#### **Review Article**

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# Comprehensive review of the properties of fly ash-based geopolymer with additive of nano-SiO<sub>2</sub>

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Abstract: Nano-SiO<sub>2</sub> is a non-toxic, tasteless, and pollution-free material with hydroxyl groups that facilitate the adsorption of water on its surface. Nano-SiO<sub>2</sub> is characterized by small particle size, high purity, low density, large surface area, and good dispersion properties. In addition, nano-SiO<sub>2</sub> has excellent stability, reinforcement, thixotropy, and optical and mechanical properties. The additive of nano-SiO<sub>2</sub> can enhance the mechanical properties and microstructure of concrete. Therefore, nano-SiO<sub>2</sub> is widely used as an additive in the field of building materials. Geopolymers have excellent mechanical properties, acid-alkali resistance, fire resistance, and high-temperature resistance. In addition, mineral waste and construction waste can be used as raw materials for geopolymers. Therefore, geopolymers have the potential to substitute ordinary Portland cement and have good prospects for application as construction materials. The application of nanomaterials in geopolymer products has shown that nano-SiO<sub>2</sub> is effective in increasing the rate of geopolymerization reaction and reducing the setting time of geopolymers in a controlled quantity. Related results indicate that an appropriate quantity of nano-SiO<sub>2</sub> can make the microstructure of fly ash-based geopolymers denser and produce higher mechanical strength. In this study, based on the mechanism of geopolymerization, the effects of nano-SiO<sub>2</sub> on the properties of fly ash-based geopolymers including compressive strength, microstructure, hardening properties, shear bond strength, durability, and practical applications have been summarized. This study can provide

a basis for understanding the effects of nano-SiO<sub>2</sub> on the mechanical properties and durability of fly ash-based geopolymers.

Keywords: geopolymer, nano-SiO<sub>2</sub>, mechanical properties, durability

# 1 Introduction

In recent years, environmental problems such as energy consumption, dust pollution, and greenhouse gas emissions have become issues of high priority for society. Approximately four billion tons of ordinary Portland cement is produced per year, and the demand is increasing every year. The amount of carbon dioxide emitted during cement production accounts for approximately 5% of the total carbon dioxide emissions worldwide annually [1]. As the main cause of air pollution, the large-scale emission of particulate matter and nitrogen oxides has kept this industry at the forefront of key industries that cause pollution in China throughout the year [2]. Because of excessive energy consumption and the high emission of greenhouse gases, new environment-friendly building materials must be developed. Consequently, many researchers worldwide have focused on geopolymer materials in recent years. Several organic materials and low-cost industrial by-products, such as metakaolin [3], fly ash [4], silica fume [5], slag, mining waste [6], and rice husk ash [7], can be synthesized into geopolymers by applying alkaline activation.

The concept of geopolymers was proposed in 1978 by Davidovits [8]. Geopolymers are inorganic silicon aluminum gel materials that consist of three-dimensional stereo mesh structures of AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedral structure units, belonging to the class of non-metals [8]. In the preparation of geopolymer, fly ash is the commonly used base material due to its advantages compared to the other base materials. The unique network structure of the fly ash-based geopolymer results in its improved high-temperature and mechanical properties than cement in many

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ways [9]. Compared with cement, the strength loss of fly ash-based geopolymer after the high temperature is little, and the strength loss rate of geopolymer after 1,000°C is still less than 50%. Geopolymers have a considerable superiority in the preparation process compared to silicate cement. The preparation process does not require calcination or sintering at high temperatures, indicating that geopolymerization can be performed at room temperature and with limited emissions of  $NO_x$ ,  $SO_x$ ,  $CO_x$ , and carbon dioxide [10]. Energy consumption and carbon dioxide emissions of geopolymer production are much lower than those in cement production. Furthermore, the geopolymerization process is a dehydration reaction between aluminum silicates and is reversible under strongly alkaline conditions. Moreover, the raw material becomes a product, and there is no loss of substances except during dehydration [11]. Therefore, after the geopolymer waste is crushed, it can be directly used as raw material, thus saving a substantial amount of raw materials and energy and reducing the environmental pollution. As a potential alternative to traditional silicate cement-based building products, there are good practical cases of concrete composite materials for making cement, ceramics, and adhesives in the field, such as Pyrament cement in the United States and Gepolyceram ceramics in France. The application of geopolymer materials in heavy-metal curing [12,13] and wastewater treatment [14] is also under active research; however, most of these are still in the experimental research stage, and only a few are used in practical applications.

In July 1990, the first international academic conference on nanometer technical science and technology was held in the United States, and it formally established nanomaterial science as a new branch of material science [15]. For a long time, most researchers were improving the performance of concrete by using different types of materials, mixing proportions, and maintenance methods of concrete [16-19]. Nanomaterials have attracted the attention of researchers owing to their size, quantum, and surface effects. Nanomaterials such as nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub>, and nano-ZnO have a significant impact on the mechanical properties of cement-based materials and their microstructure owing to their unique nanoscale effect and certain volcanic ash activity [20-24]. Numerous studies on nano cement-based materials have been conducted. The results of many studies have shown that adding nanomaterials can significantly enhance the mechanical properties of cement concrete, the microstructure of dense materials, and the durability of materials [25,26]. An evaluation of the enhancement of concrete properties by nanomaterials such as nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub>, and nano-ZnO was done by Onaizi et al. [27]

and the results of the study showed that the content, type, water-cement ratio, and curing age of nanomaterials had a significant effect on the enhancement of compressive and flexural strengths of concrete. Concrete with nano-SiO<sub>2</sub> has a higher compressive strength in the early stages compared to concrete with other nanomaterials. Moreover, the flexural strength of concrete with nano-SiO<sub>2</sub> alone is relatively higher than concrete with nano-SiO<sub>2</sub> and other nanomaterials. As a result, most of the researchers have selected nano-SiO<sub>2</sub> to modify the properties of cementitious composites or geopolymer composites. Nano-SiO<sub>2</sub> is an amorphous substance with a particle size of only 20 nm, extremely strong ash activity, crystal nuclei action, and micro aggregate filling effect. Nano-SiO<sub>2</sub> can fill smaller voids with small particle sizes and is more active than fly ash and ordinary silica mixed with concrete [28]. Adding the appropriate amount of nano-SiO<sub>2</sub> to cement can significantly enhance the mechanical properties and durability of concrete [29,30].

Owing to the excellent effect of nano-SiO<sub>2</sub> on the modification of cement concrete, several researchers have added nano-SiO<sub>2</sub> to fly ash-based geopolymers and found that nano-SiO<sub>2</sub> can significantly improve the mechanical performance, working performance, and durability of fly ash-based geopolymers; the studies are listed in Table 1. Wang et al. [31] found that with the addition of nano-SiO<sub>2</sub>, the compressive strength of all ages of concrete increased and the hydration process was promoted, and with the decrease in porosity, the microstructure and pore size distribution were enhanced. Ibrahim et al. [32] found that the compressive strength of geopolymers with nano-SiO<sub>2</sub> was enhanced at higher temperatures. In addition, other researchers have found that the addition of nano-SiO<sub>2</sub> improves the compressive strength and shortens the setting time. The optimal dosage of nano-SiO<sub>2</sub> was found to be 0.5% [31]. The level of enhancement of the fly ash-based geopolymer because of the addition of nano-SiO<sub>2</sub> was also different at different temperatures. At high temperatures, the compressive strength increased with the amount of nano-SiO<sub>2</sub> [33]. Compared with thermal curing, fly ashbased geopolymer concrete has better mechanical strength in ambient curing [32]. Many researchers have compared the enhancement achieved by adding nano-SiO<sub>2</sub>, nanoclay, and nano-Al<sub>2</sub>O<sub>3</sub> on geopolymers. Among the three nanometer materials, nano-SiO2 was found to be more effective in improving the compressive strength and durability [34]. Researchers have also studied the properties of fly ashbased geopolymers and obtained corresponding findings by adding a combination of PVA fiber and nano-SiO<sub>2</sub> [35], steel fiber and nano-SiO<sub>2</sub> [36], and nano-Al<sub>2</sub>O<sub>3</sub> and nano-SiO<sub>2</sub> [37]. Thus, nano-SiO<sub>2</sub> has become an active topic of research in the field of fly ash-based geopolymers.

Ref.	Cementitious	Geopolymer	Nanomaterial	aterial		Curing	Setting time	Mechanic	Mechanical strength (Range), MPa	ıge), MPa
	material	type	Type	Range	Method	Temperature (°C)/Days	range	Compressive strength	Tensile strength	<b>Flexural</b> strength
Wang <i>et al.</i> , 2018 [31]	Slag	Paste	Nano-Silica	%2-0	Ambient	20/1 days	I	48.80-54.70	I	I
lbrahim <i>et al.</i> 2018 [32]	Volcanic ash	Concrete	Nano-Silica	5%	Heat	60/7 days	190–255 min 275–330 min	10-45	I	I
Xu et al., 2018 [36]	Fly ash	Concrete	Nano-Silica	6%	Ambient	Room Temp/ 28 davs	I	29-43	I	3.56–6.91
Shahrajabian and Behfarnia.	Slag	Concrete	Nano-silica, nano-alumina.	1–3%	Ambient	23/1 days	I	30-60	I	I
2018 [35]			nano-clay							
Lo <i>et al.</i> , 2017 [33]	Spent catalyst Metakaolin	Paste	Nano-Silica	0-2%	Heat	30/1 days	193–272 min 72–360 min	30-71	I	I
Adak <i>et al.</i> ,	Class C flay ash	Concrete	Colloidal	6%	Ambient	27-60/2 days	Ι	34-47	2.78-4.33	I
2017 [38]	and Metakaolin		nano-silica		+ heat					
Deb <i>et al.</i> , 2016 [39]	Fly ash	Mortar	Colloidal nano-silica	0–3%	Ambient	20	Ι	21–65	I	I
Deb <i>et al.</i> , 2015 [40] Low-calcium fly ash	Low-calcium fly ash	Paste	Nano-Silica	0–3%	Ambient	Room temp 28 days	10–13 h 16–19 h	29–67	I	I
Phoo-ngernkham <i>et al.</i> , 2014 [41]	High-calcium fly ash	Paste	Nano-silica	1–3%	Ambient	23/28–90 days	12-30 min 26-58 min	16.80-51.80	I	1.83-6.41
Gao <i>et al.</i> , 2014 [10]	Metakaolin	Paste	Nano-silica	SiO <sub>2</sub> /Na <sub>2</sub> O ratio = 1-2	Heat	80/1 days	I	28-70	I	1.83-6.41
Riahi and Nazari, 2012 [42]	Fly ash + Rice husk ash	Paste	Nano-silica and nano- alumina	Nano-silica and nano- alumina	3%	25, 70, 90/2 h, 4 h, 8 h	I	12.60–35.10	I	I

Table 1: Effect of nano-SiO $_2$  on properties of geopolymer composites

# 2 Use of fly ash in geopolymers

China is the largest coal-producing country in the world. Currently, most of the electric power generated in China is from thermal power generation, which is based on coal combustion. Fly ash is the main by-product of coal combustion [42]. With rapid development in the electric power industry, the emission of fly ash is increasing rapidly. With the increase in fly ash year by year, the comprehensive procedure for the exploitation of fly ash requires serious consideration [43]. Fly ash can be used for soil improvement, in the construction and ceramic industry, as a catalyst, for environmental protection, and many other applications [44]. The infrastructure industry consumes a large amount of fly ash. Various new materials made of fly ash are widely available in the market. These are the main methods of absorbing the generated fly ash [45]. The comprehensive exploitation of fly ash, which has become an essential technological and economic strategy in China's economic building, has converted trash to treasure and damage to profit [46]. It has also become a significant tool for resolving the conflict between environmental contamination and scarcity of resources in the context of electric power generation in China. It is also one of the challenges encountered by industry [47].

Fly ash consists of a large number of amorphous silica aluminum structures which can depolymerize under the action of an alkaline activator, and it can be assembled to produce inorganic gel materials under certain conditions such as geopolymers [5]. Therefore, the preparation and application of fly ash-based geopolymers have important economic and environmental benefits. Fly ash is widely used as a raw material for synthetic geopolymers. Compared with cementitious materials such as metakaolin, slag, silica fume, and steel slag, fly ash contains more than 70% glass beads under the microscope. These glass beads have a complete particle shape, smooth surface, and dense texture. For geopolymer concrete, they can reduce water, densify and homogenize [48]. Fly ash has a volcanic ash effect. Under alkaline conditions, it can produce cementitious substances such as hydrated calcium silicate, which can enhance the performance of geopolymer concrete [49]. In geopolymer concrete, the micro beads with a small particle size in fly ash are equivalent to nanomaterials, which can significantly enhance the structural strength, uniformity, and compactness of the former [50]. The alkaline solution reacts with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the fly ash by the process of geopolymerization to produce sodium aluminosilicate gel [51,52]. Fly ash-based geopolymers are reported to exhibit excellent mechanical properties and durability after high-temperature curing [53]. The process of preparation of the fly ash-based geopolymer concrete is shown in Figure 1.

Fly ash-based geopolymers are converted to silo-aluminates through a series of processes such as dissolution, depolymerization, geopolymerization, and condensation, in the process of alkaline excitations [54]. The process involves dissolving silica and alumina into the solution from the raw material surface and a surface hydration reaction of the insoluble raw material particles. Then, the active components and soluble minerals on the surface are geopolymerized to form a colloidal phase and finally hardened into a geopolymer structure. Until the final hardened structure of the geopolymer is formed, the fly ash is not completely dissolved, and in several cases, undissolved fly ash particles enter the final geopolymer structure by surface reaction [55]. In the process of geopolymerization, the silicate bone chains of the crystalline phase are hydrated to form the product of the grid structure, and there are alkaline earth metals or alkali metal ions between the pores of the grid, which can balance the grid spacing. The final product is zeolite, zeolite phase, or products similar to silicate cement hydration products [56]. There is less alkali aluminum silicate hydrate in the high-calcium fly ash, and the high-calcium content also interferes with the geopolymerization process. The porosity of the geopolymer formed by alkali activation was higher, and the low-calcium fly ash was more adaptive for the preparation of the geopolymer [57]. However, geopolymer-based low calcium fly ash prepared at room temperature has a long setting time, and the intensity development is slow. The formation of a high early intensity requires high-temperature maintenance, and the geopolymer toughness of the low-calcium fly ash is poor and prone to damage due to brittleness [58]. To improve these

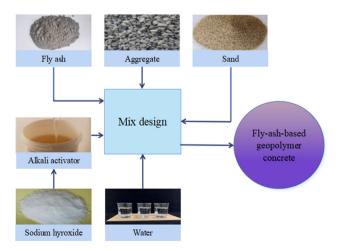


Figure 1: Preparation process of fly ash-based geopolymer concrete.

properties, some researchers have added various fibers to the geopolymer as well as various nanomaterials to improve the performance of fly ash-based geopolymers [59–61]. The common fibers used in geopolymer composites include steel fibers, polyvinyl alcohol fibers, short polymer fibers, and so on, and the most used nanomaterials added into the geopolymer composites is nano-SiO<sub>2</sub> beside nano-CaCO<sub>3</sub>.

# 3 Effect of nano-SiO<sub>2</sub> on the properties of fly ash-based geopolymer

At room temperature, the geopolymerization process of the fly ash-based geopolymer is slow, which leads to the low strength of the geopolymer [62]. Moreover, high-temperature curing is required after geopolymer molding, making the geopolymer concrete available for use only to prefabricated members, thereby limiting its scope of application scope [63]. Nanometer materials, such as nano-SiO<sub>2</sub>, nano-Al<sub>2</sub>O<sub>3</sub>, nano-Fe<sub>2</sub>O<sub>3</sub>, and others, can have a significant impact on the mechanical properties and microstructure of geopolymer composite materials owing to the nano-size effect and certain volcanic ash activity [64-67]. There are several reports of nanometer-scale materials that improve the performance of cement-based materials. Zhou et al. [68] found that a certain amount of nano-SiO<sub>2</sub> can not only enhance the compressive strength and dynamic elastic modulus of sand concrete but also improve long-term shrinkage and reduce microcracks to make the concrete more compact. Zhuang and Chen [69] researched the effect of nano-SiO<sub>2</sub> on cement slurry mobility, cement mortar strength, concrete strength, dynamic elastic modulus, and permeability performance of concrete. They observed that as the amount of nano-SiO<sub>2</sub> added was increased, within a certain range, the influence of cement hydration products gradually increased. The analysis of microstructural changes, observed using X-ray diffraction (XRD) and scanning electron microscopy (SEM), indicated good agreement with the mechanical properties and durability. Many studies have shown that adding nano-SiO<sub>2</sub> to concrete can significantly change the rheology [70], mechanical properties [69,71-73], and durability [74,75] of cement-based materials. Based on the results of several studies indicating the enhancement in the properties of cement-based composites owing to the addition of nano-SiO<sub>2</sub>, many researchers have added nano-SiO<sub>2</sub> to fly ash-based geopolymers to enhance their performance.

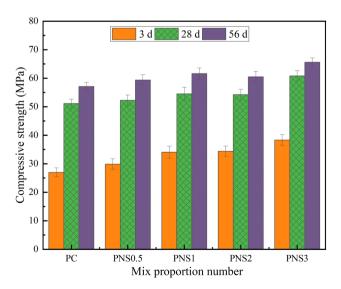
#### 3.1 Mechanism of geopolymerization

The addition of nano-SiO<sub>2</sub> to the geopolymer composite increases the soluble silica in the geopolymer composite. The increase in soluble silica leads to the formation of long-chain silicate oligomers in the geopolymer matrix, which will promote the rate of geopolymerization reactions [76]. The surface of nano-SiO<sub>2</sub> has many unsaturated bonds and a few different hydroxyl bonds which are in an active and high free-energy state. These can also accelerate the geopolymerization reaction process. Nano-SiO<sub>2</sub> has a large specific surface area and a higher activity, which may also be one of the reasons for the accelerated geopolymerization process [39,76]. Fly ashbased geopolymers use fly ash as the basic raw material, and adding nano-SiO<sub>2</sub> to fly ash-based geopolymers can enhance the activity of fly ash, thus accelerating the geopolymerization process, increasing the length of the C-S-hydrogen gel chain, and producing a small particle filling effect. Finally, fly ash and nano-SiO<sub>2</sub> were geopolymerized to form a three-site reticular inorganic gel material with Si-Al-O cross-linking [77].

Singh et al. [64] prepared geopolymers using modified nano-SiO<sub>2</sub> as an alternative activator with high mechanical strength and low permeability and found that the degree of reaction of geopolymer adhesive prepared with silica was slightly less than that prepared by industrial sodium silicate initiators, for the same fly ash; however, the mechanical strength was similar. The water demand and porosity of samples prepared with nanometer siliconbased activators are lower than those of commercially used silicate activators. This is due to the slight delay in the release of silica by the solid nanometer silicon particles which remain suspended in the solution early in the reaction and release the silica in the later stages of the reaction. Gao *et al.* [10] found that there may be a large number of unsaturated bonds and different hydroxy bonds on the surface of nano-SiO<sub>2</sub> that are in active and high freeenergy states, which increases the speed and degree of polymerization. Xu et al. [36] studied the influence of nano-SiO<sub>2</sub> particles on the structural properties of fly ash-based sustainable geopolymers. The results showed that nano-SiO<sub>2</sub> has amorphous properties, high specific surface area, and can accelerate the geopolymerization process. This may be due to the highly active silica nanometer particles reacting with sodium hydroxide and aluminum hydroxide, during hydration, to form a sodium aluminum silicate gel which acts as a nucleation site for geopolymer formation and aggregation.

#### 3.2 Compressive strength

Owing to the excellent volcanic ash activity of nano-SiO<sub>2</sub>, its inclusion in an appropriate measure improves the strength of the concrete at all ages; having a greater influence on early strength and a weaker influence on late strength [78]. From the perspective of optimizing the mechanical performance of concrete, there is a suitable range of nano-SiO<sub>2</sub> that must be considered. Any further addition of nano-SiO<sub>2</sub> will lead to a decline in the strength of concrete. The effect of the incorporation of nano-SiO<sub>2</sub> on the compressive strength of concrete varies across studies. as it also depends on the temperature, curing conditions, material composition, etc. Figure 2 summarizes the influence of the nano-SiO<sub>2</sub> content on the compressive strength of the concrete. Figure 3 shows the growth rate (%) of the compressive strength of concrete with different nano-SiO<sub>2</sub> contents. In Figures 2 and 3, PC indicates common concrete and PNS0.5 indicates that the content of nano-SiO<sub>2</sub> in the concrete is 0.5%. The ratio of the compressive strength of concrete with nano-SiO<sub>2</sub> and concrete without nano-SiO<sub>2</sub> is the growth rate of the concrete mortar. Zhang et al. [79] studied cement-based materials with nano-SiO<sub>2</sub> and found that they showed a positive growth rate of compressive strength, which was different for different dosages when compared with cement-based materials without nano-SiO<sub>2</sub>. The compressive strength of all samples increased more at an early growth rate as compared to later, which was probably due to that nano-SiO<sub>2</sub> performed the filling effect and additional calcium silicate hydrate (C-S-H) gels were produced. Kumar et al. [80] reached a



**Figure 2:** Effect of the content of nano-SiO<sub>2</sub> on the compressive strength [79].

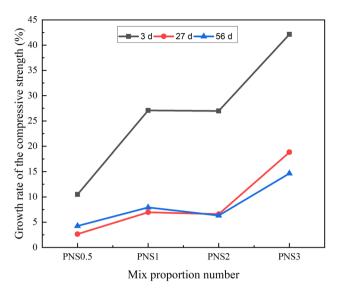


Figure 3: The growth rate of the compressive strength [79].

similar conclusion regarding the mechanical properties of cement mortar with nano-SiO<sub>2</sub>. In addition, the results showed that nano-SiO<sub>2</sub> affects cement hydration, especially at an early age [81]. In general, the cement hydration products will increase with in increase in the content of nano-SiO<sub>2</sub>, which will increase the strength and anti-permeability of concrete, and reduce the freezing-thawing resistance of concrete. Furthermore, some scholars have studied the effect of nano-SiO<sub>2</sub> on the freezing resistance of recycled concrete, and the results showed that nano-SiO<sub>2</sub> can effectively improve the compressive strength and relative elastic modulus of recycled concrete and reduce the mass-loss rate. This may also be due to nano-SiO<sub>2</sub> affecting the cement hydration products.

Owing to the significant improvement in the compressive strength of ordinary cement concrete, due to the addition of nano-SiO<sub>2</sub>, some researchers have attempted to add nano-SiO<sub>2</sub> to the geopolymer. As in the case of ordinary cement concrete, different studies have found the influence of nano-SiO<sub>2</sub> on the compressive strength of geopolymers to be varying. For high-calcium fly ash-based geopolymers, the compressive strength increased with the increase in the proportion of nano-SiO2. In a highly alkaline environment, the reaction of nanoscale silica produces C-S-H gels resulting in high-strength geopolymers. The effect of nano-Al<sub>2</sub>O<sub>3</sub> on the geopolymer properties of cured highcalcium fly ash, at room temperature, was studied by Phoo-ngernkham et al. [41]. The creation of extra C-S-H or C-A-S-H and N-A-S-H gels in the geopolymer matrix increased the compressive strength, flexural strength, and elastic modulus of the high-calcium

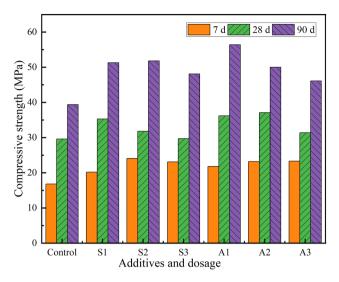


Figure 4: Compressive strength of geopolymer pastes [41].

fly ash-based geopolymer paste with nano-SiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub>. As these products are formed, they fill the pores to form dense and robust geopolymers. Other scholars have reached similar conclusions when studying high-calcium fly ash-based geopolymers [82,83]. Figure 4 shows the compressive strength of the geopolymer. In Figures 4–7, S1 indicates that the content of nano-SiO<sub>2</sub> in the geopolymer is 1% and A1 indicates that the content of nano-Al<sub>2</sub>O<sub>3</sub> in the geopolymer is 1%. Figure 5 shows the flexural strengths of the geopolymers. In comparison with ordinary silicate cement concrete, the flexural strength of the geopolymer is usually higher because the geopolymer is relatively dense and has a strength interface transition zone. Both compression

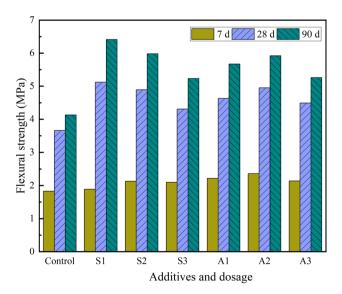
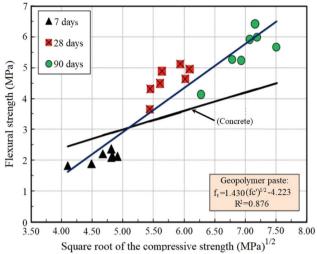


Figure 5: Flexural strength of geopolymer pastes [41].



**Figure 6:** Relationship between compressive strength and flexural strength of geopolymer pastes [41].

and discount strengths increased significantly, during the period of 28–90 days, which is a characteristic of samples cured at room temperature. Figure 6 shows the relationship between the compressive and flexural strengths of the geopolymer. The flexural strength increased linearly with the square root of the compressive strength. The equations for predicting this relationship can be written as shown in equation (1) [41]:

$$f_t = 1.430\sqrt{f_c'} - 4.223,\tag{1}$$

where  $f_t$  is the flexural strength (MPa) and  $f'_c$  is the compressive strength (MPa).

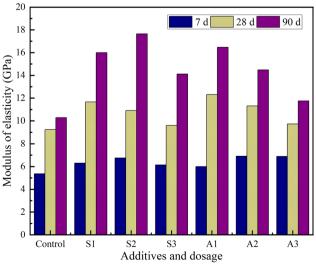
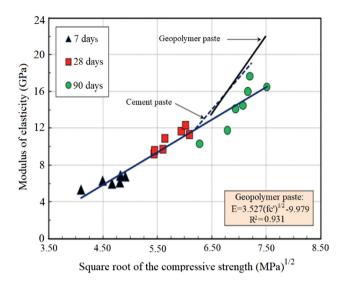


Figure 7: Modulus of elasticity of geopolymer pastes [41].



**Figure 8:** Relationship between compressive strength and flexural strength of geopolymer pastes [41].

Furthermore, the elastic modulus value tended to increase with the addition of nanoparticles. Geopolymers with nanoparticles had higher density and intensity than the geopolymer without nanoparticles, which caused an increase in the elastic modulus. Figure 7 shows the elastic moduli of the geopolymers. The elastic modulus increased linearly with the square root of the compressive strength. The relationship between the elastic modulus and compressive strength is shown in Figure 8. This relationship can be depicted using equation (2) [41]:

$$E = 3.527 \sqrt{f_c' - 9.979}, \qquad (2)$$

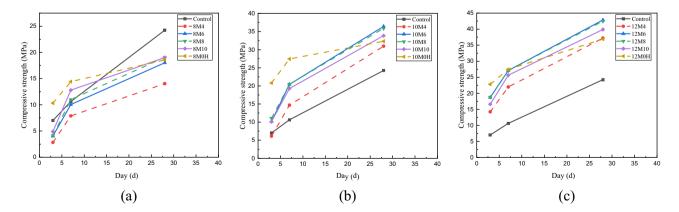
where *E* is the modulus of elasticity (GPa).

Typically, thermal activation of the fly ash-based geopolymer concrete/mortar is required to improve the early strength of the fly ash-based geopolymer. To address the aforementioned problems, Adak *et al.* [38] tested the mechanical properties of a low-calcium fly ash geopolymer

mortar at three molarities (8, 10, and 12 M) and different percentages of the added nano-SiO<sub>2</sub> (0, 6, 4, 8, and 10% fly ash). The test results showed that the compressive strength of the fly ash-based geopolymer with and without nano-SiO<sub>2</sub> at room temperature, was affected by the molar concentration, as shown in Figure 9. The compressive strength of the geopolymer mortar with and without nano-SiO<sub>2</sub> was greater at higher molarity owing to increased rates of alkali activation. The fly ash-based geopolymer with 6% nano-SiO<sub>2</sub> could still provide the best 28-day strength even without thermal curing. The compressive strength of the geopolymer matrix containing 6% nano-SiO<sub>2</sub> was higher than that of the geopolymer mortar or conventional mortar. This could be because, once nano-SiO<sub>2</sub> was present in the geopolymer mixture, the geopolymerization process in the matrix of the fly ash-based geopolymer was accelerated. The acceleration of the geopolymerization process is due to the amorphous nature and high specific surface area of nano-SiO<sub>2</sub>, which transforms amorphous compounds into crystalline compounds. However, certain researchers [58], who studied the mechanical properties and carried out the microanalysis of low-calcium fly ash-based geopolymer with nano-SiO<sub>2</sub>, found that the highest compression strength of nano-SiO<sub>2</sub> was 1%. When the added nano-SiO<sub>2</sub> is more than 1%, the nanomaterials are prone to reunite, which is unfavorable to the improvement of the compressive strength of the geopolymer. Different scholars studying the enhancement of geopolymers due to nano-SiO2 would have considered different materials, dosages, temperature, and environment. Hence, their conclusions would be different.

#### 3.3 Tensile strength

In the tensile test of geopolymer mortar mixed with nano- $SiO_2$ , the residual stress stage occurs after failure [84–86].



**Figure 9:** Compressive strength of fly ash-based geopolymer mortar (with or without nano-SiO<sub>2</sub>) with different molarity [38]. (a) 8 M, (b) 10 M, and (c) 12 M.

The reason for the residual stress is that the nano-SiO<sub>2</sub> fills the pores and forms a good matrix with epoxy resin. Geopolymers with nano-SiO<sub>2</sub> cannot bear the tensile load after cracking and the addition of nano-SiO<sub>2</sub> reduces the maximum tensile strength of the geopolymer [87]. However, it is still recommended that nano-SiO<sub>2</sub> should be added to geopolymers because it can enhance the residual strength. Therefore, geopolymer cement mortar can fare better in the face of damage, without collapsing immediately.

Different materials were selected to modify the geopolymer, and the modification produced by different substances varied. Rahmawati et al. [87] added 0, 2, 3, and 4% nano-SiO<sub>2</sub> to the geopolymer and found that there was no obvious improvement in the geopolymer tensile strength due to the addition of nano-SiO<sub>2</sub>. However, unlike in the case of the geopolymers in tensile tests, when a failure occurred, the stress did not immediately drop to zero. This indicates that the decrease in stress in the geopolymer after the incorporation of nano-SiO<sub>2</sub> does not occur suddenly and that the incorporation of nano-SiO<sub>2</sub> does not cause sudden failure of the material. Figure 10 shows the typical stress-strain curves of the geopolymers supplemented with nano-SiO<sub>2</sub> at 28 days. Figure 11 shows the maximum tensile strength of the geopolymer mortar supplemented with nano-SiO<sub>2</sub> after 28 days. In Figure 11, Control indicates common concrete, and NS2 indicates that the content of nano-SiO<sub>2</sub> in the concrete is 2%.

Nano-SiO<sub>2</sub> is better than corn whiskers (0.4-0.6 MPa)[88] in improving the tensile strength of geopolymers. However, the enhancement in the tensile strength due to the addition of metakaolin and rice shell ash (0.92-1.19 MPa) [89], steel slag (0.66–1.30 MPa) [90], and polyethylene fiber

mented with nano-SiO<sub>2</sub> [87].

NS2

1.4

1.2

1.0

0.8

0.6

0.4

0.2

0.0

Control

**Fensile strength (MPa)** 

(3.25-3.43 MPa) [91] is better than nano-SiO<sub>2</sub>. Corn whisker fiber wrapping has a significant effect on the stress-strain curve of the soil cement. With the same modification effect as that caused by nano-SiO<sub>2</sub>, the addition of corn whisker fibers led to the emergence of residual stress. However, the tensile strength of the corn whiskers was relatively low. To achieve a better tensile effect, a natural fiber with higher tensile strength is recommended [88]. The research results of Billong et al. [89] show that the tensile strength of the specimens increased by 12.5 and 25%, respectively. The reaction continues as the cement ages, and the strength at the interface between the fiber and the matrix constantly increases, which can better bridge the matrix and promote stress redistribution. Guo and Yang [90] studied the properties of ultra-high toughness fly ash and steel slag-based geopolymer and the characteristics of the microcrack at different strains and ages. They found that when the content of steel slag was 21%, the compressive strength, apparent density, tensile properties, and microcrack properties of the fly ash/steel slag-based polymer could achieve the best performance. Alrefaei and Dai [91] added steel fiber and polyethylene fiber to slag engineering geopolymer composites (EGC) to research the tensile strength of slag EGC. The results show that for slag EGC, the ultimate tensile strength of slag EGC with steel fiber is 26% higher than that of slag EGC with polyethylene fiber. In addition, the research results of Rahmawati et al. [87] show that the addition of nano-SiO<sub>2</sub> cannot increase the maximum tensile stress of geopolymer, which is mainly because nano-SiO<sub>2</sub> can only fill pores and cannot bear the expansion of cracks.

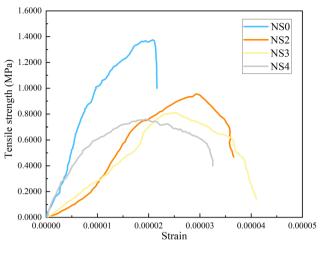
Figure 10: Typical stress-strain curves of geopolymers with nano-SiO<sub>2</sub> [87].

Figure 11: Maximum tensile strength of geopolymer mortar supple-

Nano-SiO<sub>2</sub> content (wt%)

NS3

NS4



#### 3.4 Microstructure

Geopolymers have excellent high-temperature resistance, and Figure 12 shows the microstructure of the geopolymer at different high temperatures. The geopolymer mortar colloid, without high temperature, was tightly bound, dense, and continuous, with a complete microstructure and highly reactive, and the geopolymerization products were in a good state, with no decomposition or absence of crystalline water. After 200°C heat, the geopolymer mortar colloid was tightly bound and had a complete microstructure, with a small number of cracks inside the colloid due to free water loss. Beyond 400°C, the damage to the geopolymer mortar microstructure was large, showing a crisp shape, crisscross cracks, serious colloidal block, and did not have a tight connection. The microstructure of the geopolymer which was not mixed with nano-SiO<sub>2</sub> was investigated and it was observed that the geopolymer had excellent high-temperature resistance performance. In a high-temperature environment, geopolymers will further react and a small amount of chemically bound water will be lost, leading to a denser internal structure of the geopolymer [92].

The addition of appropriate amounts of nano-SiO<sub>2</sub> can make the microstructure of the fly ash-based geopolymer denser and there were fewer particles that do not participate in the reaction. Therefore, the pores of the geopolymer were filled such that the fly ash-based geopolymer will have higher strength, higher density, and lower porosity. Figure 13 shows the microstructure of the geopolymer mixed with nano-SiO<sub>2</sub> at 200°C and 400°C. It can be seen from the figure that the incorporation of nano-SiO<sub>2</sub> greatly improved the pore distribution and pore size inside the geopolymer mortar [92].

Adak *et al.* [38] analyzed the microstructural properties of geopolymers, with and without nano-SiO<sub>2</sub>, using field emission SEM, energy dispersive X-ray spectroscopy, Fourier-transform infrared spectroscopy, and XRD. It was observed that the improvement in structural performance was mainly due to the presence of nano-SiO<sub>2</sub> which transformed the amorphous phase in the concrete matrix. Phoongernkham et al. [41] studied the influence of the added nano-SiO<sub>2</sub> on the properties of cured high-calcium fly ash. The SEM and XRD results showed that when the microstructure of the geopolymer with 1-2% nano-SiO<sub>2</sub> was enhanced, the density of the substrate was higher and there was an increase in reaction products. Singh et al. [64] also obtained results consistent with those obtained by Phoongernkham et al. [41]. However, Phoongernkham et al. [41] found that the structure of the geopolymer with 3% nano-SiO<sub>2</sub> became less dense. This could be because when there is too much nano-SiO<sub>2</sub> in the geopolymer, the nanometer-sized particles will have an agglomeration effect on the nanomaterial.

#### 3.5 Hardening characteristics

When mixed with ordinary cement mortar, nano-SiO<sub>2</sub> can shorten the setting time of cement and advance the start time of the cement hydration acceleration period. When nano-SiO<sub>2</sub> is used as an additive in the fly ash-based geopolymer, the setting time of the geopolymer is shortened owing to the formation of calcium silicate hydrate (C–S–H), thus accelerating the condensation and hardening of the geopolymer. The setting time of the fly ashbased geopolymer with nano-SiO<sub>2</sub> was reduced. As shown in Figure 14, when nano-SiO<sub>2</sub> was mixed with the geopolymer and ordinary cement mortar, the initial and final setting times of the geopolymer and ordinary cement mortar were shortened with the addition of nano-SiO<sub>2</sub>. In Figure 14, NS1 indicates the content of nano-SiO<sub>2</sub> in the geopolymer is 1%.

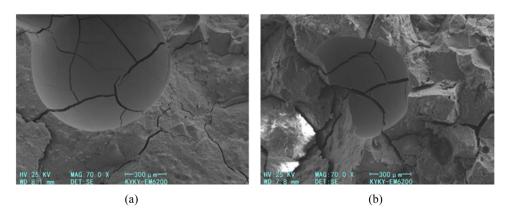
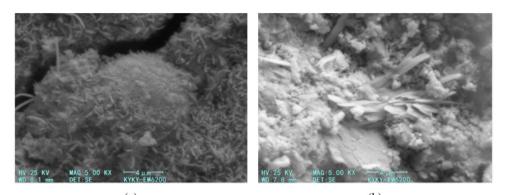
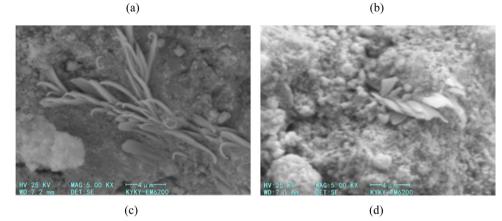


Figure 12: Micrographs of geopolymer without nano-SiO<sub>2</sub> to different temperature phases [92]. (a) 200°C:Si-0 and (b) 400°C:Si-0.





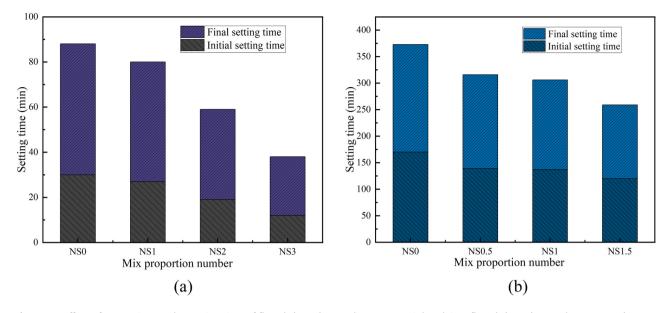
**Figure 13:** Micrographical diagram of geopolymer with different content nano-SiO<sub>2</sub> at 200°C and 400°C [92]. (a) 200°C:Si-0.5, (b) 200°C:Si-2.5, (c) 400°C:Si-0.5, and (d) 400°C:Si-2.5.

The influence of nano-SiO<sub>2</sub> on the setting time of highcalcium fly ash-based geopolymer is shown in Figure 14(a). Nano-SiO<sub>2</sub> was used as an additive for high-calcium fly ashbased geopolymer to shorten the setting time due to the formation of calcium silicate hydrate (C-S-H), thus accelerating the condensation and hardening of the geopolymer. The high-calcium fly ash-based geopolymer with nano-SiO<sub>2</sub> has rapid solidification properties and can be used as a bonding material for repair. The influence of nano-SiO<sub>2</sub> on the setting time of the low-calcium fly ash-based geopolymer is shown in Figure 14(b). The incorporation of nano-SiO<sub>2</sub> in a low-calcium fly ash-based geopolymer shortens the condensation time of the geopolymer. The higher the incorporation of nano-SiO<sub>2</sub>, the shorter is the setting time. This is mainly because of the unique "surface effect" of nano-SiO2. The nano-SiO<sub>2</sub> with a large surface area has high activity and surface energy, which enriches the surrounding free phase on the surface of the nanomaterial, thus accelerating the process of geopolymerization. At the same time, the concentration of monomers such as -OSi(OH)<sub>3</sub>-, -OSi(OH)<sub>2</sub>O-, and silicon monomers in the system promotes the formation of geopolymers in the system, accelerates the hydration and condensation hardening of fly ash, and shortens the condensation time [58].

The setting time of the fly ash-based geopolymer is affected by the content of nano-SiO<sub>2</sub> and fly ash material. Gao *et al.* [10] reported that the setting time of a geopolymer with nano-SiO<sub>2</sub> was also affected by the SiO<sub>2</sub> /sodium oxide (Na<sub>2</sub>O) ratio. The setting time of the geopolymer with nano-SiO<sub>2</sub> increased with the SiO<sub>2</sub>/Na<sub>2</sub>O ratio due to the viscosity of sodium silicate. A small SiO<sub>2</sub>/Na<sub>2</sub>O ratio aided the dissolution of the raw material and shortened the setting time. This was consistent with the results of Bernal *et al.* [93].

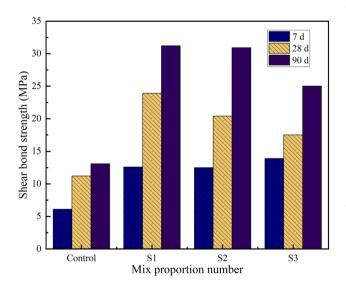
#### 3.6 Shear bond strength

Phoongernkham *et al.* [41] found that the shear bond strength of geopolymer mortar with nano-SiO<sub>2</sub> was significantly higher than that of the control group. This was due to an increase in the reaction outcome in the transition zone at the interface between the concrete substrate and the geopolymer, as well as the enhancement in the strength of the geopolymer. With the addition of nano-SiO<sub>2</sub>, the nanoparticles take part in the hydration reaction of geopolymer composites, and more hydration products are produced which contribute to the bond strength of



**Figure 14:** Effect of nano-SiO<sub>2</sub> on the setting time of fly ash-based geopolymers. (a) High-calcium fly ash-based geopolymer [38]. (b) Low-calcium fly ash-based geopolymer [41].

geopolymer. The interaction between the alkaline activator and the surface products of aged concrete causes an increase in the reaction products. As a result, the contact area of the matrix was denser, and its strength was higher [22]. Figure 15 shows the influence of the nano-SiO<sub>2</sub> content on the shear bond strength of the geopolymer. In Figure 15, Control indicates the geopolymer without nano-SiO<sub>2</sub> and S1 indicates the content of nano-SiO<sub>2</sub> in the geopolymer is 1%. The failure of formation of the geopolymer 28 days after the shear bond tests is shown in Figure 16. The failure state of the observed geopolymer paste revealed that the addition of



**Figure 15:** Shear bond strength of geopolymer with or without nano-SiO<sub>2</sub> [41].

1-3% nano-SiO<sub>2</sub> improved the binding of the geopolymer to the concrete substrate.

Adak *et al.* [38] studied the enhancement of nano-SiO<sub>2</sub> on the bonding properties of fly ash-based geopolymers by testing the bonding performance between steel bars and concrete. The results showed that for both deformed and low-carbon steel tendons, the bonding stress of geopolymer concrete was higher at a molar concentration of 12 M, and the bonding performance of nano-SiO<sub>2</sub> modified geopolymer concrete was better than that of geopolymer without nano-SiO<sub>2</sub>. Other scholars have reached the same conclusion as Zhang *et al.* [94–96]. These results prove that nano-SiO<sub>2</sub> enhances the bonding properties of geopolymers.

#### 3.7 Durability

#### 3.7.1 Anti-permeability

Anti-permeability is a basic property that characterizes the durability of the concrete because it determines the level of permeation of corrosive material under a pressure gradient, which causes the degradation of concrete. Concrete is a high-permeability medium and the incorporation of nano-SiO<sub>2</sub> changes the concrete. A certain amount of nano-SiO<sub>2</sub> can improve the anti-permeability performance of concrete, but the addition of excessive nano-SiO<sub>2</sub> can also reduce it. The addition of nano-SiO<sub>2</sub> can enhance the dynamic elastic modulus and chloride permeability of concrete. From a macro

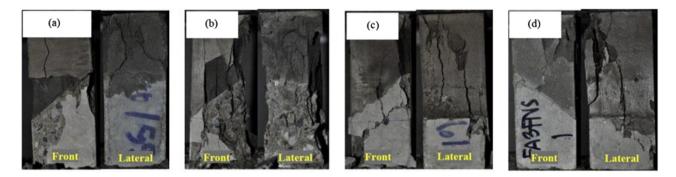
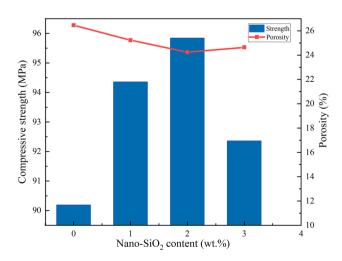


Figure 16: Failure of formation of specimens at 28 days [41]. (a) Control, (b) S1, (c) S2, and (d) S3.

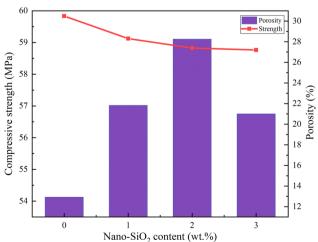
point of view, with an increase in the content of nano-SiO<sub>2</sub> within a certain range, the dynamic elastic modulus of the concrete gradually decreases and chloride permeability is gradually reduced. The reason for this is that nano-SiO<sub>2</sub> can promote the hydration reaction in cement, and the micro filling effect of the gel material increases the hydration gel content in the corresponding hydration stage. This improves the ductility of concrete; however, it makes the structure of the concrete denser and reduces its permeability. Guo et al. [97] studied the effect of nano-SiO<sub>2</sub> and nano-y-Al<sub>2</sub>O<sub>3</sub> on the durability of geopolymers. The results showed that the dry shrinkage performance of the geopolymer improved, and the improvement due to nano-SiO2 was greater than due to nanoy-Al<sub>2</sub>O<sub>3</sub>. In addition, Guo et al. [97] further confirmed using SEM and BET that nano-SiO<sub>2</sub> enhanced the microstructure and pore structure of the geopolymer significantly, reducing the pore volume of the geopolymer, increasing the density of the architecture, and enhancing the durability of the geopolymer. The results of Gao [98] et al. showed that nano-SiO<sub>2</sub> doping of 1–3% could reduce the porosity of the geopolymer.

When the mass of fly ash and slag is 70/30, the porosity of 28 days decreases from 30.5 to 27.2%, and when the mass ratio is 30/70, the porosity decreases from 26.4 to 24.2%. Figures 17 and 18 show the relationship between compressive strength, nano-SiO<sub>2</sub> content, and permeable porosity of alkali-activated slag-fly ash geopolymers after 28 days of curing. It can be seen that compressive strength increases with decreasing porosity, porosity usually decreases with increasing nano-SiO<sub>2</sub> content, and anti-permeability increases with increasing nano-SiO<sub>2</sub> content in an appropriate range.

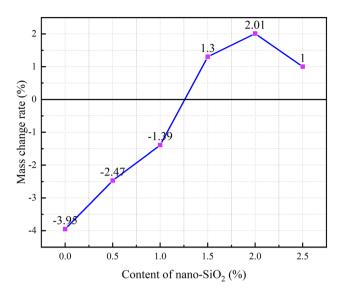
Certain scholars have reported that the optimal performance of geopolymer can be obtained for a proportion of nano-SiO<sub>2</sub> of 6% [41]. When nano-SiO<sub>2</sub> is not added, the geopolymer mortar cured at room temperature is less charged than that cured using thermal curing. This indicates that the increase in the number of crystal compounds in nano-SiO<sub>2</sub> modified geopolymer mortar reduces the diffusion coefficient of the mortar and thus improves its durability.



**Figure 17:** Relations between 28 days strength, porosity and nano-SiO<sub>2</sub> content (slag/fly ash = 70/30) [98].



**Figure 18:** Relations between 28 days strength, porosity and nano-SiO<sub>2</sub> content (slag/fly ash = 30/70) [98].

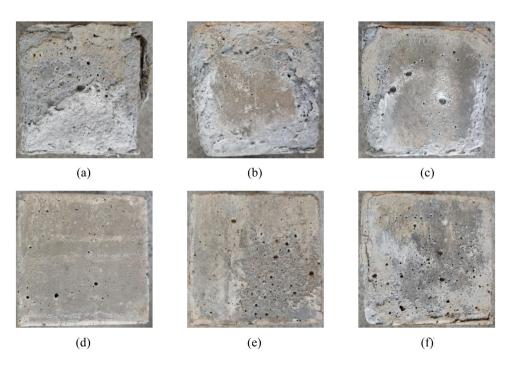


**Figure 19:** Effect of nano-SiO<sub>2</sub> content on resistance to sulfate erosion properties of geopolymer [99].

#### 3.7.2 Resistance to sulfate erosion

Geopolymer mortar is subjected to physical and chemical erosion in a sulfate environment. Physical erosion mainly refers to sodium sulfate invading the geopolymer when the dryness and humidity or concentration conditions are altered. This causes fatigue loss and damages the internal structure and mechanical properties of the geopolymer.

Chemical erosion mainly refers to the reaction of calcium in the geopolymer after sulfate has invaded the geopolymer. This produces gypsum and calcium alum stone causing the geopolymer to expand and disintegrate. If the geopolymer does not have good anti-permeability, ion exchange occurs after sulfate in harsh environments invades the geopolymer. Ion exchange decomposes the geopolymer matrix and produces crystals such as sodium silicate and silica on the surface of geopolymer materials. In addition, they result in a decline in the mechanical performance of materials. In the dry and wet cycle erosion tests on the sulfate, the change in the mortar specimen quality can reflect the degree of reaction and erosion of the mortar specimen. After the geopolymer mortar specimen without nano-SiO<sub>2</sub> underwent sulfate dry and wet cycle erosion, the surface fell off, resulting in a greater mass reduction of the specimen. After mixing with nano-SiO<sub>2</sub>, the mass of the geopolymer mortar specimen decreased relative to the geopolymer mixed with nano-SiO<sub>2</sub>, but the continued increase in the mixing amount of nano-SiO<sub>2</sub> causes the crystallization within the geopolymer to increase the specimen mass, as shown in Figure 19. Wang [99] observed that during the dry and wet cycles of sulfate erosion of the geopolymer, the geopolymer mortar specimen was exchanged with the sulfate solution. The unreacted alkali and sodium silicate in the mortar specimen dissolved into the solution, the sulfate solution eroded into the specimen and was repeatedly

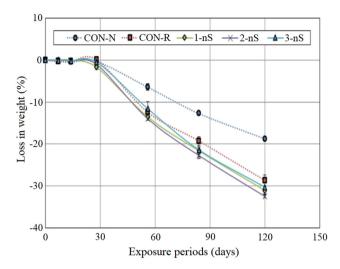


**Figure 20:** Form of geopolymer mortar destroyed by sulfate erosion in different content of nano-SiO<sub>2</sub> [99]. (a) NS-0.0, (b) NS-0.5, (c) NS-1.0, (d) NS-1.5, (e) NS-2.0, and (f) NS-2.5.

crystallized during the dry and wet cycles, filling the pores inside the specimen, resulting in an increase in the specimen mass. However, there is also some proportion of mortar in the sulfate during the dry and wet cycle erosion; the surface structure becomes loose and falls off, resulting in the reduction of the specimen mass.

The apparent damage to geopolymer mortar mixed with nano-SiO<sub>2</sub> was reduced relative to the geopolymer specimens not mixed with nano-SiO<sub>2</sub>, and the specific pattern of damage pattern is shown in Figure 20. In Figure 20, NS-0.5 indicates the content of nano-SiO<sub>2</sub> in the geopolymer is 0.5%. The geopolymer mortar specimen not mixed with nano-SiO<sub>2</sub> was seriously damaged, the surface material over a large area fell off, and the internal structure became loose due to erosion, resulting in more sulfate crystallization residue. The intermediate areas of the geopolymer mortar specimens with 0.5% and 1.0% were intact, with the edges and corners severely eroded, showing a loose structure and serious failure of form. The geopolymer mortar specimens with a nano-SiO<sub>2</sub> content of 1.5% were completely intact, with minimal damage to the edges and corners, and the overall degree of erosion was minimal, indicating that the test block structure had excellent corrosion resistance. The surface layer of geopolymer mortar specimens with nano-SiO<sub>2</sub> content of 2.5% falls off slightly, but its internal structure is loose and has more pores than geopolymer mortar specimens with nano-SiO<sub>2</sub> content of 1.5 and 2.0% [99]. It can also be observed from the difference in apparent damage of forms that different amounts of nano-SiO<sub>2</sub> can affect the sulfate erosion resistance of geopolymer to varying degrees and reduce the apparent damage of geopolymer mortar.

Nano-SiO<sub>2</sub> can enhance the sulfate corrosion resistance of the geopolymer mortar, not that of geopolymer concrete. Scholars [100] who studied recycled aggregate high-calcium fly ash geopolymer concrete (RAGC) mixed with nano-SiO<sub>2</sub> found no obvious difference in the sulfate resistance of RAGC mixed with nano-SiO2. After adding nano-SiO<sub>2</sub> to the geopolymer, the permeability of RAGC decreased, but the sulfate attack was more serious. Figure 21 shows the impact of nano-SiO<sub>2</sub> on weight loss, due to sulfuric acid corrosion, in geopolymer concretes. Figure 22 shows the specimen of the geopolymer concrete sample after immersion in 3% sulfuric acid for 120 days. In Figures 21 and 22, 1-nS indicates the content of nano-SiO<sub>2</sub> in the geopolymer is 1%; CON-N indicates the geopolymer with natural aggregate and without nano-SiO<sub>2</sub>; CON-R indicates the geopolymer with recycled aggregate and without nano-SiO<sub>2</sub>. From Figure 21, it can be found that the weight loss of RAGC mixed with nano-SiO<sub>2</sub> was higher than that of RAGC without added nano-SiO<sub>2</sub>.



**Figure 21:** Effect of nano-SiO<sub>2</sub> on the weight loss of geopolymer concretes due to sulfuric acid assault [100].

This may be because the unreacted nano-SiO<sub>2</sub> particles fill the large pores, reducing the available space for the expansion due to the reaction, leading to increased additional stress. Therefore, the deterioration rate increases, causing the concrete to collapse [100]. Therefore, the weight loss curve of CON-N is quite different from the curves of the other groups.

#### 3.7.3 Freezing-thawing resistance

The freezing-thawing resistance of the geopolymer can be determined by the loss rate of the compressive strength of the geopolymer. Research shows that, with an increase in the content of nano-SiO<sub>2</sub>, the freezing-thawing resistance of the geopolymer is gradually strengthened at first and then declines. After mixing with nano-SiO<sub>2</sub>, the geopolymer became dense, the pore size inside the material decreased, and the number of pores decreased, which reduced the damage to the internal structure during the freezing-thawing cycle. Wang [99] tested the geopolymer mortar mixed with nano-SiO<sub>2</sub> and found that the compressive strength and loss rate of the compressive strength of the geopolymer was as shown in Figure 23. As shown in the graph, with the increase in nano-SiO<sub>2</sub>, the loss rate of the compressive strength of the geopolymer first decreased and then increased. When the nano-SiO<sub>2</sub> content was 1.5%, the loss rate reached a minimum. This shows that the freezing-thawing resistance of the geopolymer gradually strengthened initially and then gradually declined. This is because adding a spot of nano-SiO<sub>2</sub> can improve the density of the geopolymer mortar, reducing the internal holes in the mortar, and decreasing the water absorption rate. This causes less damage during the freezing-thawing



Figure 22: Geopolymer concrete specimens after 120 days immersion in 3% sulfuric acid [100].

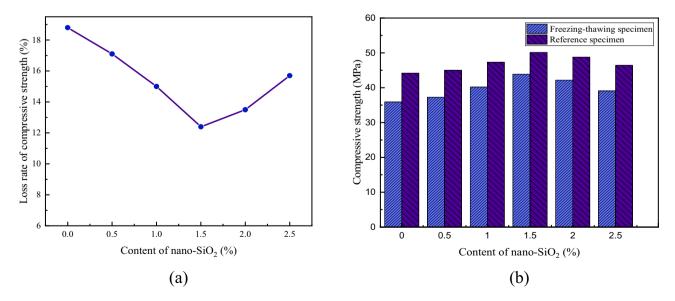
cycle. However, when the amount of nano-SiO<sub>2</sub> added during the preparation of geopolymer mortar was higher, water absorption reunion may have occurred in nano-SiO<sub>2</sub> dioxide, resulting in an incomplete mortar reaction, caused due to nano-SiO<sub>2</sub> reunion inside. This leads to the easy structural damage of the geopolymer mortar during the freezing-thawing cycle, and the freezing-thawing resistance decreased.

# **4** Application prospect

The rapid change in China's energy usage has resulted in massive consumption of coal, minerals, and other resources, resulting in a large amount of solid waste ("solid waste") being generated, which is increasing year after year [101]. According to the data from the National Bureau of Statistics, the output of industrial solid waste in 2017 reached 3.315 billion tons, a year-on-year increase of 7.24%. These wastes

not only occupy a large number of land resources but are also highly polluting, which poses a great threat to both health and the environment [102–104]. Solid wastes such as fly ash, slag, and garbage incinerator fly ash or bottom ash have amorphous silicate aluminate properties and can be utilized as raw materials for geopolymer production [105–107]. The use of solid waste in the production of geopolymers can not only provide an economic and effective treatment of industrial solid waste but also recycle waste, which is conducive to the sustainable development of the economy and environment [108–110].

Nano-SiO<sub>2</sub> fly ash-based geopolymers can store and adsorb heavy metals and their compounds. The material itself has a unique three-dimensional network crystal structure, and its skeleton is composed of a ring molecular chain and forms a good airtight cage shape so that it can wrap heavy metal ions and toxic waste substances in the cage cavity, to achieve the environmental protection goal of making waste profitable. Therefore, it has good application prospects in materials, construction, and environmental protection [39,111].



**Figure 23:** Effect of nano-SiO<sub>2</sub> content on the freezing-thawing resistance of geopolymer [99]. (a) The loss rate of compressive strength and (b) compressive strength.

The results of this study show that nano-SiO<sub>2</sub> can effectively improve the performance of geopolymer concrete. Despite the good modification effect of nano-SiO<sub>2</sub>, its high cost greatly limits the development and application of nano-SiO<sub>2</sub> reinforced geopolymers. Therefore, it is imperative to optimize the production process of nano- $SiO_2$  to reduce the production cost of nano-SiO<sub>2</sub>, or to find low-cost materials that can replace nano-SiO<sub>2</sub>. Most of the current research on nano-SiO2 enhanced geopolymers is at an early stage of exploration, and few studies have focused on its value for engineering applications. Besides, the dynamic properties and the properties after elevated temperature are important for the safety of concrete structures. However, the results of this study focus on the static mechanical properties of geopolymer composites modified with nano-SiO<sub>2</sub>, and few studies involve the dynamic mechanical properties and the properties after elevated temperature. Therefore, more research on the dynamic properties and the properties after the elevated temperature is needed to advance the development of nano-SiO<sub>2</sub> enhanced geopolymers and their application value.

# **5** Conclusion

The influence of nano-SiO<sub>2</sub> on the geopolymerization mechanism, compressive strength, microstructure, tensile strength, setting time, shear bond strength, durability, and the application of nano-SiO<sub>2</sub> geopolymer are summarized. The conclusions are as follows:

- Nano-SiO<sub>2</sub> has amorphous properties and a high specific surface area and hence can accelerate geopolymerization reaction. Moreover, the surface of nano-SiO<sub>2</sub> has many unsaturated bonds and different hydroxyl bonds, which are in the active and high free-energy states, and they can accelerate the geopolymerization process of the fly ash-based geopolymer.
- Within a certain range, the compressive strength of the fly ash-based geopolymer showed an increasing trend and then decreased with an increase in the amount of nano-SiO<sub>2</sub> added. Although the addition of nano-SiO<sub>2</sub> to the geopolymer reduces the maximum tensile strength of the geopolymer, the addition of nano-SiO<sub>2</sub> to the geopolymer is still recommended. The production of residual stress can lessen the face destruction of the geopolymer preventing immediate collapse.
- The addition of an appropriate amount of nano-SiO<sub>2</sub> can make the microstructure of the fly ash-based geopolymer more compact, with fewer unreacted particles, and the resulting geopolymerization products fill the

voids, resulting in higher strength, higher density, and lower porosity of the fly ash-based geopolymer. However, excessive addition of nano-SiO<sub>2</sub> also leads to too many nanoparticles and a non-dense structure.

• The addition of nano-SiO<sub>2</sub> improved the shear bond strength of the geopolymer. The bonding performance of geopolymers with nano-SiO<sub>2</sub> was better than that of geopolymers without nano-SiO<sub>2</sub>. The addition of nano-SiO<sub>2</sub> can effectively improve the durability of fly ashbased geopolymers within a certain range.

The properties of fly ash-based geopolymers are related to their chemical composition, curing conditions, and environmental conditions. At a certain amount, nano-SiO<sub>2</sub> has an influence on the setting time, compressive strength, shear bond strength, microstructure, and durability of the fly ashbased geopolymer. This study provides a basis for understanding the effects of nano-SiO<sub>2</sub> on the mechanical properties and durability of fly ash-based geopolymers.

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