, as well as the aggregate type.

In contrast to cement concrete, the thermal expansion rate of geopolymers varies less. However, thermal expansion of the geopolymers is a complex process. In order to prepare superior thermal insulation materials, it is necessary to design the geopolymer concretes through optimization of geopolymer composites, aggregates, and activator types to achieve the appropriate permeability and dehydration temperature.

### 2.2.2. Thermal Expansion/Shrinkage Process of Geopolymers.

According to the thermal deformation mechanism of geopolymers under various temperatures, previous studies have revealed and defined six stages throughout a completely heating process [45], as shown in Figure 3.

A slight expansion is generated at the first stage (below 100°C) due to the evaporation of absorbed water contained in geopolymers. At the second stage (100~300°C), the

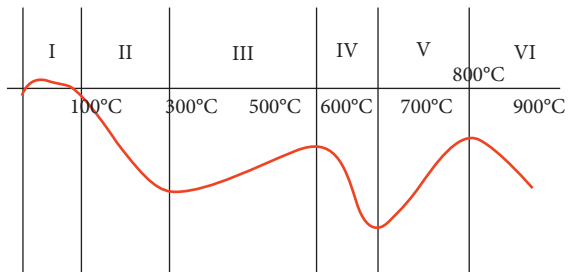


FIGURE 3: Thermal expansion process of the geopolymers.

capillary shrinkage after dehydration of the geopolymers resulted in high strain. When the temperature reaches 300~350°C, shrinkage of geopolymers remains stable. The geopolymers (such as FA geopolymers) can densify at the fourth stage (550~650°C). In some cases, the aluminosilicate gel is densified into a glass or ceramic state at an increasing heating rate due to softening and viscous sintering. Rapid expansion or contraction occurs at the fifth stage (650~800°C). Rapid contraction can be observed in some cases. However, the region does not necessarily exist. It can be due to the mixing ratio of aluminosilicate types (FA, MK, rice husk ash (RHA), etc.) or geopolymers themselves. However, the causes of their sudden expansion or contraction have not been studied. When temperature exceeds 800°C, the pore structure collapsed, the geopolymers begin to melt, and further contraction could be observed [45–50]. The effects of different measures on thermal contraction are listed in Table 1 [26, 51–53]. It can be seen that the thermal deformation results of FA and MK geopolymers are consistent with the thermal strain process.

It is urgent to solve the problem of how to restrain the thermal deformation of geopolymers after the change of expansion/contraction of geopolymers when exposed to elevated temperature. The common way to reduce thermal expansion/shrinkage is to add filler such as silica fume and alumina to the geopolymers or to add ceramic particles or refractory aggregates. The silica fume filler and the alumina filler are added to the FA geopolymers. Compared with the FA geopolymers without any filler, the shrinkage of the composite geopolymers is reduced by 40~60% at 1000°C. And the sample containing silicon powder improved the heat shrinkage effect better than the alumina containing sample [51]. Addition of fine ceramic particles to MK geopolymers can also significantly reduce the thermal shrinkage [52]. Chamotte aggregates are added to FA and MK geopolymers, and the effect of inhibiting thermal shrinkage is very significant compared with geopolymer slurry [53]. In view of the advantage of short fibers in reinforcing ordinary concrete, it was also used to improve the thermal stability of geopolymer [54]. The results show that carbon fiber reduces the thermal shrinkage of geopolymers from approximately 4% at 500°C to less than 0.1%, due to the deformation restraint imposed by carbon fibers.

In conclusion, thermal expansion of geopolymers usually has six stages and the expansion or contraction rate varies from stage to stage. It is an effective method to incorporate silicon-type filler, fine ceramic particles, and short

fibers for the objective of inhibiting the thermal deformation of geopolymers.

### 2.3. Thermal Conductivity Analyses of Geopolymers

**2.3.1. Conductivity of Geopolymers.** Generally, thermal conductivity of geopolymers is lower than that of the conventional building materials. For instance, when the density of the MK geopolymers is 1430~1890 kg/m<sup>3</sup>, its thermal conductivity is 0.550~0.650 W/(m·K). And the thermal conductivity of Na-based geopolymers is higher than that of K original geopolymers. It is also found that the thermal conductivity of MK geopolymers is 0.067 W/(m·K) when the density is 270 kg/m<sup>3</sup> and increases to 0.160 W/(m·K) when the density is 350~400 kg/m<sup>3</sup> [12]. However, these reports do not mention the methods and conditions for measuring thermal conductivity. Rashad [55] showed that the thermal conductivity of geopolymer mortar (the highest thermal conductivity of geopolymer mortar is 0.930 W/(m·K)) is lower than that of cement mortar (1.400 W/(m·K)). And FA geopolymer mortar seems to be more effective in insulation than MK geopolymer mortar. The lower thermal conductivity of FA powder can be associated with higher territorial powders.

Kamseu et al. [56] found that the thermal conductivity of the MK geopolymers varied between 0.300 and 0.590 W/(m·K). Moreover, the variation of thermal conductivity was linear with the molar ratio of Si/Al. The thermal conductivity of geopolymers increases with the increase of Si/Al molar ratio. The insulation property of the geopolymers depends on its porosity and the amorphous properties of the main phases. The increase of Si/Al molar ratio leads to the excessive content of Si, which is helpful to strengthen the polysilicates formed or as fillers, so as to improve the mechanical properties of the matrix. However, the increase of silicon content has no positive contribution to insulation performance.

The data of the thermal conductivity of the geopolymers show that the geopolymers have good thermal insulation; the smaller the geopolymer density, the lower the thermal conductivity. Interestingly, the increase of Si/Al ratio has the opposite effect on decreasing the thermal conductivity of geopolymers.

**2.3.2. Thermal Conductivity Improvement Techniques for Geopolymers.** Ordinary geopolymers, however, are not able to be used as refractory and thermal insulation materials for buildings. Therefore, the modifications for ordinary geopolymers are purpose-designed in previous research studies. To this end, engineering fibers are employed to improve thermal insulation of ordinary geopolymers. For instance, Samal et al. [57] compared the thermal conductivity of the various fiber-reinforced MK geopolymers under increasing ambient temperature. The results indicated that the fiber incorporation greatly contributes to thermal insulation improvement of the geopolymers. When the temperature gradually increases to 250°C, the maximum thermal conductivity of the fibers geopolymers is less than 0.700 W/

TABLE 1: Effects of different measures on thermal contraction.

Researchers	Villaquirán-Caicedo et al. [26]	Vickers et al. [51]	Kovářík et al. [52]	Rovnaník and Šafránková [53]
Raw materials	MK	FA	Clay and MK	MK and FA
Method	Adding RHA and silica fume.	Adding silica ash and aluminum base type filler.	Adding ceramic particle material.	Choosing chamotte as the thermally stable aggregate of mortar.
Conclusions	The geopolymer curve with silica fume is gentler, while the thermal shrinkage of geopolymers added with boiler slag is obvious.	The addition of filler can reduce the thermal shrinkage of geopolymers, and the effect of adding silica fume is better.	The higher content of fine ceramic particles can improve the thermal shrinkage of geopolymers.	The thermal shrinkage of MK paste is much larger than FA paste, but the difference of mortar is small.

(m·K), which is similar to that of insulating concrete (thermal conductivity is less than 0.750 W/(m·K)). Comparatively, fiber is proven to be most effective for geopolymers to get a lowest thermal conductivity. The large porosity of the fibers results in high air content in the geopolymers, and thus the rate of heat transfer through the geopolymers is decreased.

In addition to fiber addition, Lee et al. [58] found that the addition of aluminum powder to the FA geopolymer mixture reduces apparent density and thermal conductivity (thermal conductivity of 0.506 W/(m·K)). This is because aluminum powder reacts with sodium hydroxide in geopolymer slurry to produce hydrogen. The hydrogen in the slurry causes the formation of a porous structure in the geopolymer mortar. The porous structure contributes to the insulating properties of the geopolymer mortar. Rashad [55] found that the addition of expanded perlite to the FA geopolymers can also increase its thermal insulation performance, with thermal conductivity of at least 0.37 W/(m·K).

The thermal insulation of the geopolymers can be improved more significantly by making foamed concrete from the FA geopolymers. Through the simultaneous introduction of air foams and hollow glass bubbles (HGBs) in FA-based geopolymer matrix, the foamed geopolymers achieved low density, relative high strength, and ultralow thermal conductivity at the same time [59]. The properties of the optimized foamed geopolymers in terms of density between compressive strength and thermal conductivity are listed as (300 kg/m<sup>3</sup>, 2.84 MPa, and 0.0711 W/(m·K)), (250 kg/m<sup>3</sup>, 1.57 MPa, and 0.05509 W/(m·K)), and (200 kg/m<sup>3</sup>, 1.06 MPa, and 0.05223 W/(m·K)). Compared with the former research about the thermal insulation materials, these fabricated geopolymers exhibit promising performance.

The use of similarly improved techniques in MK geopolymers also has an improved effect on thermal insulation properties. For example, the alternative silica-based activators, such as rice husk ash (RHA), silica fume (SF), and slag, are separately added to MK to prepare MK geopolymers. The thermal conductivity of the composites was 0.170~0.353 W/(m·K), and the thermal insulation property of the prepared composite is equivalent to that of the thermal insulation material (heat-insulating gypsum (0.260~0.300 W/(m·K)) [36]. The geopolymer with MK/RHA has the lowest thermal conductivity of 0.17 J/m·K. Similarly, the addition of organic

particles to the geopolymers can also improve the thermal insulation of the geopolymers. It is reported that the dry density and thermal conductivity of composite geopolymers decreased with the increase of polystyrene particles [60].

Table 2 shows a summary of the methods for improving the thermal insulation properties of geopolymers [25, 55–60]. It can be seen from Table 2 that the addition of HGBs to the foam FA geopolymer concrete appears to be the most effective method for reducing thermal conductivity. However, the cost of polystyrene is unclear, so this method is not suitable for a wide range of applications. At the same time, it is difficult to compare the thermal insulation properties of MK-based geopolymers and FA-based geopolymers from the results of Table 2. The thermal conductivity data of the two are not much different. However, the environmental driving from these test data is not the same. Therefore, it is more convincing to compare the difference in thermal insulation properties of the two geopolymers while controlling the same variables.

The geopolymers exhibit thermal stability at high temperatures. The mass loss is small, and the expansion ratio and thermal conductivity are low. Moreover, the thermal properties of the geopolymers are usually closely related to the constituents of the geopolymers and the raw materials. Silicon-type fillers have a good effect on improving the expansion of geopolymers but have opposite effects on thermal conductivity. In pursuit of further improvement about the thermal insulation performances, the foamed porous geopolymer materials have become the most promising alternative with great potential. The foamed geopolymers are fabricated by incorporating solid ingredients (silicon and aluminum), liquid activator, expanding agents, HGBs, and/or porous aggregates.

### 3. Mechanical Properties of Geopolymers under High Temperature

*3.1. Differences of Aluminosilicate Raw Materials.* Compressive strength of ordinary cement concrete is reported to decrease sharply when temperature exceeds 400°C [19]. And cement exhibits brittle failure of compression tests at all experimental temperatures [61]. It is different from traditional cement concrete that the high-temperature residual mechanical properties of geopolymers are much desirable. Tables 3 and 4 show some of the research results

TABLE 2: Effects of different measures on thermal insulation properties.

Methods	Geopolymer type	Thermal conductivity
Silica-based activators [25]	MK	0.170–0.353 W/(m·K)
Expanded perlite [55]	FA	0.37 W/(m·K)
Fibers [57]	MK	Less than 0.700 W/(m·K)
Aluminum powder [58]	FA	0.506 W/(m·K)
Foam concrete with air and HGBs [59]	FA	0.052–0.071 W/(m·K)
Foam concrete with polystyrene [60]	MK	0.09 W/(m·K)

on mechanical property changes of geopolymers at high temperature [27–84]. It can be seen that the high-temperature mechanical properties of the geopolymers are greatly affected by various factors. Moreover, the properties of different geopolymers with different raw materials are also quite different. It can be obviously obtained from Tables 3 and 4 that the high-temperature mechanical properties of FA geopolymers are better than those of the MK geopolymers.

The difference in aluminosilicate raw material is the important reason for the difference in mechanical properties at high temperature for the geopolymers. The change of strength between geopolymer mixtures is largely due to the different geological polymerization levels among the mixtures. The ratio of Si/Al in diverse types of FAs is different. At high temperature, the higher the Si/Al ratio of FA is, the higher the conversion of FA into amorphous aluminosilicate geopolymer gels is and the better the retention of strength is (or even increase). The increase of strength is due to the greater intergranular connectivity of the aluminosilicate and the unreacted FA resulting from the sintering [62].

The performance of FA and MK geopolymers at high temperature is compared in some former research studies [53, 80]. The results show that the strength of MK geopolymers decreases more significantly after high-temperature exposure. This difference may be due to the different microstructures of the two geopolymers. The mechanical strength of FA geopolymers decreases due to the presence of unreacted particles and crystals at ambient temperature. With the increase in temperature, the moisture in geopolymers begins to evaporate. MK geopolymers still have a very dense structure at elevated temperatures and the vapor pressure on porous walls increases continuously because there is no channel for dissipating the vapor pressure. Therefore, when the vapor pressure reaches the maximum limit, the dense matrix cannot withstand the high thermal stress caused by temperature, resulting in the development of cracks and eventually a complete collapse of the microstructure. A number of pores are created in the FA geopolymers, which provide an escape path for the dissipation of vapor pressure, and thus the microstructure of these samples is relatively less damaged. Therefore, high compressive strength of FA geopolymers is maintained at high temperature [53].

The geopolymers are usually prepared from a variety of aluminosilicate materials, which helps to improve the strength of the geopolymers at room temperature, but does not necessarily have the same effect on the residual strength of the geopolymers after high temperature. The maximum compressive strength of FA geopolymer mortar is observed,

and it decreases with the increase in POFA. In high-temperature applications, low water content is usually required. It can reduce dehydration and shrinkage during heating. The higher specific surface area of the POFA particles results in a higher water demand of the geopolymer mortar. Therefore, the strength of composite geopolymers is directly affected [27]. The increase of BFS in the geopolymers mainly results in the increase in compressive strength at room temperature. The strength loss at high temperature is caused by the disappearance of chemically bound water in calcium rich gel containing high concentration slag, which results in cavity structure and phase separation [73].

However, the effect of raw materials on the stress-strain behavior of geopolymers does not appear to be significant. For example, Martin et al. reported that both the FA geopolymers and FA/bauxite geopolymers exhibit linear elastic behavior of brittle materials at temperature of 400°C and 600°C. But, the behavior of the alkali cement was plastic and permanently deformed at a higher temperature (800–1000°C) [61]. Unlike the role of aluminosilicate precursors, the incorporation of fiber reinforcements, such as CF, SCF, BMF, and so on, changes the failure mode of the geopolymer composites after exposure to high temperatures from brittle failure into plastic failure, which has an extended period of plastic deformation [81, 82]. This is mainly due to the interface debonding, fracturing, and pulling-out of fiber reinforcements.

In a word, the raw materials have great influence on the high-temperature residual strength of the geopolymers. The strength of FA with high silicon aluminum is desirable at high temperature. In some cases, the loss of high-temperature residual strength of geopolymers prepared from various aluminosilicate materials is more than that of single raw material geopolymers. However, the effect of raw materials on the stress-strain relationship of the geopolymers at high temperature is relatively small. Nonetheless, the inclusion of fiber reinforcements which possesses good thermal resistance for geopolymers would be feasible to promote its use in structural fire resistance applications.

**3.2. Chemical Compositions.** Auxiliary materials are usually added to the geopolymers to improve the performance of the geopolymers. Other materials (such as QP, CF, and polystyrene particle) are added directly into geopolymers; however, the performance improvement results are different. Adding materials such as QZ and SF into the FA geopolymers can enhance the mechanical properties of the composite geopolymers at high temperature. Fine filler

TABLE 3: Strength characteristics of FA geopolymers at high temperature.

Researchers	Thokchom et al. [62]	Rickard et al. [44]	Shaikh and Vimonasitt [63]	Rickard et al. [64]	Junaid et al. [65]	Ze et al. [66]	Vickers et al. [51]	Timakul et al. [67]	Chithambaram et al. [68]	Pan et al. [69]	Abdulkareem et al. [29]	Saavedra and de Gutiérrez [70]	Hussin et al. [71]	Ranjbar et al. [27]	Rashad and Ouda [72]	KURKLU [73]	Messina et al. [74]	Yang et al. [75]
Additive	None	None	None	None	None	None	$\alpha$ -Alumina and wollastonite fillers	TiO <sub>2</sub>	Ground granulated blast furnace slag (GGBFS)	None	None	Granulated blast furnace slag (GBFS)	Pulverized fuel ash (PFA) and POFA	POFA	Quartz powder (QP)	Blast furnace slag (BFS)	BFS and MK	Red mud (RM)
Variable	Si/Al ratio in 1.7–2.2	Amorphous Si/Al ratio in 1.2–8.8	Aggregate sizes	Pretreatment	Duration of exposure time	None	Filler types and amounts	TiO <sub>2</sub> additive amount	Amount of GGBFS	OPC/ geopolymer paste and concrete	Fine aggregate and lightweight aggregate (LWA)	FA/GBFS and FA/ OPC concrete	Blended ash geopolymer (BAG) and OPC concrete	The addition of POFA	The addition of QP	The addition of BFS	Different curing temperatures (CT)	Different temperatures
The result of strength	The residual strength of geopolymers with Si/Al of 2.2 is the highest.	The fly ash geopolymers with high Si/Al (>5) has high compressive strength at 1000°C.	Small size aggregate can reduce strength loss.	Leaching in water and gradually drying prior to heating improve the residual strength.	Most of the changes in strength occurred in the first two hours. Then, the duration of exposure has insignificant effect on the strength.	The strength of geopolymers with SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio of 3.8 is the highest after firing.	The addition of inorganic filler exhibits high-level strength after firing, and wollastonite is much better.	TiO <sub>2</sub> is significant for improving the compressive strength and thermal shock resistance when the content is 5 wt%.	30% partial replacement of FA by GGBFS reaches the highest strength irrespective of NaOH concentration.	The strength of geopolymer and OPC paste increases by 192% at 500°C. But, a significant loss of strength appears after cooling.	The addition of aggregates (fine or fine +LWA) can promote the fire resistance significantly.	The residual strength of FA/GBFS and FA/ OPC concrete at 1100°C is 15 MPa and 5.5 MPa, respectively.	The strength of BAG concrete increases with the temperature and reaches its peak at 600°C, while OPC concrete only reaches at 200°C.	All FA/POFA samples can obtain strength when exposed up to 500°C. The content of POFA delays after firing temperature of peak strength.	With the increase of QP content, the compressive strength before and after firing increases.	The compressive strength of the mortars increases with the amount of BFS, while the flexural strength decreases with that of FA.	BFS and MK can increase the reactivity at early age and improve mechanical performances without higher CT.	It keeps good retention while the strength drops quickly above 600°C.
Residual strength	For the Si/Al ratio of 1.7 and 2.2, respectively, it is about 90% and 79% at 600°C and 62% and 52% at 900°C.	It is about 100% at 600°C and 97% at 800°C for the aggregate size of 10 mm, while it is about 87% at 600°C and 84% at 800°C for 20 mm.	It is about 290% at 800°C and 260% at 1000°C for the geopolymers with SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio of 3.8.	It is about 90%, 185%, and 279% at 600°C, 800°C, and 1000°C, respectively.	It is about 55% and 58% at 600°C and 900°C, respectively.	It is about 290% at 800°C and 260% at 1000°C for the geopolymers with SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio of 3.8.	It is about 52%, 72%, and 247% at 600°C, 800°C, and 1000°C, respectively.	It is about 50% and 37% for composites with 5% and 0 content of TiO <sub>2</sub> after 15 thermal cycles (800°C).	It is about 53% at 600°C and 45% at 800°C, respectively.	It is about 61.4% and 73.3% at 600°C and 47.7% and 61.0% for mortar and concrete with LWA, respectively.	It is about 40% and 36% for geopolymer and OPC concretes, respectively, at 550°C.	It is about 41% and 25% at 900°C and 33% and 24% at 1100°C for FA/GBFS and FA/ OPC concrete, respectively.	It is about 120% and 67% at 600°C and 84% and 45% at 800°C for BAG and OPC concrete, respectively.	It is about 163%, 185%, and 233% at 600°C, 800°C, and 1000°C, respectively, for the compressive strength of 25:30% QP.	It is about 77.5%, 44.7%, and 41.9% at 600°C, 800°C, and 1000°C, respectively, for the compressive strength of 100% BFS content.	After exposure to 800°C, it is about 75% (MK/FA) and 66% (BFS/FA) for 20°C CT, 76% (MK/FA) and 64% (BFS/FA) for 40°C CT, and 61% (MK/FA) and 73% (BFS/FA) for 60°C CT.	It is about 82% at 600°C and 27% at 800°C.	



TABLE 4: Strength characteristics of MK geopolymers at high temperature.

Researchers	Tchakoutte et al. [76]	Lahoti et al. [77]	Aygörmez et al. [78]	Duan et al. [43]	Duan et al. [79]	Šafránková [53]	Duan et al. [60]	Zhang et al. [80]	Roviello et al. [81]	Yan et al. [82]	Villaquirán-Cácedo et al. [83]	Kovářík et al. [52]	Burciaga-Díaz and Escalante-García [84]
Additive	Sodium waterglass (NWG)	Silica fume (SF)	SF and colemanite waste (CW)	FA	FA	FA	Polystyrene particles (PP)	FA	Basalt microfibril (BMF)	Carbon fiber (CF) and SIC fiber (SCF)	Aluminosilicate particles (AP), CF, and alumina fibers (AF)	Ceramic particle (CP)	BFS
Variables	The addition of NWG from RHA and waste glass (WG)	Si/Al molar ratio in 1.03–2.00	The addition of SF, CW, and polypropylene fiber (PF)	The addition of OPC and FA	The addition of OPC and FA	FA and MK geopolymers	The addition of PP	The addition of FA	The addition of BMF	Different temperatures and fiber lengths	The addition of reinforcing materials	The addition of CP	The addition of BFS
The result of strength	The strength decreases from room temperature to 400°C and then increases until up to 800°C.	Geopolymers with Si/Al ratio of 1.75 possess highest strength (6 MPa) after exposure to 900°C.	The inclusion of SF up to 20% and CW up to 10% increased the residual compressive and flexural strengths, while PF yields slight decrease.	The strength of OPC paste is almost zero at 600°C, while that of FA/MK geopolymer decreases to 46 MPa at 1000°C.	The compressive strength of OPC paste decreases significantly after 400°C, while that of geopolymer increases after 400°C.	MK geopolymer shows better mechanical properties compared to FA geopolymer under laboratory conditions. But high temperature turns the results into opposite.	The strength of geopolymers decreases with the increase of PP content, but still shows sufficient strength.	Blended MK/FA show higher bending and compressive strength both at ambient temperature and after exposure to 800°C.	The incorporation of BMF increases the strength due to its increased thermal resistance and dense microstructure. The composite of 10 wt% BMF possesses the best residual strength.	The room temperature mechanical properties are improved remarkably due to the inclusion of hybrid fibers. The SCF with the length of 3 mm exhibits the highest retention of strength.	The reinforcement composites of AF/AP and CF/AP achieve remarkable mechanical performance both at room and high temperature.	The geopolymers incorporating fine CP (under 90 mm) at the amount of 250% of MK weight have a constant flexural strength of ~12 MPa and a compressive strength of ~90 MPa, both before and after exposure at 1000°C.	The binders of 50%BFS-50%MK and 100%BFS retain the strength better than 100%MK at the range of 600–800°C. But the trend changes when the temperature is over 1000°C.
Residual strength	It is about 103% and 117% at 600°C and 92% and 98% at 800°C for NWG-RHA and NWG-WG respectively.	It is about 0, 11%, 3%, 9%, and 4% at 900°C for the Si/Al ratio of 1.03, 1.25, 1.5, 1.75, and 2.00.	It is about 48.1% (10% SF) and 47.3% (10% CW) at 600°C and 17.1% (10% SF) and 15.8% (10% CW) at 800°C.	It is about 100%, 81%, and 78% at 600°C, 800°C, and 1000°C, respectively, for the geopolymer pastes.	It is about 97%, 84%, and 72% at 600°C, 800°C, and 1000°C, respectively, for the geopolymer pastes after 3 days of curing.	It is about 72%, 72%, and 64% at 600°C, 800°C, and 1000°C, respectively, for MK pastes and 217%, 410%, and 422% for FA paste.	It is about 32%, 29%, 28%, 25%, and 17% at 800°C for the 0, 25%, 50%, 75%, and 100% addition of PP, respectively.	The retention ratio in bending and compressive strength is 4% and 44%, respectively, after exposure to 500°C.	It is about 68% and 57% at 400°C and 800°C, respectively, for the incorporation of 10 wt% BMF.	It is about 108%, 72%, and 77% at 800°C, 1000°C, and 1200°C, respectively, for the SCF length of 3 mm.	It is about 265% and 227% after exposure to 1200°C for reinforcements of CF/AP and AF/AP, respectively.	It is about 100% and 98% for the flexural and compressive strengths at 1000°C.	It is about 58%, 55%, and 30% at the temperature of 800°C, and 1000°C, and 1200°C, respectively, for the binder of BFS: MK = 1:1.

particles can significantly improve the pore size and pore shape distribution of the matrix. For silica powder (SP) and SF, the increase of Si/Al ratio also increases the compressive strength of the mixture [62]. The addition of silica fume into the geopolymers of MK can increase the residual strength after high temperature because the SP as filler can help reduce the thermal shrinkage. Moreover, quartz can maintain the dimensional stability of the matrix at high temperature [72]. The MK geopolymers with fine CPs have higher compressive strength after exposure at 1000°C because fine particles fill the gap between larger aggregates [52]. Therefore, the fine particles form an effective stress/strain barrier against the collapse of the geopolymer matrix during exposure to high temperature.

Zhang et al. [85] mixed FA with MK to prepare composite geopolymers and added chopped carbon fibers to the geopolymers. It was found that the flexural strength of the geopolymers increased after the high temperature, but the addition of the carbon fiber to the geopolymers had little effect on the compressive strength. The addition of APs and CFs to geopolymers made from RHA and MK has similar effects [85].

The addition of organic matter into MK can significantly reduce the thermal conductivity of the geopolymers. However, the mechanical properties at high temperature do not necessarily increase. For example, increasing polystyrene particles reduce the compressive strength of the polystyrene foam geopolymers. Because the strength of the polystyrene particles is close to zero and the compressibility is high. The flexural strength of the polystyrene foam geopolymers decreased at 800°C, and the compressive strength was negligible [60]. However, the addition of melamine resin to MK geopolymer has the opposite result. The incorporation of the resin has the effect of fixing water molecules and effectively delaying the evaporation of water. Organic phase can not only absorb partial load by plastic deformation but also exert toughening effect through typical crack deviation mechanism [86], so the residual strength of MK geopolymers can be improved by adding resin.

In general, the filling effect of the silicon-type filler results in an increase in the high-temperature residual strength of the geopolymers. A small portion of organic fillers can increase the toughness of the geopolymers, but most organic fillers are detrimental to mechanical properties of geopolymers exposed to high temperature.

**3.3. Preparation Conditions.** The preparation conditions also affect the mechanical properties at high temperature of the geopolymers. Firstly, in the preparation of geopolymers, it is considered that the higher the design of Si/Al ratio, the greater the residual compressive strength of the geopolymer made of the same kind of FA [62, 66]. The X-ray diffraction spectrum shows a higher Si/Al ratio is relatively undisturbed and the diffraction peaks are narrow.

The type and concentration of activator used to prepare the geopolymers also have a significant impact on the

high-temperature mechanical properties of the geopolymers. Keng et al. [87] found that the compressive strength of potassium-based FA geopolymers increased at temperatures exposed to 500°C, while the strength of sodium-based geopolymers decreased. The reason for this phenomenon may be that the crack damage of potassium-based geopolymers is small at 500°C, and the densification of geopolymer matrix caused by capillary strain leads to the increase of compressive strength. Sodium-based geopolymers are subject to higher cracking damage, which has a negative effect on the compressive strength. Under the action of high temperature, the development of cracks and the expansion of pores reduce the strength, while the densification of the matrix is beneficial to the improvement of strength. These competing mechanisms depend on the type of alkali metal cation used and determine the strength durability of the geopolymers. Rashad and Zeedan [88] found that the concentration of the activator had a significant effect on the initial strength and residual strength after heating. As the concentration of the activator increases, the compressive strength increases. Conversely, as the concentration of the activator increases, the relative residual compressive strength after firing decreases. It is preferred to use a lower concentration of sodium silicate to activate the FA required for the refractory bonding material.

The addition of aggregate has an effect on the mechanical properties of geopolymers at high temperature. It is reported that the compressive strength of FA geopolymer paste decreases with the increased temperature. At 800°C, the strength of geopolymer paste is completely lost, but the strength loss rate of geopolymer mortar and lightweight geopolymer concrete is low [29].

In order to discuss the effect of different aggregates on the stress-strain behavior of FA geopolymers at high temperature, three different FA geopolymer concretes (M1, M2, and M3) were prepared by using typical basalt natural aggregates and nonparticulate light ceramics. Tables 5 and 6 show the maximum values of stress-strain curves of geological polymers obtained at room temperature and high temperature [89].

It can be seen that the stress-strain relationship of different geopolymers is much different, which indicates that the composition of geopolymers had a greater influence on the strain curve. The stress-strain curve of M3 at high temperature shows that as the temperature increases, the peak strength of the geopolymer samples changes little, but the strain corresponding to the peak intensity increases. It shows that the deformation of the geopolymers before it breaks is greater as the temperature increases.

It can be concluded that the preparation conditions also have an important influence on the high-temperature mechanical properties of the geopolymers. The higher the ratio of Si to Al, the better the properties of the geopolymers. The strength loss rate of geopolymers is decreased by adding aggregate, but the stress-strain curves of geopolymers were different from different kinds of aggregates.

TABLE 5: Stress-strain curves for different geopolymers at room temperature.

Samples	M1	M2	M3
Peak stress (MPa)	60	46	39
Peak strain (mm/mm)	0.0038	0.0041	0.0035
Variation trend after peak stress	Stress drops rapidly	Stress drops rapidly	Stress decreases slowly

TABLE 6: Stress-strain relationship for M3 samples at elevated temperatures.

Temperature (°C)	Ambient	100	200	300	400	800
Peak stress (MPa)	39	34	33	37	37	41
Maximum strain (mm/mm)	0.0035	0.006	0.0043	0.0039	0.0038	0.0062

**3.4. Test Conditions.** Finally, the test conditions such as heating time and heating temperature are also considered to be an important factor related to the properties of the geopolymers. For instance, pretreatment can remove water and excess alkali before exposure to high temperature without damaging the structure [54]. Therefore, proper pretreatment can increase the residual strength of the geopolymers. It has been reported that the effect of high temperature action on the strength of the geopolymer is within 2 hours. For more than 2 hours, the heating time has little effect on the properties of geopolymers [55].

Some researchers have studied the stress-strain behavior of geopolymers at different heating temperatures. Zhu et al. [90] showed that the failure behavior of geopolymers varies with temperature in the investigated temperature range. At the temperature of 575°C, FA geopolymers undergo brittle failure soon after reaching their peak strength. At 680°C, geopolymers retain most of their deformation before fracture, indicating that the behavior of geopolymers is viscoelastic at this temperature. However, the pattern remains brittle after reaching its peak stress at this temperature [90], as shown in Table 7. The stress-strain curve of the FA geopolymers from room temperature to 1000°C was tested by Muhammad, et al. [91]. The relationship shows that at all temperatures, the sample reaches its peak strength and is rapidly brittle to failure. When heating to 200°C, the peak strength of the sample slightly increases compared with room temperature, and the temperature continues to increase, and the peak intensity decreases significantly. And as the peak intensity decreases, the corresponding peak strain increases significantly. It can also be obtained from reference [91] that the stress-strain curve of the specimen tends to be flat before deformation and fracture, but it still maintains brittle failure after reaching the peak strain. The peak intensity is the maximum at 200°C and the peak strain is the smallest. At 800°C, the peak intensity is significantly reduced and the corresponding strain is greatly enhanced.

In a word, the heating time which has an effect on geopolymer properties is short. The failure behavior of geopolymers varies with temperature, but rapid brittle failure occurs when the stress comes to the peak strength for all temperatures.

TABLE 7: Stress-strain relationship of FA geopolymers at different temperatures.

Temperature (°C)	23, 100, and 200	290	380	520	575	680
Peak stress (MPa)	74	112	104	124	116	122
Peak strain (mm/mm)	0.02	0.01	0.02	0.03	0.07	0.45
Stress decline trend	When the peak stress is reached, the sample stress at all temperatures decreases rapidly and linearly.					

**3.5. Summary.** The aforementioned favorable factors affecting the strength of the geopolymer after high temperature are summarized in Table 8. It can be seen from Table 8 that it is beneficial for the high-temperature mechanical properties of the MK geopolymers and the FA geopolymers to add a filler such as SF and QP, and this method is also simple and available. The addition of FA to the MK geopolymer can increase the compressive strength after high temperature. It also proves that the high-temperature mechanical properties of the MK geopolymers are inferior to the FA geopolymers. Changing the concentration of the activator and the type of alkali metal seems to be a relatively simple method, but this method takes much time. Therefore, in general, the addition of silica fume or quartz powder to the geopolymers is an excellent choice for improving its high-temperature performance.

Based on the analyses of the mechanical properties of the geopolymers after high-temperature exposure, it can be concluded that the geopolymer properties are closely related to the raw materials, the chemical composition of the geopolymers, the preparation conditions, and the test conditions of the geopolymers. The high-temperature residual strength of the geopolymers can be obtained by using suitable raw material of aluminum silicate and large designed silicon aluminum and adding silicon-type filler in it. At the same time, the failure behavior of geopolymers has been studied. The stress-strain curves of geopolymer are changed by the composition of geopolymers and the measured temperature. However, the failure behavior of geopolymers under thermal conditions is less. Therefore, in the further study of geopolymers, it is necessary to study its high-temperature stress-strain behavior.

TABLE 8: Summary of methods for improving residual strength of geopolymers.

Geopolymer type	High-temperature mechanical performance improvement methods
MK geopolymers	Adding melamine resin Adding fine CP Adding FA
FA geopolymers	Reducing the concentration of activating agent; alkali metal ion is potassium Adopting high Si/Al ratio Adding fine aggregate
MK or FA geopolymers	Adding SF and QP Adding fiber reinforcement

#### 4. Microstructure and Mineralogical Characterizations of Geopolymers Exposed to High Temperature

*4.1. Microstructures of Geopolymers.* It is widely acknowledged that variation in mechanical properties of geopolymers is mainly attributed to changes of inner microstructure. Therefore, microstructure formation and development that occurs during thermal exposure have been characterized using scanning electron microscopy (SEM) by a lot of researchers [38, 43, 60, 79, 80]. The morphological changes of OPC and geopolymer after heating are compared and analyzed [79]. It is pointed out that the corresponding microstructure of OPC becomes more and more looser with the increasing of heating temperature, while the microstructure of geopolymer remains to be stable after exposure to high temperatures. Even after the exposure to 400 °C, geopolymer microstructures become denser. These results provide a strong evidence that geopolymers possess better thermal resistance than OPC [79].

Furthermore, the morphological difference of fired geopolymers derived from different aluminosilicate source materials is also analyzed [38, 80]. The SEM photographs show that the FA geopolymers are loose in microstructure and contains a large number of spherical unreacted FA and a small amount of voids at room temperature [80]. The ratio of aluminosilicate gels is much lower than that in MK geopolymers. Therefore, the bending and compressive strengths of FA geopolymers are smaller at room temperature. When the temperature rises to 500°C, more large pores are observed on the surface of FA geopolymers. These pores may be related to pore aggregation and connection due to dehydration and sintering of unreacted FA particles at high temperature. These large holes provide an escape route for the dissipation of steam pressure in the heating process, so the damage to the microstructure of FA geopolymers is small and the residual strength is large. Different from FA geopolymers, the MK geopolymers have fine and uniform microstructures and few surface cracks at room temperature, which make the MK geopolymers possess high strength at room temperature. However, the microstructure of the MK geopolymers does not change significantly after exposure to 500°C, which does not provide an escape route for the dissipation of vapor tension. Therefore, the residual strength of MK geopolymers in the high temperature is lower than that of FA geopolymers.

FA/MK geopolymers can combine the advantages of FA geopolymers and MK geopolymers, which exhibit dense and almost uniform microstructure at room temperature [80]. There are some FA particles on the surface, but the composite geopolymers have a high proportion of aluminosilicate gels, which increase the mechanical properties of geopolymers. At 500°C, some voids also appear on the surface of the composite geopolymers, but the pore size was smaller than that of the FA geopolymers. Therefore, the geopolymers have good residual strength after high temperature [80].

However, the addition of other materials to the geopolymers does not necessarily improve its microstructure. For instance, the microstructure of POFA/FA geopolymers mortar at room temperature indicates that there is a very tiny amount of microcracks on the surface of the specimen and there are unreacted particles (FA and POFA) [27]. All of the samples are denser at 500°C despite their coarser surface. There is considerable pore formation of the POFA-based geopolymers, and unreacted particles are still present. After heating to 800°C, the average pore size of the sample surface significantly increases, which can be due to the collapse of the geopolymer matrix. For geopolymer concretes, the thermal incompatibility between geopolymers and aggregate may damage the microstructure [92]. The microstructures of geopolymer concrete present potholed texture at 400°C, and the spherical FA particles are being fused. The geopolymer matrix melts into a homogeneous phase at 800°C and cracks at 1000°C due to thermal incompatibility between geopolymers and aggregates.

In short, the microstructural damage to FA geopolymers is less than that of MK during high-temperature heating. The thermal incompatibility between aggregates and geopolymers is the main reason for the destruction of microstructures of geopolymers.

*4.2. Mineralogical Characteristics of Geopolymers.* The phase analysis of FA geopolymers and MK geopolymers after high temperature-exposure shows that the phase transition occurs in the heating process of both geopolymers. The diffraction patterns of FA geopolymers with Si/Al ratio of 1.9 at room temperature show that the phases of the geopolymers are mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), hematite ( $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 9(\text{H}_2\text{O})$ ), quartz ( $\text{SiO}_2$ ), and amorphous aluminum silicate gel. At 300°C, sintering resulted in a small amount of albite ( $\text{NaAlSi}_3\text{O}_8$ ) and nepheline ( $\text{AlNaSiO}_4$ )

peaks. At 900°C, mullite appears earlier and more albite peaks appear [73]. XRD analysis of MK geopolymers shows that the main phases of MK geopolymers are feldspar and quartz without heating. When heated to 1000°C, the main phases in the geopolymers are nepheline [93]. Similarly, Kljajević et al. [94] reported that at room temperature, there are amorphous structures for MK geopolymers and the amorphous phase disappears and nepheline appears at 900°C. It is reported that the main phase of MK geopolymers is completely transformed into nepheline at 1000°C, and the strength of nepheline phase decreases after annealing [33, 34].

The addition of quartz powder to geopolymers can increase residual strength at high temperature because of the phase change. XRD analysis of the MK-based geopolymers with quartz powder showed that the main phases of the geopolymer at room temperature were kaolinite and quartz [31]. At 400°C, the image shows no phase change in phase composition. At 1000°C, the peak values of quartz and nepheline ( $\text{NaAlSi}_3\text{O}_8$ ) are detected and the peaks of kaolinite disappear. It is reported that the crystallinity of the N-A-S-H phase increases at the temperature of 200~400°C, maintains at 800°C, and then recrystallizes to form a structurally stable anhydrous phase. The peak of nepheline appears at 1000°C. The quartz phase increases with the increase of powder content. The appearance of nepheline can maintain dimensional stability and high mechanical strength of the material. Therefore, the geopolymers still maintain high compressive strength at high temperature [95–97].

Similarly, the phase analysis of the FA geopolymers with quartz powder showed that the main phases of geopolymers at room temperature were quartz, mullite, hematite, and magnetite [72]. When the temperature was 400°C, the phase did not change significantly. Quartz, mullite, and hematite are detected at 1000°C. The melting point of mullite phase is about 1830°C, the thermal expansion rate is low, and the mechanical stability is good. The melting point of quartz phase is about 1711°C, so the appearance of quartz seems to allow geopolymers to obtain higher compressive strength under thermal load. At the same time, albite ( $(\text{NaAlSi}_3\text{O}_8)$ ) and nepheline ( $\text{NaAlSi}_3\text{O}_8$ ) were also detected at 1000°C. These phases can help maintain the dimensional stability of the material [98–102].

The phase analysis of the geopolymers after high-temperature exposure shows that there is phase transition in the heating process of the geopolymers. Nepheline phase becomes the main phase of geopolymers at high temperature. The addition of silicon-type filler increases the quartz phase in geopolymers and makes the geopolymers maintain relatively high strength value after high temperature treatment.

In general, during the high-temperature heating process, the damage to the microstructure of the prepared geopolymer during the high-temperature heating process is different due to the difference in the raw materials. However, similar phase transitions occurred in the process of heating the geopolymers to high temperatures. And microscopic analysis proves that the addition of silicon-type fillers improves the mechanical properties of geopolymers.

## 5. Conclusions

In this work, the thermal and mechanical properties of geopolymers exposed to high temperature were reviewed. The conclusions are as follows.

The geopolymers exhibit good thermal stability at high temperatures. The mass loss, expansion ratio, and thermal conductivity of fired geopolymers are much smaller than those of OPC. Moreover, the thermal properties of the geopolymers are usually closely related to the constituents of the geopolymers and the raw materials. Silicon-type fillers have a good effect on improving the expansion of geopolymers but have opposite effects on thermal conductivity.

The mechanical properties of geopolymers are closely related to the raw materials, the chemical composition of the geopolymer, the preparation conditions, and the test conditions. The stress-strain relationships of geopolymers are changed by the composition of geopolymers and the measured temperature. However, the failure behavior of geopolymers under thermal conditions is less influenced by the composition than the strength. Therefore, in the further study of geopolymers, it is necessary to study its high-temperature stress-strain behavior.

Upon elevated temperatures, the damage in the microstructure of the geopolymers is much different due to the derivation of aluminosilicates. However, similar phase transitions can occur when the geopolymers are under severe high temperature. The magnitude and the effect of the dehydration, deformation, and phase changes vary with precursor materials, permeability, and the aggregate type. Therefore, additional performance enhancements can be achieved via optimizing the paste formulation to be less susceptible to dehydration damage, changing the alkali type to increase the critical temperature, such as using a  $\text{K}^+$ -based activating solution and incorporating reinforcements.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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