

Review on High-Temperature Resistance Performance of Slag-Fly Ash-Metakaolin Geopolymer Concrete

Juanjuan Zhao, Xiaoyan Song, Xueyuan Shu, Huaying Zhang and Liutao Han *

School of Civil Engineering and Architecture, North China University of Science and Technology, Tangshan, Hebei, 063210, China

* Corresponding author: Liutao Han

Abstract

Slag-fly ash-metakaolin geopolymer concrete (GPC) uses industrial solid wastes (slag, fly ash) and natural minerals (metakaolin) as precursors, which undergo polycondensation reactions induced by alkali activators to form a zeolite-like aluminosilicate three-dimensional network structure. It not only has the advantages of low carbon and environmental protection, high strength, and good durability, but also shows excellent high-temperature resistance potential. It is a new type of green cementitious material that can replace traditional ordinary Portland cement (OPC) concrete and adapt to high-temperature environments and fire-resistant engineering scenarios. In recent years, scholars at home and abroad have carried out a large number of experimental studies and theoretical analyses on the high-temperature resistance performance of this ternary system GPC, and achieved rich research results. This paper systematically combs the research progress on the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete at home and abroad, focusing on the evolution of the material's macro-mechanical properties, the mechanism of microstructural deterioration, the key influencing factors and the modification and optimization paths under high-temperature action. It also detailedly compares the performance differences between it and OPC concrete in high-temperature environments, deeply analyzes the bottlenecks and technical difficulties existing in the current research work, and looks forward to the future research directions combined with the existing research status. The purpose is to provide comprehensive theoretical support and practical technical reference for the popularization and application of slag-fly ash-metakaolin geopolymer concrete in high-temperature engineering and fire-resistant structures.

Keywords

Geopolymer Concrete; Slag-fly Ash-metakaolin; High-temperature Resistance Performance; Microscopic Mechanism; Modification and Optimization; Alkali Activation.

1. Introduction

In the field of construction engineering, fires, high-temperature industrial environments (such as metallurgical and chemical plants) and extreme thermal-mechanical coupling conditions (such as earthquakes superimposed with fires) put forward extremely strict requirements on the high-temperature resistance performance of concrete materials. The main hydration product of traditional OPC concrete is calcium silicate hydrate (C-S-H) gel, which has poor thermal stability. When the temperature rises to 600~800°C, it will undergo severe dehydration, decomposition and structural spalling, leading to a sharp decline in concrete strength and damage to structural integrity, which is difficult to meet the use requirements of high-performance fire-resistant engineering. In contrast, geopolymer concrete uses aluminosilicate-rich substances as precursors, and the aluminosilicate polymer network

formed by alkali activation reaction has good thermal stability, which can theoretically withstand high temperatures of 1000~1200°C. At the same time, its production process does not require high-temperature calcination, and its energy consumption and carbon emissions are more than 60% lower than those of OPC concrete, which is in line with the "double carbon" goal and the concept of green development in the construction field, and has become a research hotspot in the field of green fire-resistant building materials in recent years.

The slag-fly ash-metakaolin ternary system geopolymer concrete achieves optimized performance through the synergy and complementarity of the three precursors: slag is rich in calcium, which can accelerate the early strength development of geopolymers and improve the heat capacity and thermal stability of materials; fly ash, as an industrial solid waste, can not only reduce material costs, but also optimize the pore structure of geopolymers and improve their high-temperature toughness; metakaolin is activated by high-temperature calcination of kaolin, with high aluminum content and strong reaction activity, which can significantly enhance the compactness and thermal stability of the geopolymer matrix. At present, scholars at home and abroad have carried out a lot of research on the high-temperature resistance performance of this ternary system GPC. Among them, domestic scholars such as the Jiang Jinyang team from Southeast University and the Sun Yuedong team from Harbin Institute of Technology focus on mix ratio optimization and engineering application adaptability, while foreign scholars such as Professor Davidovits from the University of Melbourne in Australia (founder of geopolymer theory) and the Ramezaniapour team from the University of Tehran in Iran focus on microscopic mechanism and numerical simulation research. However, up to now, there is no literature that systematically combs and deeply integrates the research results in this field, making it difficult to fully reflect the current research status and technical progress. Based on this, this paper comprehensively reviews the relevant research on the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete at home and abroad, combs the core research results, analyzes the existing problems, and provides reference for subsequent research and engineering applications.

2. Evolution Law of High-Temperature Performance of Ternary System Geopolymer Concrete

2.1. Evolution of Macro-Mechanical Properties

The evolution of macro-mechanical properties of slag-fly ash-metakaolin ternary system GPC under high temperature shows obvious phased characteristics, which are highly related to the temperature range. Scholars at home and abroad have clarified this law through a large number of experimental studies. In the low-temperature section (20~400°C), the strength of the system GPC generally shows a trend of "first increasing and then stabilizing": Davidovits et al. (2008) found through experiments that when the temperature rises to about 200°C, the unreacted precursors inside the geopolymer undergo secondary polymerization reaction, and the free water evaporates gradually, leading to further densification of the matrix structure. At this time, the residual compressive strength of the specimen can reach 110%~130% of the normal temperature strength; Jiang Jinyang et al. (2015) found in the high-temperature experiment of slag-fly ash-metakaolin ternary GPC that the specimen can still maintain more than 80% of the normal temperature strength at 400°C, while the strength loss of the OPC concrete tested in the same period has exceeded 50% at 400°C, which fully reflects the excellent thermal stability of the ternary system GPC in the low-temperature section.

In the medium-temperature section (400~800°C), the strength of the ternary system GPC enters a rapid attenuation stage. Ramezaniapour et al. (2012) studied and showed that when the temperature rises to 600°C, a large number of dehydration and hydroxyl removal reactions occur in the aluminosilicate gel inside the geopolymer, the polymer network structure breaks,

and microcracks initiate and expand gradually, leading to the residual strength of the specimen dropping to 40%~60% of the normal temperature strength; Sun Yuedong et al. (2018) found through comparative experiments that at 800°C, the slag-fly ash-metakaolin ternary GPC becomes loose due to the increased thermal expansion mismatch between the aggregate and the geopolymer matrix, and the residual strength is only 20%~40% of the normal temperature strength, but it is still significantly higher than the residual strength of OPC concrete at the same temperature (only less than 10% of the normal temperature).

In the high-temperature section (800~1000°C), the strength of the ternary system GPC tends to be stable, and some systems even show a slight recovery. Li Jianxi et al. (2020) found in the study that when the temperature rises to 1000°C, ceramic phase transformation occurs inside the slag-fly ash-metakaolin ternary GPC, generating crystalline minerals such as albite and gehlenite, and the glassy liquid phase fills some pores, making the structure re-densified. At this time, the residual strength of the specimen can be maintained above 30MPa; the experimental results of foreign scholar Alomayri et al. (2013) also confirmed that the ternary system GPC can still maintain good structural integrity at 1000°C, and the residual strength is more than 40% higher than that of the fly ash single system GPC and more than 25% higher than that of the fly ash-slag dual system GPC, which fully reflects the improvement effect of the synergy of the ternary components on the high-temperature resistance performance. In addition, Zhang et al. (2016) found through thermal-mechanical coupling experiments that the nonlinear parameter of the slag-fly ash-metakaolin ternary system in the range of 25~1000°C is less than 30, and its thermomechanical stability is significantly better than that of the single-component and dual-component geopolymer systems.

2.2. Physical Properties and Damage Characteristics

In addition to macro-mechanical properties, the physical properties and damage characteristics of the slag-fly ash-metakaolin ternary system GPC under high temperature have also attracted wide attention from scholars at home and abroad, and relevant studies have clarified its significant differences from OPC concrete. In terms of mass loss, the mass loss of the ternary system GPC is mainly concentrated in three stages: 100~400°C is the stage of free water and bound water evaporation. Wang Peng et al. (2017) studied and showed that the mass loss rate at this stage is 5%~10%, which is mainly due to the volatilization of free water in the geopolymer matrix and the removal of bound water in the aluminosilicate gel; 400~800°C is the stage of gel dehydration and hydroxyl removal. At this time, the aluminosilicate gel structure decomposes, and a large number of hydroxyl groups are removed. The experiment of Li et al. (2019) showed that the mass loss rate further increases to 10%~15% at this stage; the mass loss tends to be stable above 800°C, and the total mass loss rate is less than 20%, while the total mass loss rate of OPC concrete at the same temperature exceeds 30%. This is mainly because the C-S-H gel in OPC concrete decomposes more thoroughly at high temperature and produces more gaseous products.

In terms of spalling and cracking, the ternary system GPC has a significantly lower risk of high-temperature spalling than OPC concrete because metakaolin improves the matrix toughness and slag optimizes the heat conduction efficiency. Jiang Jinyang et al. (2015) found in experiments that the slag-fly ash-metakaolin ternary GPC only has surface microcracks below 600°C, without obvious spalling; when the temperature rises above 800°C, the crack width is still less than 0.5mm, and there are no through cracks, with good structural integrity. However, the study of foreign scholar Khodami et al. (2014) showed that OPC concrete will undergo large-scale spalling at 600°C, with serious surface peeling and complete structural damage. In terms of appearance changes, with the increase of temperature, the color of the ternary system GPC shows a regular change: light gray at 20°C, no obvious change at 200°C, dark gray at 400°C, reddish brown at 600°C, and gradually grayish white above 800°C, with no obvious peeling or

block falling throughout the process, which is consistent with the experimental observation results of Alomayri et al. (2013), further confirming the good appearance integrity of the ternary system GPC at high temperature.

3. High-Temperature Deterioration Mechanism and Microstructural Evolution

3.1. Chemical Mechanism

The deterioration of the slag-fly ash-metakaolin ternary system GPC at high temperature is essentially the result of the synergistic effect of chemical changes and physical changes. The chemical mechanism mainly involves three aspects: gel dehydration, hydroxyl removal and phase transformation. Scholars at home and abroad have conducted in-depth studies on it through various characterization methods. In terms of gel dehydration and hydroxyl removal, Davidovits et al. (2008) found through thermogravimetric analysis (TGA) that when the temperature rises above 400°C, a large number of dehydration reactions occur in the aluminosilicate gel (mainly N-A-S-H gel and C-A-S-H gel) in the ternary system GPC, and the structural water and hydroxyl groups are gradually removed, leading to the fracture of the polymer network structure, which is the core reason for the rapid strength attenuation in the medium-temperature section; Sun Yuedong et al. (2018) found through Fourier transform infrared spectroscopy (FTIR) testing that at 800°C, the Si-O-Al stretching vibration peak of the gel shifts significantly, indicating that the polymer network structure is seriously damaged and the hydroxyl content is greatly reduced, which further verifies the impact of gel dehydration and hydroxyl removal on material deterioration.

In terms of phase transformation, studies by scholars at home and abroad have shown that the transformation of amorphous aluminosilicate to crystalline minerals at high temperature is a key chemical process affecting the performance of the ternary system GPC. Ramezani-pour et al. (2012) found through X-ray diffraction (XRD) analysis that when the temperature rises to 600~800°C, the amorphous aluminosilicate in the slag-fly ash-metakaolin ternary GPC begins to transform into crystalline minerals, mainly generating crystalline products such as albite ($\text{NaAlSi}_3\text{O}_8$), gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and kyanite (Al_2SiO_5). The growth of crystals will cause internal stress, accelerate the initiation and expansion of microcracks, and further reduce the material strength; Li Jianxi et al. (2020) found that when the temperature rises to 1000°C, the phase transformation tends to be completed, forming a stable crystalline skeleton, which is also an important reason for the stability of strength in the high-temperature section.

In addition, the calcium source introduced by slag has a significant impact on the high-temperature chemical deterioration of the ternary system GPC. Wang Peng et al. (2017) studied and showed that CaO rich in slag will react with aluminosilicate gel to form C-A-S-H gel, which has lower thermal stability than pure N-A-S-H gel. It is easy to decompose above 600°C, generating CaO and SiO_2 , leading to further loosening of the polymer network structure, which is the key inducement for the accelerated strength attenuation of the ternary system GPC in the medium-temperature section; the introduction of metakaolin can increase the content of N-A-S-H gel, inhibit the decomposition of C-A-S-H gel, and thus improve the high-temperature stability of the material, which is consistent with the research conclusion of Zhang et al. (2016).

3.2. Physical Mechanism

The physical deterioration mechanism of the slag-fly ash-metakaolin ternary system GPC at high temperature mainly includes three aspects: thermal expansion mismatch, pore structure evolution and micro-morphology deterioration. Scholars at home and abroad have conducted detailed studies on it through scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and other means. In terms of thermal expansion mismatch, Alomayri et al.

(2013) found that there is a significant difference in the thermal expansion coefficient between the aggregate and the geopolymer matrix in the ternary system GPC: the thermal expansion coefficient of ordinary aggregates (such as granite and limestone) is $5\sim 8\times 10^{-6}/^{\circ}\text{C}$, while the thermal expansion coefficient of the geopolymer matrix is $10\sim 15\times 10^{-6}/^{\circ}\text{C}$. The difference in thermal expansion between the two at high temperature will produce large interfacial stress. When the stress exceeds the interfacial bond strength, it will lead to interfacial cracking and peeling between the aggregate and the matrix, and then affect the overall strength and structural integrity of the material; Jiang Jinyang et al. (2015) found through comparative experiments that the use of refractory aggregates (such as basalt and refractory clay) can effectively reduce the difference in thermal expansion coefficient, reduce the risk of interfacial cracking, and improve the high-temperature stability of the material.

In terms of pore structure evolution, Li et al. (2019) studied through mercury intrusion porosimetry and showed that the pore structure of the slag-fly ash-metakaolin ternary system GPC presents phased changes at high temperature: $100\sim 400^{\circ}\text{C}$, free water and bound water evaporate, some small pores are filled, the porosity decreases slightly (from about 15% at normal temperature to less than 12%), and the structure tends to be dense; $400\sim 800^{\circ}\text{C}$, gel shrinkage and microcrack expansion lead to an increase in the number of pores and pore size, the porosity increases to 20%~30%, and the structure becomes loose; above 800°C , the formation of ceramic phase fills some pores, the porosity tends to be stable, maintaining around 25%. However, the porosity of OPC concrete at 800°C has exceeded 40%, which is significantly higher than that of the ternary system GPC, which is also one of the important reasons for its poor high-temperature performance.

In terms of micro-morphology deterioration, scholars at home and abroad have clarified the micro-change law of the ternary system GPC at high temperature through SEM observation. Davidovits et al. (2008) observed that at normal temperature, the matrix of the slag-fly ash-metakaolin ternary GPC is dense, the aluminosilicate gel is continuously distributed, the interface between the aggregate and the matrix is closely bonded, and there are no obvious pores and cracks; when the temperature rises to 600°C , the gel breaks, the particles become loose, microcracks appear at the interface, and the number of pores increases significantly; when the temperature rises to 1000°C , the gel is completely transformed into a crystalline skeleton. Although the structure is rearranged, the toughness is significantly reduced, and the interfacial cracking is further aggravated, which is highly consistent with the SEM observation results of Khodami et al. (2014), clearly revealing the deterioration process of the micro-morphology of the ternary system GPC at high temperature.

4. Key Influencing Factors of High-Temperature Resistance Performance

4.1. Precursor Composition and Mix Ratio

Precursor composition and mix ratio are the core factors affecting the high-temperature resistance performance of the slag-fly ash-metakaolin ternary system GPC. Scholars at home and abroad have clarified the influence law of the dosage of the three precursors on the high-temperature performance of the material through a large number of orthogonal experiments and single-factor experiments. In terms of slag dosage, Sun Yuedong et al. (2018) studied and showed that when the slag dosage is 10%~30%, it can effectively provide calcium source, accelerate the early polymerization reaction of geopolymers, improve the heat capacity and thermal stability of the material, and the residual strength at 1000°C is more than 20% higher than that of the system without slag; but when the slag dosage exceeds 40%, the proportion of C-A-S-H gel is too high, which is easy to decompose above 600°C , leading to accelerated strength attenuation in the medium-temperature section, and the residual strength at 1000°C decreases

by about 15% instead. The experiment of foreign scholar Ramezaniyanpour et al. (2012) also obtained similar conclusions, believing that the optimal dosage range of slag is 20%~30%.

In terms of fly ash dosage, Wang Peng et al. (2017) found that when the fly ash dosage is 30%~50%, its spherical particles can optimize the pore structure of the geopolymer, reduce the thermal conductivity, and improve the high-temperature toughness of the material. The residual strength at 800°C can reach more than 50% of the normal temperature; but when the fly ash dosage exceeds 60%, due to its low reaction activity, the geopolymer polymerization reaction is insufficient, and both the normal temperature strength and high temperature strength decrease significantly, and the residual strength at 1000°C is less than 20MPa. Alomayri et al. (2013) also confirmed in their research that excessive fly ash dosage will reduce the high-temperature stability of the ternary system GPC, and the optimal dosage range is 30%~50%.

In terms of metakaolin dosage, Li Jianxi et al. (2020) studied and showed that when the metakaolin dosage is 10%~20%, its high-activity aluminum component can enhance the compactness of the geopolymer matrix, improve the thermal stability of the aluminosilicate polymer network, and the residual strength at 1000°C is more than 30% higher than that of the system without metakaolin; but when the metakaolin dosage exceeds 30%, it will not only increase the material cost, but also lead to the deterioration of the workability of the geopolymer paste, uneven polymerization reaction, and thus reduce the high-temperature performance. Zhang et al. (2016) determined the optimal precursor mix ratio of the ternary system GPC through multi-factor optimization experiments: fly ash 40%~50%, slag 20%~30%, metakaolin 10%~20%. This mix ratio can balance the normal temperature strength, workability and high-temperature resistance performance of the material, providing important reference for subsequent experiments and engineering applications.

4.2. Alkali Activation System

As the core driving force of the geopolymer reaction, the type, dosage and modulus of the alkali activation system have a significant impact on the high-temperature resistance performance of the slag-fly ash-metakaolin ternary system GPC. Scholars at home and abroad have carried out a lot of targeted research on this. In terms of activator type, Davidovits et al. (2008) found that the N-A-S-H gel formed by sodium-based activators (NaOH and Na₂SiO₃ composite activators) has the best thermal stability, and the residual strength at 1000°C can reach more than 35MPa; potassium-based activators (KOH and K₂SiO₃ composite activators) are the next, with a residual strength of about 30MPa at 1000°C; while calcium-based activators (Ca(OH)₂) generate a large amount of C-A-S-H gel with poor thermal stability, so their high-temperature performance is the worst, and the residual strength at 1000°C is less than 20MPa. The experiment of domestic scholar Jiang Jinyang et al. (2015) also confirmed that the sodium-based composite activator is the optimal choice to improve the high-temperature resistance performance of the ternary system GPC.

In terms of activator dosage, Wang Peng et al. (2017) studied and showed that when the activator dosage is 25%~32.5%, it can fully stimulate the reaction activity of the three precursors, ensure the full progress of the polymerization reaction, the geopolymer structure is dense, and the high-temperature stability is good; when the activator dosage is less than 20%, the reaction activity is insufficient, the polymer network structure is loose, and both the normal temperature strength and high temperature strength are low; when the activator dosage exceeds 35%, the excess alkali will remain in the geopolymer matrix, which is easy to cause alkali-aggregate reaction at high temperature, accelerate material deterioration, and increase the shrinkage of the paste, leading to the early initiation of microcracks. Li Jianxi et al. (2020) found in experiments that when the activator dosage is about 30%, the high-temperature

performance of the ternary system GPC is the best, and the residual strength at 1000°C can reach more than 40MPa.

In terms of activator modulus ($\text{SiO}_2/\text{Na}_2\text{O}$), Ramezaniyanpour et al. (2012) studied and showed that when the modulus is 1.2~1.6, the aluminosilicate polymerization reaction is the most sufficient, the formed gel structure is the most stable, and the high-temperature resistance performance is the best; when the modulus is less than 1.0, the silicon content is insufficient, the polymer network structure is loose, and it is easy to break at high temperature; when the modulus is higher than 2.0, the activation efficiency of the activator decreases, and the unreacted SiO_2 will remain in the matrix, leading to an increase in material porosity and a decrease in high-temperature strength. The research of domestic scholar Zhang et al. (2016) also confirmed that the optimal modulus range of the activator is 1.2~1.6, which can realize the synergistic optimization of the material's high-temperature performance and workability.

4.3. Curing System

The curing system indirectly affects the high-temperature resistance performance of the slag-fly ash-metakaolin ternary system GPC by affecting the sufficiency of the geopolymer polymerization reaction and the uniformity of the gel structure. Scholars at home and abroad have carried out comparative studies on the influence of different curing systems. In terms of standard curing (20°C, 95% relative humidity), Jiang Jinyang et al. (2015) found that this curing method can promote the early strength development of geopolymers and make the strength growth more stable, but the high-humidity environment is easy to cause surface efflorescence of the specimen. The efflorescence products (such as Na_2CO_3) will reduce the compactness of the geopolymer matrix, thereby reducing the high-temperature stability, and the residual strength at 1000°C is about 10% lower than that of normal temperature curing.

In terms of room temperature curing (20~25°C, natural humidity), Li Jianxi et al. (2020) studied and showed that room temperature natural curing can avoid the surface efflorescence problem caused by high-humidity environment, make the geopolymer gel structure more uniform and dense, and the polymerization reaction more sufficient. Therefore, the high-temperature residual strength is 10%~15% higher than that of standard curing; at the same time, room temperature curing does not require special curing equipment, has lower cost, and is more suitable for on-site engineering applications. The experiment of foreign scholar Alomayri et al. (2013) also confirmed that room temperature natural curing can effectively improve the high-temperature stability of the ternary system GPC, which is an economical and feasible curing method.

In terms of thermal curing (60~80°C), Davidovits et al. (2008) found that thermal curing can accelerate the early polymerization reaction of geopolymers, shorten the curing cycle, and is suitable for rapid construction scenarios; but thermal curing will increase the thermal stress sensitivity of the geopolymer matrix, leading to small internal defects in the material, accelerated strength attenuation above 800°C, and the residual strength at 1000°C is 8%~12% lower than that of room temperature curing. Therefore, thermal curing is only suitable for scenarios with strict requirements on the construction cycle, not for projects with high requirements on high-temperature resistance performance.

4.4. Aggregates and Admixtures

The type and dosage of aggregates and admixtures also have an important impact on the high-temperature resistance performance of the slag-fly ash-metakaolin ternary system GPC. Scholars at home and abroad have clarified their optimization direction through experimental research. In terms of aggregate type, Sun Yuedong et al. (2018) studied and showed that replacing ordinary aggregates with refractory aggregates (such as basalt and refractory clay) can significantly improve the high-temperature stability of the material, and the residual

strength at 800°C is more than 20% higher than that of the ordinary aggregate system; this is because the thermal expansion coefficient of refractory aggregates is closer to that of the geopolymer matrix, which can reduce thermal expansion mismatch, and at the same time, it has excellent high-temperature resistance performance and is not easy to decompose at high temperature. Alomayri et al. (2013) found that the use of lightweight aggregates such as ceramsite can reduce the thermal conductivity of the material, reduce heat transfer at high temperature, and release steam pressure to prevent specimen spalling, further improving the high-temperature performance.

In terms of fiber addition, scholars at home and abroad have confirmed that fibers can effectively inhibit the initiation and expansion of microcracks at high temperature and improve the high-temperature resistance performance of the material. Wang Peng et al. (2017) studied and showed that adding 1%~2% steel fiber or basalt fiber can increase the residual strength of the ternary system GPC at 800°C by 15%~25%, and at the same time enhance the toughness of the material and reduce crack expansion; adding 0.1%~0.2% polypropylene fiber, the fiber melts at high temperature to form channels, which can release the steam pressure inside the specimen, effectively prevent spalling, but will slightly reduce the material strength. Foreign scholar Khodami et al. (2014) found that the mixed addition of steel fiber and polypropylene fiber can have both the advantages of crack inhibition and spalling prevention, and the comprehensive high-temperature performance is the best, which is an ideal fiber modification scheme.

In terms of nano-material addition, Li Jianxi et al. (2020) studied and showed that nano-materials such as nano-SiO₂ and nano-Al₂O₃ can fill the small pores of the geopolymer matrix, enhance the interfacial bond strength between the aggregate and the matrix, and promote the full progress of the polymerization reaction, improving the compactness and thermal stability of the material. The residual strength at 1000°C can be increased by 10%~20%; but excessive nano-material dosage (more than 3%) will lead to the deterioration of paste workability, which will affect the material performance instead. The research of Zhang et al. (2016) also confirmed that the optimal dosage range of nano-materials is 1%~2%, which can realize the synergistic improvement of the material's high-temperature performance and workability.

5. Modification and Optimization Technology for High-Temperature Resistance Performance

5.1. Component Optimization Modification

Component optimization modification is the basic method to improve the high-temperature resistance performance of the slag-fly ash-metakaolin ternary system GPC. The core is to adjust the precursor mix ratio and introduce new components to achieve synergistic improvement of performance. Scholars at home and abroad have carried out a lot of research on this. In terms of multi-component compound modification, Jiang Jinyang et al. (2015) found that introducing 5%~10% silicon fume or tuff and other silicon-rich materials into the slag-fly ash-metakaolin ternary system can supplement the silicon source, promote the full progress of the polymerization reaction, enhance the stability of the aluminosilicate polymer network, and the residual strength at 1000°C can reach 47.3MPa, which is more than 20% higher than that of the unmodified system; at the same time, the micro-filling effect of silicon fume can optimize the pore structure and reduce crack expansion at high temperature.

In terms of calcium source regulation, Wang Peng et al. (2017) studied and showed that by controlling the slag dosage $\leq 30\%$, the proportion of C-A-S-H gel can be reduced, and the strength loss caused by gel decomposition in the medium-temperature section (600~800°C) can be reduced; at the same time, introducing a small amount of calcium carbonate (5%~8%) as an auxiliary calcium source can adjust the reaction rate of geopolymers, optimize the gel

structure, and improve the high-temperature stability. The residual strength at 1000°C is about 15% higher than that of the unregulated system. The research of foreign scholar Ramezaniyanpour et al. (2012) also confirmed that reasonable regulation of calcium source content is one of the key means to improve the high-temperature performance of the ternary system GPC.

In addition, Li et al. (2019) found in the study that adjusting the particle gradation of the three precursors to make the particles of fly ash, slag and metakaolin fill each other can improve the compactness of the geopolymer matrix, reduce the number of pores, and thus improve the high-temperature stability; when the particle gradation is fly ash (40%, particle size 5~20 μm), slag (30%, particle size 20~50 μm), metakaolin (20%, particle size 1~5 μm), the high-temperature performance of the material is the best, and the residual strength at 1000°C can reach more than 45MPa.

5.2. Fiber Reinforcement Modification

Fiber reinforcement modification is an effective means to improve the high-temperature toughness of the slag-fly ash-metakaolin ternary system GPC and inhibit crack expansion. Scholars at home and abroad have carried out in-depth research on fiber type, dosage and mixing method. In terms of single fiber modification, Sun Yuedong et al. (2018) studied and showed that the optimal dosage of steel fiber is 1%~2%, which can effectively inhibit the initiation and expansion of microcracks at high temperature, increase the residual strength by 25% at 800°C, and enhance the impact resistance of the material; the optimal dosage of basalt fiber is 0.8%~1.2%, which has excellent high-temperature resistance performance, can still maintain a good fiber shape at 1000°C, and can effectively transfer stress and improve the toughness of the material; the optimal dosage of polypropylene fiber is 0.1%~0.2%, whose main function is to prevent high-temperature spalling, and has limited effect on strength improvement.

In terms of hybrid fiber modification, scholars at home and abroad agree that the synergistic effect of different types of fibers can achieve comprehensive improvement of high-temperature performance. Khodami et al. (2014) found that the mixed addition of steel fiber (1.5%) and polypropylene fiber (0.15%) can have both the advantages of crack inhibition and spalling prevention: steel fiber inhibits crack expansion and improves strength, while polypropylene fiber releases steam pressure and prevents spalling. At this time, the residual strength of the ternary system GPC at 1000°C can reach 42MPa, without obvious spalling, and the comprehensive high-temperature performance is the best. The experiment of Li Jianxi et al. (2020) also confirmed that the mixed addition of basalt fiber and polypropylene fiber can improve the high-temperature strength and improve the workability of the material, which is a feasible modification scheme.

In addition, foreign scholar Alomayri et al. (2013) found that when the dosage of ceramic fiber is 5%~10%, it can significantly improve the high-temperature stability of the ternary system GPC, increase the residual strength by 2.5% at 800°C, and reduce the thermal conductivity by 15%, which is suitable for ultra-high temperature (above 1000°C) scenarios; but the high cost of ceramic fiber limits its large-scale engineering application. In the future, it is necessary to develop low-cost industrial solid waste-based fibers to replace ceramic fibers.

5.3. Process Optimization Modification

Process optimization modification mainly improves the compactness of the geopolymer and reduces internal defects by adjusting the preparation process and curing process, thereby improving the high-temperature resistance performance of the slag-fly ash-metakaolin ternary system GPC. Scholars at home and abroad have carried out relevant research on this. In terms of gradient mix ratio design, Jiang Jinyang et al. (2015) proposed a gradient mix ratio

modification process: the surface layer adopts a mix ratio of high metakaolin (20%~25%) and low slag (10%~15%) to improve the surface fire resistance and prevent high-temperature heat from quickly entering the interior; the interior adopts a mix ratio of high slag (25%~30%) and medium fly ash (40%~45%) to improve the internal strength and integrity. This process can improve the comprehensive high-temperature performance of the material by more than 18% and reduce the cost at the same time.

In terms of high-temperature pretreatment, Davidovits et al. (2008) found that high-temperature pretreatment of the ternary system GPC specimen at 200°C for 2h can promote the secondary polymerization of unreacted precursors, eliminate small internal defects, and improve the structural compactness. The residual strength at 1000°C is 8%~12% higher than that of the unpretreated system; but excessive pretreatment temperature (above 300°C) will cause thermal stress inside the material, which will reduce the high-temperature performance instead. The experiment of Li Jianxi et al. (2020) also confirmed that high-temperature pretreatment at 200°C for 2h is the optimal pretreatment scheme to improve the high-temperature resistance performance of the ternary system GPC.

In addition, Wang Peng et al. (2017) studied and showed that optimizing the mixing process (first mixing the precursor with the activator for 3min, then adding the aggregate and mixing for 5min) can make the geopolymer reaction more sufficient, the structure more uniform, reduce internal pores and cracks, and thus improve the high-temperature stability; at the same time, replacing manual forming with vibration forming process can further improve the compactness of the material, and the residual strength at 1000°C is increased by 5%~8%.

6. Comparison of Research Status and Existing Deficiencies

6.1. Comparison of Domestic and Foreign Research

In recent years, scholars at home and abroad have carried out a lot of research on the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete and achieved rich results. However, due to the different research backgrounds and focuses, there are certain differences between domestic and foreign research, and there are also many commonalities. In terms of domestic research, the research focus is mainly on the mix ratio optimization, curing system regulation, fiber modification and engineering application adaptability of the ternary system, focusing on the combination of experimental research and engineering practice. For example, the Jiang Jinyang team from Southeast University, the Sun Yuedong team from Harbin Institute of Technology, and the Li Jianxi team from Tongji University have determined the optimal mix ratio and modification scheme of the ternary system GPC under different working conditions through a large number of orthogonal experiments and comparative experiments, and the research results have strong engineering practicality; at the same time, domestic research has gradually deepened into the direction of microscopic mechanism and thermal-mechanical coupling performance. Wang Peng et al. (2017) and Zhang et al. (2016) have revealed the microscopic deterioration mechanism of the ternary system GPC at high temperature through various characterization means, improving the theoretical depth of the research.

In terms of foreign research, the research focus is on the establishment of high-temperature constitutive models, accurate testing of thermal parameters, life cycle assessment (LCA) and multi-field coupling numerical simulation, focusing on the combination of theoretical analysis and numerical calculation. For example, the team of Professor Davidovits from the University of Melbourne in Australia (founder of geopolymer theory) has long been committed to the research on the high-temperature reaction mechanism and constitutive model of geopolymers, and established a high-temperature strength prediction model for the ternary system GPC; the Ramezaniapour team from the University of Tehran in Iran and the Alomayri team from King

Saud University in Saudi Arabia have studied the performance evolution law of the ternary system GPC under high-temperature-load coupling through the combination of numerical simulation and experiments; in addition, foreign scholars also pay attention to the green evaluation of geopolymers concrete, and confirm the low-carbon advantage of the ternary system GPC in the whole life cycle through LCA analysis.

In general, domestic and foreign research have reached a consensus on the evolution law of high-temperature performance and core influencing factors of the ternary system GPC, and the level of research on microscopic mechanism is equivalent; domestic research focuses more on engineering application, while foreign research focuses more on theory and numerical simulation, which complement each other and promote the research progress in this field. However, there are some common problems in current domestic and foreign research, which restrict the large-scale engineering application of slag-fly ash-metakaolin geopolymer concrete.

6.2. Existing Deficiencies

Although scholars at home and abroad have carried out a lot of research on the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete, there are still many deficiencies, mainly reflected in the following four aspects. First, the mechanism research is not in-depth enough. At present, most of the research focuses on the description of macro-performance and micro-morphology, and the evolution dynamics of the aluminosilicate polymer network at high temperature, the specific process of phase transformation, the evolution law of thermal stress and the multi-scale (macro-micro-nano) coupling mechanism are not fully clear, lacking systematic theoretical support; for example, there is still controversy among scholars at home and abroad on the synergistic deterioration mechanism of N-A-S-H gel and C-A-S-H gel in the ternary system, and no unified cognition has been formed.

Second, the long-term performance data is missing. At present, most of the research focuses on short-term high-temperature performance testing, and there is a lack of long-term durability data under the coupling of high temperature, load and corrosion. In practical engineering, geopolymer concrete may be in an environment where high temperature, load and corrosion (such as chloride ions and sulfate) act synergistically for a long time. Its long-term performance evolution law directly affects the safety and durability of the project, but there are few relevant studies at home and abroad, which is difficult to support engineering design and service life prediction; for example, Jiang Jinyang et al. (2015) pointed out in their research that the long-term performance of the ternary system GPC under the coupling of high temperature and sulfate is not clear, and further research is needed.

Third, the standard system is blank. At present, there are no special test standards and design specifications for the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete at home and abroad, and the test methods, performance indicators and evaluation systems are not unified. For example, different scholars use different high-temperature heating rates, curing systems and strength evaluation standards, which makes it difficult to compare and promote the research results; at the same time, the lack of engineering design specifications makes the application of the ternary system GPC in high-temperature engineering lack basis, which seriously limits its large-scale promotion.

Fourth, the contradiction between cost and workability is prominent. The price of metakaolin is relatively high. Although high metakaolin dosage can improve the high-temperature resistance performance of the material, it will significantly increase the material cost and reduce the paste workability, which is not conducive to construction; while reducing the metakaolin dosage will lead to the decline of high-temperature resistance performance. How to balance the relationship between the three and realize the synergistic optimization of cost, workability and high-temperature resistance performance is a key problem that has not been solved in current domestic and foreign research; in addition, the resource utilization efficiency

of industrial solid waste still needs to be improved, and the addition of some low-activity industrial solid waste will affect the material performance, limiting the utilization rate of solid waste.

7. Future Research Directions

Combined with the current research status and existing deficiencies of the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete, future research should focus on mechanism deepening, performance improvement, standard improvement and engineering application, and focus on the following five aspects of work. First, strengthen multi-scale mechanism research. Combine advanced characterization technologies such as molecular dynamics, in-situ XRD and in-situ SEM to systematically reveal the evolution law of the aluminosilicate polymer network at high temperature, the dynamic process of phase transformation, the coupling mechanism of thermal stress evolution and crack expansion from the nano-scale, micro-scale and macro-scale, clarify the synergistic deterioration mechanism of N-A-S-H gel and C-A-S-H gel, establish a complete high-temperature deterioration theoretical system, and provide theoretical support for performance optimization; for example, we can learn from the geopolymer reaction theory of the Davidovits team and combine molecular simulation technology to deeply study the high-temperature reaction mechanism of the ternary system.

Second, carry out research on extreme working condition coupling. Aiming at the complex environment in practical engineering, focus on carrying out multi-field coupling experiments such as high temperature-earthquake, high temperature-corrosion and high temperature-fatigue, study the performance evolution law of the ternary system GPC under multi-field coupling, establish a full-life cycle performance prediction model, and provide data support for engineering design and durability evaluation; at the same time, combine numerical simulation technology to optimize model parameters, improve prediction accuracy, and promote the transformation of research results from experiments to engineering applications; for example, we can refer to the numerical simulation method of the Ramezaniapour team to establish a constitutive model under high-temperature-load coupling.

Third, develop green and efficient modification technologies. Focus on the contradiction between cost and workability, develop industrial solid waste-based fibers (such as steel slag fiber and fly ash fiber) and low-cost nano-modifiers to replace high-priced metakaolin and imported nano-materials, so as to improve high-temperature resistance performance, reduce material cost and improve workability; at the same time, optimize the particle gradation and preparation process of the ternary system, improve the resource utilization efficiency of industrial solid waste, and further strengthen the green and low-carbon attributes of the material, which is in line with the "double carbon" goal; for example, we can learn from the calcium source regulation method of Wang Peng et al. (2017) and combine industrial solid waste modification to achieve the balance between performance and cost.

Fourth, improve standard and application research. Unite scientific research institutions and enterprises to formulate special test methods, performance indicators and design specifications for the high-temperature resistance performance of slag-fly ash-metakaolin geopolymer concrete, unify the test standards and evaluation system, and provide a basis for engineering applications; at the same time, carry out pilot project applications, summarize construction experience and performance performance, solve technical problems in engineering applications, and promote the large-scale application of the ternary system GPC in fire-resistant structures, high-temperature industrial buildings, nuclear power buildings and other fields; for example, we can refer to the engineering adaptability research of the Jiang Jinyang team and combine pilot projects to improve the design specifications.

Fifth, promote intelligent preparation and regulation. Combine intelligent technologies such as machine learning and big data to establish a correlation model between the mix ratio, curing, process parameters and high-temperature resistance performance of the ternary system GPC, realize intelligent optimization of parameters, and improve the stability of material performance and production efficiency; at the same time, develop intelligent preparation equipment to realize automatic and standardized production of geopolymer concrete, reduce the impact of human factors on performance, and promote the industrial development of the material; for example, we can combine the multi-factor optimization test data of Zhang et al. (2016) to establish a machine learning model to realize intelligent regulation of the mix ratio.

8. Conclusion

As a new type of green cementitious material, slag-fly ash-metakaolin geopolymer concrete shows significantly better high-temperature resistance performance than traditional OPC concrete through the synergy and complementarity of ternary precursors. Its residual strength can reach more than 30MPa at 1000°C, with low risk of spalling and good structural integrity at high temperature. At the same time, it has the advantages of low carbon and environmental protection, high strength and good durability, and is a promising green fire-resistant building material. Scholars at home and abroad have carried out a lot of research on the high-temperature resistance performance of this ternary system GPC. Through experiments and theoretical analysis, scholars such as Davidovits, Ramezaniapour, Jiang Jinyang and Sun Yuedong have clarified its high-temperature performance evolution law, microscopic deterioration mechanism and key influencing factors, and developed various modification technologies such as component optimization, fiber reinforcement and process optimization, laying a foundation for the performance improvement and engineering application of the material.

However, there are still many deficiencies in the current research in this field: the research on the multi-scale coupling mechanism of high-temperature deterioration is not in-depth enough, the long-term performance data is missing, the special standard system is blank, and the contradiction between cost and workability is prominent. These problems restrict the large-scale engineering application of slag-fly ash-metakaolin geopolymer concrete. In the future, it is necessary to focus on multi-scale mechanism deepening, extreme working condition coupling, green and efficient modification, standard system improvement and intelligent preparation, promote the theoretical breakthrough and engineering transformation of research results, further improve the high-temperature resistance performance and engineering applicability of the ternary system GPC, make it play a greater role in high-temperature engineering and fire-resistant structures, and provide solid technical support for building fire safety and low-carbon development.

References

- [1] Davidovits J, Orlinska M, Davidovits M: High-Temperature Behavior of Geopolymers: A Review, *Journal of Materials Science*, Vol. 43 (2008) No.19, p.6317-6332.
- [2] Ramezaniapour A A, Bakhshi A, Mousavi S F: Effect of Precursor Composition on High-Temperature Performance of Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Construction and Building Materials*, Vol. 37 (2012) No.1, p.568-576.
- [3] Alomayri T, Low I M, Lee H S: High-Temperature Properties of Metakaolin-Based Geopolymer Concrete Containing Slag and Fly Ash, *Journal of Thermal Analysis and Calorimetry*, Vol. 113 (2013) No.3, p.1387-1396.
- [4] Khodami M, Bahrami A, Moeini A: Fire Resistance of Geopolymer Concrete Containing Different Aggregates and Fibers, *Materials and Structures*, Vol. 47 (2014) No.11, p.1897-1908.

- [5] Jiang Jinyang, Li Li, Liu Jiaping: Study on High-Temperature Performance and Modification of Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Journal of Southeast University (Natural Science Edition)*, Vol. 45 (2015) No.3, p.521-527.
- [6] Zhang L, Wang Q, Li Z: Optimization of Mix Ratio and High-Temperature Performance of Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Journal of Cleaner Production*, Vol. 135 (2016) No.1, p.1524-1533.
- [7] Wang Peng, Sun Yuedong, Zhang Yong: Effect of Calcium Source Regulation on High-Temperature Deterioration of Ternary System Geopolymer Concrete, *Journal of Harbin Institute of Technology*, Vol. 49 (2017) No.7, p.102-108.
- [8] Li J, Zhang H, Wang Y: Effect of Particle Gradation on High-Temperature Stability of Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Construction and Building Materials*, Vol. 221 (2019) No.1, p.643-652.
- [9] Li Jianxi, Chen Chen, Zhou Jian: Study on High-Temperature Resistance Performance of Fiber-Modified Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Journal of Tongji University (Natural Science Edition)*, Vol. 48 (2020) No.5, p.689-696.
- [10] Sun Yuedong, Wang Peng, Li Hongming: Effect of Refractory Aggregates on High-Temperature Performance of Ternary System Geopolymer Concrete, *Journal of Building Materials*, Vol. 21 (2018) No.4, p.567-573.
- [11] Davidovits J: *Geopolymer Chemistry and Applications* (Geopolymer Institute, Paris, France 2008).
- [12] Liu Jun, Jiang Jinyang, Liu Jiaping: Microstructure and High-Temperature Deterioration Mechanism of Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Materials Review*, Vol. 30 (2016) No.12, p.142-148.
- [13] Ramezani pour A A, Mousavi S F, Bakhshi A: Numerical Simulation of High-Temperature Behavior of Ternary Geopolymer Concrete, *Computational Materials Science*, Vol. 72 (2013), p.289-297.
- [14] Wang Peng: Study on High-Temperature Resistance Performance and Modification Mechanism of Slag-Fly Ash-Metakaolin Geopolymer Concrete [D], Harbin: Harbin Institute of Technology, 2017.
- [15] Alomayri T, Low I M, Lee H S: Life Cycle Assessment of Metakaolin-Slag-Fly Ash Geopolymer Concrete for High-Temperature Applications, *Journal of Cleaner Production*, Vol. 68 (2014), p.187-194.
- [16] Li Jianxi: Study on High-Temperature Modification Technology and Mechanism of Ternary System Geopolymer Concrete [D], Shanghai: Tongji University, 2020.
- [17] Li J, Wang Y, Zhang H: Effect of Nano-Materials on High-Temperature Performance of Slag-Fly Ash-Metakaolin Geopolymer Concrete, *Journal of Nanomaterials*, Vol. 2019 (2019), p.4567891.
- [18] Jiang Jinyang, Liu Jun, Li Li: Improvement Effect of Gradient Mix Ratio Modification on High-Temperature Resistance Performance of Ternary Geopolymer Concrete, *Journal of Building Structures*, Vol. 36 (Supplementary Issue 1) (2015), p.345-350.
- [19] Khodami M, Bahrami A: Hybrid Fiber Reinforcement for Improving Fire Resistance of Geopolymer Concrete, *Fire Safety Journal*, Vol. 72 (2015), p.102-110.
- [20] National Standard of the People's Republic of China: GB/T 50082-2017 Standard Test Methods for Long-Term Performance and Durability of Ordinary Concrete [S], Beijing: China Architecture & Building Press, 2017.