

Research and development of geopolymer concrete

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Abstract: Geopolymer concrete is a kind of green and environmental protection high performance building material, and its own material properties will directly affect its practical application effect and scope. The raw material of geopolymer concrete is an inorganic polymer formed by a series of reactions of some silica-alumina under the condition of alkali activator. The application of geopolymer concrete has great significance for directly reducing the emission of carbon dioxide in the atmosphere, the development of resources, and protecting the natural ecological environment. The material properties of geopolymer concrete mainly include basic mechanical properties and durability. In this paper, the current methods to enhance its mechanical properties, corrosion resistance, chloride ion penetration resistance, frost resistance are reviewed. The research shows that the basic mechanical properties of geopolymer concrete are better than that of ordinary Portland cement, and the mechanical properties and durability of geopolymer concrete can be greatly improved by adding different composite materials as long as the design is reasonable, so it is the best choice to replace ordinary Portland cement. Based on the analysis of current research and development results, some research suggestions are put forward in order to promote the development and application of geopolymer concrete.

Key word: *Geopolymer concrete ; Composite materials ; Mechanical properties ; The durable performance*

0、 Introduction

Concrete is an essential building material in modern engineering. In the past, people focused on improving the strength of concrete and extending the service life of its structure, but paid little attention to the impact on the environment. However, most of the ordinary concrete is ordinary Portland cement. In the production process of 1kg ordinary Portland cement, 0.66 ~ 0.82kg CO₂ will be emitted. In 2020, the annual output of cement is as high as 2.37 billion tons. In addition, the annual CO₂ emissions from the

cement industry account for 7% of the total global CO₂ emissions^[1]. Cement production is accompanied by a large number of NO_x, SO_x and dust particles and other harmful substances discharge. With the rapid development of modern economy and society, the global energy and environmental crisis is becoming more and more serious. It is necessary to reduce energy conservation and low-carbon emission reduction. Industrial and agricultural waste slag, slag and fly ash are used instead of cement to reduce cement consumption, protect the environment and improve the strength of concrete^[2].

Geopolymer is a new type of calcium-free aluminosilicate cementing material. The main method

of synthesizing geopolymer is to combine alkaline solution (NaOH solution, Na_2SiO_3 solution) with active aluminosilicate to form a new type of low-carbon cementitious material through geopolymerization reaction, which may become a partial substitute for Portland cement in construction [3]. The term Geopolymers was coined in 1970 by French engineer Professor Joseph Davidovits, who first discovered it [3]. Originally developed in Europe as an alternative to thermosetting polymers. In 1993, Professor Wastiel [3] et al. showed through a series of experiments that it was possible to generate reliable high-performance geopolymers through fly ash, a by-product of alkaline activation of coal combustion, which would then be gradually transferred to the construction industry. Metakaolin, steel slag, fly ash, silica fume and zeolite can all be used as raw materials for the development of geopolymers [4]. Construction waste dust can also be used as raw material for geopolymer concrete [5]. Compared with cement concrete, geopolymer concrete on mechanical properties, corrosion resistance, high temperature resistant (can be used in $1000 \sim 1200$ °C stable) stand out, also has the early high strength (4 h of ultimate strength of 70% ~ 80%), low shrinkage (only about 1/5 of the Portland cement), long life (predict its life can amount to thousands of years), and other superior performance [6-7]. Moreover, the raw material of geopolymer preparation is discarded industrial waste, which has low energy consumption and does not emit harmful gases (CO_2 , NO_x , SO_x) [8-10], which is in line with the sustainable development strategy of China. Compared with ordinary concrete, geopolymer also has some defects, such as slightly poor tensile resistance and weak carbonization resistance, so we still need to make further efforts. At present, the research on geopolymers in our country is still insufficient. The purpose of this paper is to collect and summarize some domestic and foreign scholars' research on the application properties of geopolymers.

1、 The mechanical properties of geopolymers

1.1 Add fiber to geopolymer to enhance mechanical properties

Although geopolymer has great advantages in high temperature resistance, fire resistance, low energy consumption and good compressive performance, it is not outstanding in bending and tensile performance. In order to improve this situation, different fibers are mixed into geopolymer for research. Amer Bhutta [8-9] et al. made steel fibers with length deformation, end deformation and linear deformation, and added these three different steel fibers at a volume fraction of 0.5% to study the influence of fiber geometry on high strength polymer concrete. The results showed that 28 days steel fiber polymer concrete flexural strength, splitting tensile properties and toughness has improved, and shows that the deformation of end fiber length on the bending and tensile performance than is superior to the deformation and the deformation of straight line fiber, and points out that the linear deformation of steel fiber polymer concrete enhancement effect is the worst. Li Zongjin [10] conducted a variety of short fiber doping experiments and concluded that PVA (poly-vinyl-alcohol) fibers had high stability in an alkaline environment, and PVA fibers had a good combination with geopolymer substrates. On the other hand, nano- SiO_2 has high specific surface area and high activity, which can accelerate the polymerization reaction of geopolymer. Highly active nano- SiO_2 particles react with NaOH and Al_2O_3 in geopolymer to form sodium aluminosilicate gel, which can further enhance the compactness of geopolymer mortar [11]. Zhang Peng [12-15] et al. explored the influence of nano- SiO_2 and PVA fiber on the fracture energy G_F , compressive performance, flexural resistance and elastic modulus of geopolymer mortar through the three-point bending test of beam with incision. Through research available: adding the right amount of nano - SiO_2 and PVA fiber can effectively improve the strength of the polymer mortar can fracture, when PVA fiber volume content of 0.8%, and when the quality of the nano - SiO_2 content reaches 1.5%, the polymer mortar and PVA fiber polymer composite mortar specimen compressive capacity, modulus of elasticity, flexural properties and fracture can achieve the optimal value.

Under the action of alkali activator prepared by sodium silicate and sodium hydroxide, Professor Kan Lili et al. [16] jointly prepared high ductile metakaolin - fly ash base polymer with fly ash as the main raw material and metakaolin as auxiliary material .By uniaxial tensile test, changing the temperature, metakaolin content and PVA fiber content, it was concluded that the influence degree of tensile property of high ductile metakaolin fly ash base polymerization specimen was curing temperature > Metakaolin content & gt; PVA fiber content.

Combined with the above mentioned domestic and foreign researchers, fiber can enhance the mechanical properties of geopolymer concrete, but few scholars have studied the concrete characterization after fiber is added to geopolymer concrete. At the same time, the types of fibers added are relatively small, which cannot clearly indicate the different characteristics of fiber addition. The addition of different types and different amounts of fibers may lead to the different setting rate of geopolymer concrete and the changing trend of its mechanical properties.

1.2 Nanoparticles are added to geopolymer to enhance mechanical properties

Adding certain nano-CaCO₃ particles to the cement base can promote the hydration reaction, effectively enhance the mechanical properties of the cement base and improve the pore microstructure [17-18]. Hasan Assaedi et al. [19] studied the influence of nano-CaCO₃ particles on the mechanical properties of geopolymer materials. Assaedi's team mixed nano-CaCO₃ with geopolymer mortar with different contents to study the composite material from three aspects: bending strength, compressive strength and impact strength. The final results show that nano-CaCO₃ particles can effectively enhance the mechanical strength of geopolymer. In addition, when nano-CaCO₃ particles with a mass fraction of 2% are added, a good interface and bonding force are formed between geopolymer and particles, and the dosage of nano-CaCO₃ particles cannot exceed 3%. Because of the high concentration of nanoparticles, the geopolymer matrix is prone to cluster. Abdulkadir serhan Cevik [20], such as by adding and not adding

SiO₂ nanoparticles of two kinds of low calcium fly ash (FAI and FAII) was prepared by four kinds of polymer concrete, and carries on the contrast experiment preparation of ordinary Portland cement concrete, concluded that low calcium content in the fly ash and adding nano SiO₂ in polymer concrete has better mechanical performance. Moumita Maiti made quantitative geopolymer concrete by mixing titanium oxide (TiO₂) nanoparticles with different particle sizes into industrial waste (fly ash) and adding alkali activator, and proved that the compressive and tensile properties of the composite material were significantly improved [21].

Combined with the above studies, it is found that a single nano-particle can enhance the mechanical properties of geopolymer concrete, but there are few experimental studies on the addition of two or more kinds of nano-particles into geopolymer concrete. At the same time, when the nanomaterials are added to the concrete for mixing, the phenomenon of agglomeration is obvious. How to make the nanoparticles evenly distributed in the concrete is the only way for every scholar.

1.3 Inert silicate in activated geopolymers

Because the base activator of geopolymer is synthesized by sodium hydroxide and sodium silicate, there will be some silicate after its forming, and the existence of some inert silicate will inevitably lead to the internal structure is not dense enough, the activation of inert silicate in geopolymer concrete can enhance the internal stability. There are many materials to synthesize geopolymer, among which mine tailings can also synthesize geopolymer, but mine tailings-geopolymer concrete has much lower compressive strength compared with ordinary geopolymer concrete [22]. There is a large amount of quartz in mine tailings, and the presence of quartz in the geopolymer will hinder the polymerization reaction of its geopolymer [23]. However, many researchers have broken the structure of quartz through different chemical solutions to promote the polymerization of geopolymer, but it consumes a lot of energy, and does not conform to the concept of green energy saving of geopolymer. Qian Wan et al. [24] used ball milling to strengthen its microstructure,

and the compressive strength increased by 67%. In addition, they studied the influence of mechanical living fossil on the polymer at different times.

Combined with the above studies, it seems that the inert silicate in activated geopolymer is still in the preliminary stage, and the use of a large number of chemicals is certainly not consistent with the green development we advocate. However, we can start from curing, construction process or study of different raw materials to solve the inert silicate in geopolymer concrete.

2、 Durability of geopolymers

2.1 Corrosion resistance of geopolymer composites

According to the mechanics theory of composite materials, composite materials can retain the characteristics of the original component materials and make the properties of each component complement and relate with each other through material design, so as to obtain new superior properties^[25]. Because ordinary Portland cement is alkaline, its cement mortar and acid easy to contact so it is difficult to resist the chemical attack of acid and sulfate. Ariffin et al.^[26] prepared geopolymer concrete by mixing fly ash and palm oil fly ash with alkaline activator, took ordinary Portland cement concrete as control concrete, and put the two groups of concrete specimens in 2% sulfuric acid solution for 18 months. By studying the quality, microstructure, compressive strength and degradation products of the two groups of specimens, it is concluded that the durability of geopolymer concrete is obviously better than that of ordinary concrete in the concentration of 2% sulfuric acid solution. Abdulkadir serhan Cevik etc.^[20] in order to study in geopolymer concrete mixing nanoparticles mechanics performance under acid condition, using the add and not adding SiO₂ nanoparticles two kinds of low calcium fly ash (FAI and FAII) was prepared by four kinds of geopolymer concrete, and carries on the contrast experiment preparation of ordinary Portland cement concrete, the four types of polymer and the ordinary Portland cement concrete applying concentration of 5%, 5% and 3.5% respectively (H₂SO₄) sulfate, magnesium

sulfate (MgSO₄) and water (NaCl) solution. The experimental results show that geopolymer concrete mixed with nano-SiO₂ particles has better durability in chemical environment and nano-SiO₂ can prolong the structure life. Suleman Afridi^[27] et al added SAP (superabsorbent polymer) into geopolymer mortar, then soaked the specimen in HCl solution with a concentration of 5% for 24 hours, and soaked the specimen in solution with a concentration of 5% Na₂SO₄ and 5% CaCl₂ for 180 days. Finally, it was shown that SAP particles could enhance the chemical durability of geopolymer concrete. SAP particles can refine the porosity and reduce the porosity, thus improving the durability of concrete. In addition, SAP particles have certain feasibility in controlling freeze-thaw resistance, crack self-healing, chloride ion migration and oxygen permeability^[28-29].

Combined with the above studies, the addition of composite materials can effectively improve the corrosion resistance of geo-polymer concrete, but generally through filling the internal environment to improve its performance, should be able to study its corrosion resistance under different environments, different factors, and then can be carried out a systematic in-depth study.

2.2 Chloride ion penetration resistance of geopolymer composites

The influence of chloride ion (Cl⁻) on the durability of concrete is mainly reflected in that it will destroy the passivation film on the surface of steel bar after invading concrete, and then lead to corrosion of steel bar. The migration mechanism of chloride ion in concrete mainly includes diffusion, capillarity and penetration^[30]. Chloride ion has 2 kinds of existence form in concrete, namely free state and solidified state (physical adsorption and chemical combination 2 kinds), if solidified more, then free less. And concrete chloride ion permeability resistance and free chloride ion is closely related, that is, the less free, the better its permeability resistance. There are four main methods to detect the chloride ion permeability resistance of concrete, namely, rapid chloride ion migration coefficient method (RCM method), electric flux method, rapid chloride ion diffusion coefficient detection method (NEL method) and

natural diffusion method .Stephen A Alabi et al. [31] used rapid migration test (RMT) to measure the chloride ion permeability of concrete mixed with different amounts of geopolymer (FA and RHA) when it partially replaced ordinary Portland cement (OPC), indicating that the performance of geopolymer mixed with recycled concrete is better. Douglas et al. [32] tested the total electric flux of the slag geopolymer using Na_2SiO_3 , NaOH and Na_2CO_3 as activators and tested its pore structure by mercury injection method. It was found that when Na_2SiO_3 was used as activator, its electric flux was much higher than that using NaOH and Na_2CO_3 as activators, but its porosity was smaller and its pore structure was more complete. Zhang Junzhi et al. [33] discussed the variation of free chloride ion concentration in fly ash concrete under natural tidal range environment, and found that the peak concentration of free chloride ion in concrete increased with the increase of exposure time, and the peak concentration of chloride ion decreased with the increase of fly ash content during the same exposure time. The effect of fly ash on chloride ion concentration in concrete is smaller in the early exposure period and larger in the late exposure period. In general, the thickness of the convection zone eroded by chloride ion is not affected by exposure time and fly ash content, and is stable at about 4mm. Shaikh et al. [34] pointed out that the chloride ion permeability resistance of geopolymer concrete increases with the increase of alkali content and the ratio of Na_2SiO_3 to NaOH in alkali activator (2.5-3.5). Some researchers believe that geopolymer concrete can improve its resistance to chloride penetration by fixing chloride ions and reducing free chloride ions [35-37]. Shi [38] found that pore network is the primary factor affecting chloride ion transport, followed by porosity and pore solution. For example, the Na^+ and OH^- concentrations in the hole solution of alkali-excited slag are high, and the high Na^+ concentration reduces the Cl^- concentration, which also reduces the electric flux of its solution. Yang Yongmin [39] found that the porosity of geopolymer concrete was lower than that of Portland cement concrete, and it had good resistance to chloride ion permeability.

Combined with the above studies, geopolymer concrete has better performance of chloride ion permeability resistance than ordinary Portland cement concrete. However, there is no uniform conclusion on the anti-chloride penetration ability of geopolymer concrete with different raw materials, different activator components or alkali concentration conditions, and different researchers pay different attention to different emphases and use different evaluation methods. Therefore, further research should be conducted.

2.3 Freezing resistance of geopolymer concrete

Different researchers have drawn different conclusions on the antifreeze properties of alkali - excited geopolymer. Brooks et al. believed that geopolymer has dense structure and strong freeze-thaw damage resistance [40]. Fu et al. [41] found that after 300 freeze-thaw cycles, the elastic modulus loss and mass loss of slag powder ground polymer concrete are 12% and 6% less than those of ordinary concrete, respectively, indicating that its freeze-thaw resistance is better than that of ordinary concrete. This is because the compact structure with low Ca/Si ratio makes it difficult for water to penetrate. According to Duxson's research, geopolymer prepared with metakaolin as raw material requires more water, has more porosity, and has reduced frost resistance [42]. Xu Yan [43] concluded that geopolymer concrete had poorer frost resistance than Portland cement concrete, and the mixed slag and air entraining agent could better improve the frost resistance of geopolymer concrete.

In conclusion, the frost resistance of geopolymer concrete is generally better than that of ordinary Portland cement concrete. But at the same time, adding different materials can also promote the improvement of its frost resistance. However, there are still few researches on the antifreeze performance under different environments and under no factors, and further researches are still needed.

3、 Conclusion and Prospect

In this paper, the mechanical properties,

corrosion resistance, chloride penetration resistance and frost resistance of reinforced geopolymer concrete are summarized. Some properties of geopolymer concrete mentioned above are controversial due to the different testing methods, but most properties are better than Portland cement concrete. As long as the design of geopolymer concrete is reasonable and the construction technology is accurate, geopolymer concrete may replace Portland cement in engineering application.

In China, the research on geopolymer concrete is still in the initial stage, so the content and results of the research are relatively few, different raw material components have certain differences, its performance also has a big difference, but if it wants to be widely applied, there is still a lot of research. For the current study, there are the following recommendations:

(1) At present, the construction technology, mix ratio, mechanical properties and durability evaluation index of geo-polymer concrete are all borrowed from the specification of cement concrete or imitating foreign research methods, which should be further studied to improve its theoretical system.

(2) Although there are a wide range of materials for the production of geo-polymer concrete, most scholars focus on slag and fly ash geo-polymer concrete, while there are few studies on the use of construction dust and other materials as raw materials for the production of geo-polymer concrete, which should be strengthened and further studied.

(3) There is no clear conclusion on the research of alkali activator, and the research on the production, ratio, concentration and construction sequence of alkali activator is not thorough enough.

(4) After adding some composite materials into geopolymer concrete, it should not only study its performance, but also conduct in-depth research on its setting time, forming process and its microscopic characterization.

(5) At present, most of the research on geopolymer concrete is in a single environment, and the mechanical properties and durability properties under a single factor variable are studied. There are few studies on the properties under the combined action of multiple environments and multiple factors, which should be further studied.

(6) Compared with the research on the material properties of geopolymer concrete, the research on reinforced geopolymer concrete and other structures of geopolymer concrete is less, and the research on its specific practical application is also less. It is necessary to carry on the thorough study of its various structures, and combine with the ordinary cement concrete to analyze and study its seismic performance.

(7) The interface bond of geopolymer concrete can be studied, such as the grip with steel bars and the bond performance of ordinary Portland cement concrete research and analysis, so as to speed up its application.

(8) At present, the strength research of geo-aggregated concrete is mostly medium and high strength concrete, and the research on ultra-high strength geo-aggregated concrete is relatively few. Therefore, it is necessary to conduct in-depth research on high strength and ultra-high strength concrete.

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