Review Article

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Review on the research progress of cement-based and geopolymer materials modified by graphene and graphene oxide

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Abstract: In recent years, with the higher requirements for the performance of cement-based materials and the call for energy conservation and environmental protection, a wave of research on new materials has set off, and various high-performance concrete and more environmentally friendly geopolymers have appeared in the public. With a view to solving the defects of energy consumption, environmental protection and low toughness of traditional cement-based materials. At the same time, nanomaterials have become a focus of current research. Therefore, the research on the properties of cement-based materials and geopolymers modified by graphene and its derivatives has aroused extensive interest of researchers. Graphene-based nanomaterials are one of them. Because of their large specific surface area, excellent physical properties have been favored by many researchers. This paper reviews the research progress of graphene-based nanomaterials in improving the properties of cement-based materials and geopolymer materials, and points out the main challenges and development prospects of such materials in the construction field in the future.

Keywords: graphene; cement-based materials; geopolymer; graphene oxide; development prospects

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1 Introduction

With the rapid development of the global construction industry, the number of new buildings in various countries has grown rapidly. As a result, concrete has become the largest and most widely used civil engineering material [1]. It requires a lot of ordinary Portland cement (OPC) when make concrete. The production of OPC not only consumes a lot of natural resources, such as limestone and fossil fuel, but also produces 0.8 tons of CO_2 for each ton of cement clinker, which intensifies the greenhouse effect. In addition, cement consumes a lot of energy during the production process [45]. The environmental costs of cement production will be higher and higher with more and more strict restrictions on pollutant emissions. The continuously rising environmental costs have forced scientific research and industrial enterprises to invest in energy-saving and environmentally-friendly cement alternatives to cement.

At present, geopolymer is a more mature alternative to cement. The concept of geopolymer was first proposed by Joseph Davidovits [3] in 1978. It is based on metakaolin [4], slag [5], fly ash [6], silica fume [7], red mud [8] and other silicon aluminum materials. A new type of inorganic polymer material with special three-dimensional oxide network structure of inorganic polycondensation was obtained by proper processing and chemical reaction of these raw materials at low temperature. The geopolymer not only has better properties than polymer materials, ceramics, cement and metals, but also has the advantages of wide sources of raw materials, simple process, less energy consumption and less environmental pollution. It is a kind of environment-friendly material with sustainable devel-

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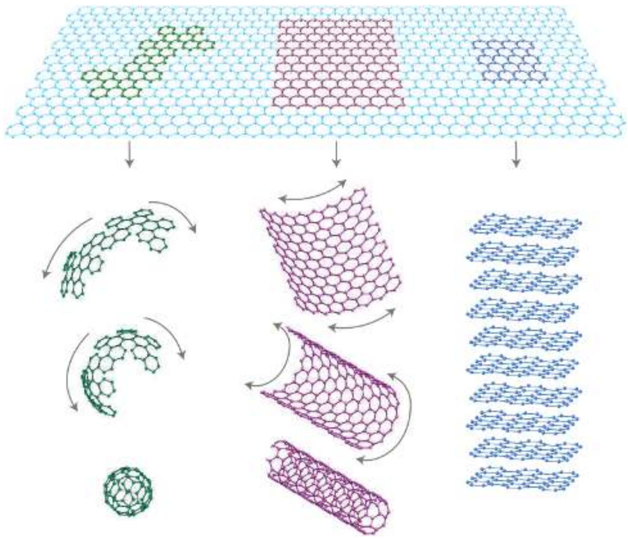

Figure 1: Different forms of graphene [12]

opment. Therefore, it is considered to be able to replace cement or as a supplement for cement materials in some fields [9]. In order to improve the defects of cement-based materials and geopolymer matrices, such as large brittleness, easy cracking, and poor impermeability, researchers attempt to introduce different modifiers to enhance the performance of cement-based materials and geopolymer matrices. Graphene is one of the representative modifiers.

Graphene is a flat single-layer carbon atom film tightly packed in a two-dimensional honeycomb lattice [10]. In 2004, British physicists Geim and Novoselov [11, 12] (Figure 1) successfully isolated graphene from graphite by mechanical peeling in experiments, thus confirming that it can exist alone. Its unexpected existence and excellent properties quickly triggered a wave of theoretical and applied research. Since then, graphene preparation methods have emerged endlessly. Graphene has been successfully prepared by epitaxial growth method [13], chemical vapor deposition (CVD) method [14], and graphite oxide reduction method [15, 16]. According to relevant research, graphene has excellent mechanical properties [17], Young's modulus of TPa level [18], optical properties [19], biological properties [20], electrical conductivity [21], thermal properties [22], catalytic properties [23] and ferromagnetism [24].

Graphene Oxide (GO) is one of the important derivatives of graphene. It is an intermediate product obtained during the preparation of graphene by redox method (product obtained after the oxidation process is completed). Its properties and microstructure are derived from primitive graphene is also commonly used in building materials. GO is the most studied graphene-based nanomaterial in cement composites [25] (Figure 2). At present, the common preparation methods of GO are Brodie method [26], Staudemnaier method [27] and Hummers method [28]. The structure of GO has introduced oxygen-containing functional groups on the basis of graphene by chemical method, so that its surface contains hydroxyl (-OH), epoxy (C-O-C), and carboxyl (-COOH) on the edges [29]. These hydrophilic groups make GO have good dispersibility in water and provide a large number of active sites for connecting other functional groups and organic molecules. The similar advantages of GO and graphene and it's more cost-effective [30] make it the most widely used and most representative graphene nanomaterial [31].

Researchers have made many advances in the application of nanomaterials including graphene. Nanotechnology has been widely used in the fields of biomedicine and environment [32]. Such as electrochemical carbon nanotube filters can be widely used in the field of water purification [33]; new biosensors for bio-nanotechnology can be used for early diagnosis and treatment of tumors [34]. Mohan *et al.* [35] gave a detailed review of the production, application, and product limitations of graphene-based materials and their composites. The environmental applications, toxicity and safety treatment schemes of graphene nanomaterials are summarized. It is pointed out that graphene and its composite materials with polymers, ceramics and metals have unique characteristics and significant advantages in different application fields. For example, the application of graphene pulverized by freeze grinding technology for graphene/chitosan nanocomposites can enhance the dispersibility, graphitization characteristics, and thermal stability of graphene powder, and tensile performance of the corresponding chitosan nanocomposite significantly improved [36]. Surudžić *et al.* [37] showed that synthetic polyvinyl alcohol/graphene (PVA/Gr) nanocomposites are good candidates for biomedical soft tissue implants and wound dressing. Jiao *et al.* [38] found that polymers made by grafting carboxymethyl cellulose (CMC) to GO could be used as drug carriers. Wan *et al.* [39] pointed out the potential of graphene and carbon-based nanomaterials as efficient adsorbents for oils and organic solvents. Yu *et al.* [40] and Park *et al.* [41] showed that graphene-based nanocomposites have great potential for improving photocatalytic efficiency. In addition, graphene can also be applied as a sensor element in miniaturized, biomedical sensor devices [42]. But at present, the use of graphene-based nanomaterials for the preparation of cement-based composites and geopolymer composites is also one of the main research directions of current researchers. Its unique lamellar structure and rich surface functions can effectively improve the mechanical

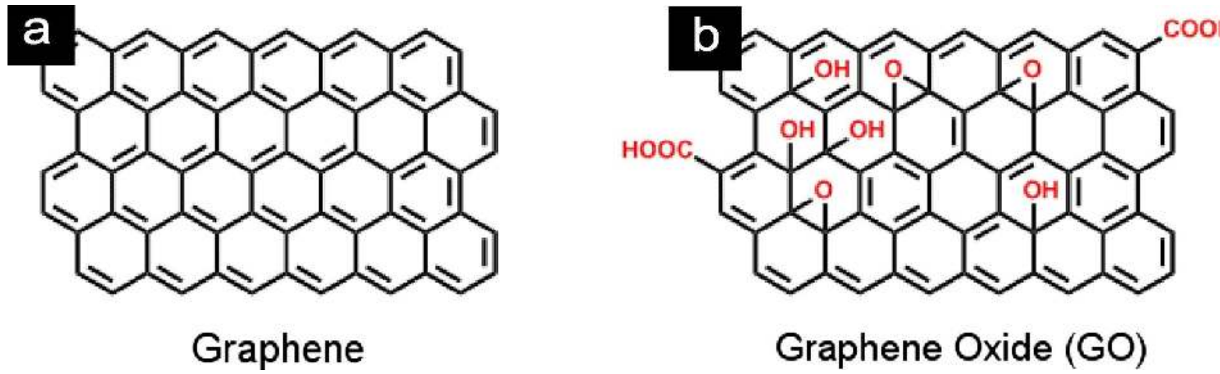

Figure 2: Representation of (a) graphene; (b) graphene oxide (GO) [25]

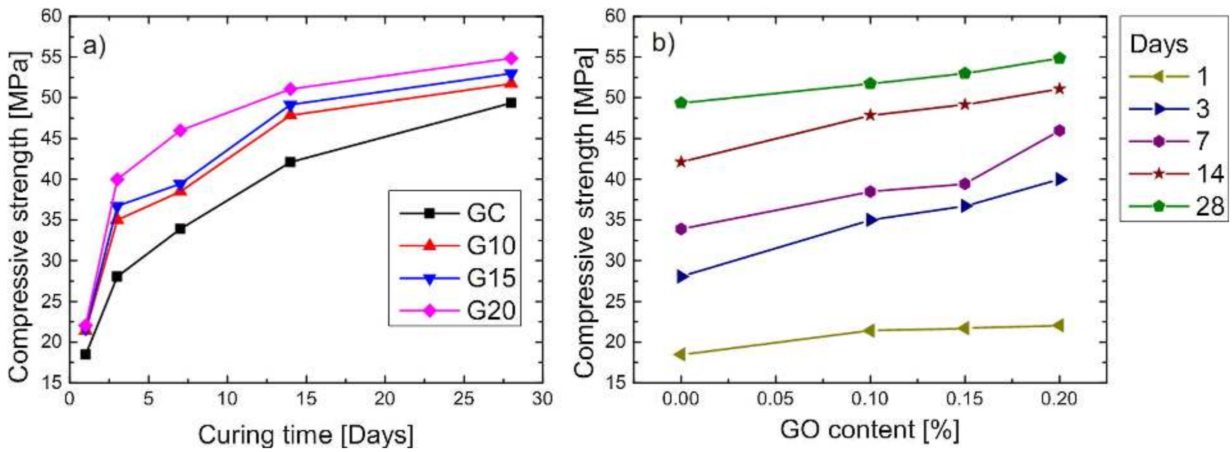

Figure 3: Compressive strength development of cement paste. (a) Effect of curing time on compressive strength of cement paste; and (b) effect of GO content on compressive strength of cement paste [70]

properties of cement-based materials and geopolymer materials, such as compressive strength, flexural strength, elastic modulus and tensile strength. At the same time, it has a good improvement effect on anti-freezing, fire resistance and impermeability. A large number of studies have proved that graphene-based nanomaterials are promising in the field of cement-based materials and geopolymers. This article will review the research progress of cement-based and geopolymer materials based on graphene modification for many years, and provide ideas for the future application and development of geopolymer materials and graphene materials.

2 Research progress of graphene modified cement-based materials

Ordinary portland cement (OPC) was invented and applied in the 19th century, and later played an important role in human construction activities. As construction behaviors around the world begin to become "faster, taller, and stronger", people have put forward higher requirements for the performance of cement-based materials. Cement-based materials mainly refer to materials formed by using cement as a binder, such as concrete and cement mortar. Because it is a brittle material, its compressive strength is high, but tensile strength and flexural strength are low. Therefore, it is easy to produce cracks in actual application, which leads to its performance degradation and shortened service life [43, 44]. In addition, the heavy application of cement-based materials will also cause huge energy consumption and severe environmental pollution [2, 45].

Cement-based materials are a naturally heterogeneous and porous material, which makes the tiny gaps inside them easily communicate and extend after loading, resulting in low tensile strength and deformation capacity of cement-based materials. In addition, due to the high proportion of pores, hydration products of cement are easily eroded, which not only makes the long-term durability of cement-based materials poor, but also has high maintenance costs [46, 47]. In general, the methods to enhance the strength and durability of cement-based materials mainly include add supplementary cementitious materials, using chemical admixtures or reducing water binder ratio [48]. Compared with traditional methods, nanomaterials provide a new method for improving the mechanical properties and durability of cement-based materials. The mechanical, chemical, thermal, and magnetic properties of nanomaterials are very different from those of macromaterials. This gives them the ability to solve problems that cannot be solved by traditional methods [49]. In cement-based materials, the size of most hydration products and gel pores are on the order of nanometers, therefore, in response to cracks in cement-based materials, nanomaterials can effectively control the development of nanoscale cracks into microcracks [50, 51]. Studies have shown that processes that occur at the nanoscale will ultimately affect the properties of bulk materials [52–54]. Graphene is a modifier that people have been very optimistic about in recent years. Graphene-based nanomaterials are the modifiers that people are very optimistic about in recent years. Their planar structure and surface function determine that they can be better combined with the cement matrix. They can effectively control the number and expansion of cracks and improve the performance of cement-based materials at a micro level. Therefore, the application of graphene in cement-based materials has received widespread attention.

2.1 Effect of graphene on the working performance of cement-based materials

Good working performance can ensure that the mixture has a high degree of fluidity, and will not delaminate after molding, maintain high strength and stability, and effectively avoid engineering accidents such as collapse and cracks. There are currently many studies on the working properties of GO cement-based materials, and all conclusions show that GO will reduce the fluidity of cement slurry. Wang *et al.* [55] believe that GO improves the hydration of cement and reduces the free water content in the cement slurry, thereby reducing the fluidity of the cement slurry. Li *et al.* [56] showed that the reduction of free water in cement slurry caused the GO aggregates formed by chemical cross-linking of GO nanoflakes with calcium ions to have higher water retention capacity, thereby reducing the fluidity of cement slurry. Other research results also show that: GO mixed with cement slurry reduces the fluidity of cement slurry and slump of concrete [57]. However, the use of naphthalene-based superplasticizers, polycarboxylic acid-based superplasticizers or the incorporation of silica fume can improve the problem of the decline in workability of cement-based composites caused by the incorporation of GO [58–60].

There are some truth for the two explanations in paper [55] and [56] referring to the decrease in liquidity. But the paper [56] is explained more thoroughly. Because of its unique lamellar structure and large number of active functional groups on the surface, GO can fully react with the cement matrix, thereby promoting cement hydration, which will indeed reduce the free water content in the cement slurry. But the impact of the formation of new microstructures on macro performance is the more important reason. From the characteristics of GO, it is easy to aggregate with calcium ions, so new aggregates are bound to be formed in the cement slurry. Such agglomerates have a higher water-retaining capacity, which results in reduced fluidity of the cement slurry.

2.2 Microstructure and mechanical properties of graphene modified cement-based materials

At present, there are many related studies on the effect of GO on the microstructure and mechanical properties of cement-based composites. Many studies have shown that changes at the micro level are the root cause of changes in mechanical properties. Lyu *et al.* [61] believed that the incorporation of a suitable amount of GO can significantly improve the microstructure of the mortar because it plays a template effect in the formation of cement hydration products. The research results by Mohammed *et al.* [62] pointed out that the incorporation of GO can not only improve the micro compactness and pore structure of cement mortar, but also inhibit the expansion of micro cracks in cement mortar. Many other studies have shown that GO can produce a more dense microstructure of cement-based materials and reduce the total pore volume of cement composite slurry [63–68]. The research of Wang *et al.* [69] showed that the main reason for GO to improve the mechanical strength of cement-based materials is to promote secondary hydration, reduce pore volume and refinement of CH crystal. In another study, experiments by Yang *et al.* [70] showed that GO has no effect on the structure of C-S-H, and the improvement of its mechanical properties mainly comes from the acceleration of hydration and chemical reactions. The experimental results show that the compressive strength of the cement-based composite increases by 42.3% and 35.7% respectively in 3 days and 7 days with 0.2wt% (weight percentage) of the ultrasonic dispersed GO. From Figure 3, it can be found that GO increases the compressive strength

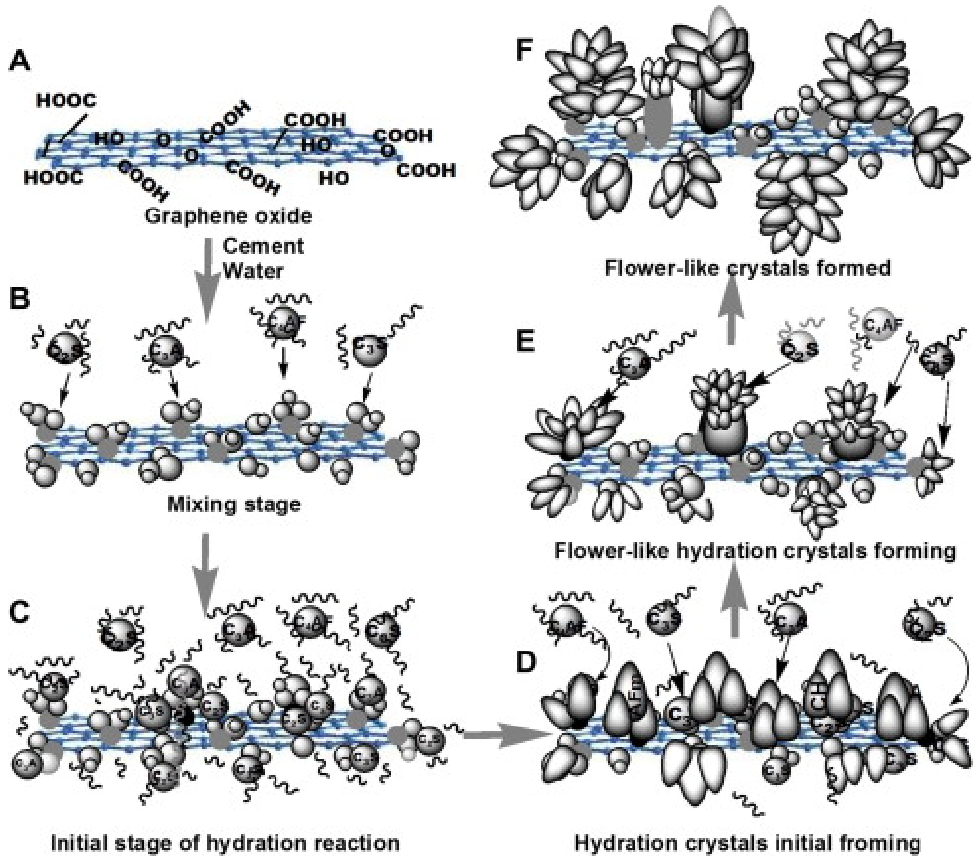

Figure 4: Schematic diagram of regulation mechanism of GO on cement hydration crystals [71]

of cement-based materials more dramatically in the early stage, and the higher the GO content in cement, the slower the increase in strength in the later stage. Lv *et al.* [71] found that at a low content of GO (0.01-0.03 wt%), the tensile and flexural strength of cement mortar showed an increasing trend when the amount of GO was gradually increased. When the added amount is 0.05 wt%, the increase in the compressive strength of the cement stone for 28 days appears to be a peak, and the improvement rate is 47.9%. If the GO added amount is further increased, the compressive strength will decrease; when GO was added at 0.03 wt%, the 28 days tensile strength increased by 78.6%, and the flexural and compressive strength increased by 60.7% and 38.9, respectively. The author points out that this is because the GO sheet can effectively control the aggregation and growth of cement hydration products, so that the growth of cement hydration products has a certain orientation, and the hydration products are presented to the performance of cement stones by orderly stacking and crossing a good gain effect (Figure 4). However, when the GO content is large, cement hydrated crystals should flocculate for GO and the peak value will decrease. In another study, Lü *et al.* [72] prepared a well-dispersed intercalation compound GO/P (AA-AM) by an oxidation method to solve the flocculation problem. Li *et al.* [73] carried out experimental research on the early hydration process and mechanical properties of GO cement mortar. It is proposed that when the amount of GO added is greater than 0.04 wt%, the increase in the flexural strength of the mortar begins to decrease. Pan *et al.* [74] and Du *et al.* [75] investigated the effects of the incorporation of GO on the rate of hydration of cement in cement mortar and the distribution and state of products. The study by Pan *et al.* [74] showed that when the GO content was 0.05 wt%, the compressive and flexural strength of cement sandstone 28d increased by 15-33% and 41-59%, respectively, and pointed out that the significant enhancement of GO to matrix is attributed to the strong interfacial adhesion between GO and the cement matrix. In Figure 5, they described the toughening mechanism of these composites through SEM. In graphene-cement composites, unlike ordinary matrices where cracks usually pass in a straight line, in graphene-cement composites, cracks are stopped and cannot pass through the graphene sheet. The GO flakes block and alter the propagation of microcracks in the plane. In addition, many studies have shown that the appropriate amount of

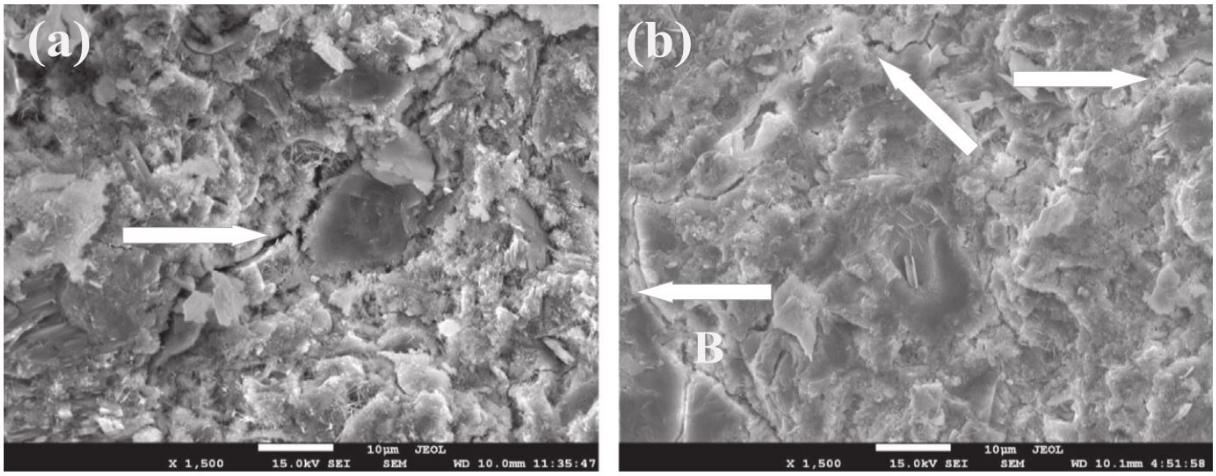

Figure 5: (a) SEM image of plain paste showing a straight-through type crack (arrow). (b) SEM image of GO–cement composite showing a number of fine cracks (arrows) with few branches [74]

GO compounded with cement-based composites can regulate the structure of hydration products and the hydration reaction process, thereby improving its mechanical properties [58, 65, 76–78]. Chuah *et al.* [79] conducted a detailed study on the dispersibility of graphene oxide in aqueous solutions, and explored the pH value of lye, ions in salts, and their combined effects in simulated pore solutions. It is proposed that GO can significantly improve the flexural strength, and it is pointed out that the incorporation of graphene oxide-compatible surfactant into cement slurry can stabilize the dispersion of graphene oxide in cement slurry.

The above research proves the potential of graphene-based nanomaterials in the modification of cement-based materials. At this stage of research, a reasonable model of the mechanism by which GO affects the properties of cement-based composite materials can be constructed, and a microscopic understanding of the action mechanism of GO cement-based materials has been initially obtained. These studies are of great significance for the macroscopic regulation and interpretation of the properties of GO cement-based materials. The disadvantages are: (1) There is no definite value for the optimal content of GO. As shown in Table 1, different researchers have given different values, and the improvement effect is also different; (2) The current micro-mechanism needs to be further improved, and deeper research is still lacking; (3) Most of the researched cements are OPC, and other special cements such as aluminate cement (AC), sulphoaluminate cement (SC) and other modification studies are based on OPC. There is still a lack of theoretical research on special cement, which needs more research.

2.3 Research progress of durability of graphene modified cement-based materials

The structure of cement-based materials is durable under various harsh conditions exposed to the outside world for a long time, which is called durability [80]. Durability is an important issue in the construction industry. Durable construction materials not only help extend service life, but also reduce maintenance costs. As the most widely used construction material, concrete is susceptible to various forms of erosion during service period, such as carbonization, alkaline silicic acid reaction (ASR), chloride attack, calcium leaching, freeze-thaw cycles, fire, thermal cracking, and bacteria attacks, etc. [81], resulted in a significant reduction in their useful life. From the existing research, the most important factors determining durability are the internal pore structure and porosity. The appropriate amount of GO added to cement mortar can significantly improve its micro-compactness and pore structure, and improve the durability of cement mortar. GO cement mortar durability research currently focuses on the resistance of cement mortar to chloride ion penetration, carbonization resistance, and freeze damage resistance.

Paper [63] pointed out that the improvement of the frost resistance of cement mortar by GO is because the incorporation of GO improves the micropore structure of cement mortar, and the incorporation of GO can inhibit the expansion of micro-cracks in cement mortar, thereby inhibiting the expansion of freeze-thaw damage. Another study by Mohammed *et al.* [82] showed that GO has layered and cross-linked structural characteristics, and when mixed into cement mortar, it can form a sponge-like struc-

Table 1: Mechanical performance of GO–reinforced cementitious composites

Matrix	GO dosage (wt%)	GNS type	Curing age (days)	Performance improvement	Highlights	Ref		
				Tensile str. increase rate (%)	Flexural str. increase rate (%)	Compressive str. increase rate (%)		
Mortar	0.03	GO	28	65.5	60.7	38.9	XRD and SEM showed that GO changed the shape and arrangement of hydrated crystals.	[61]
Paste	0.20	GO	3/7	-	-	42.3/35.7	^{29}Si-NMR, FT-IR and XRD indicated that GO has no influence on C-S-H structure.	[70]
Mortar	0.03	GO	3/28	51.0/78.6	70.7/60.7	45.1/38.9	FT-IR, XRD and SEM indicated that Go can effectively regulate the microstructure of hydrated crystals.	[71]
	0.05		3/28	24.2/35.8	28.1/30.2	59.0/47.9		
Paste	0.04	GO	28	-	14.2	37.0	SEM indicated that GO makes the microstructure more compact.	[73]
Mortar	0.05	GO	28	-	41-59	15-33	SEM indicated that Go controls the generation of cracks.	[74]
Concrete	2.00	GO	28	-	- 65.2	57	SEM showed that GO does not influence the hydration of the concrete.	[76]
	4.00	GO	28	-		50		
Paste	0.03	GO/ Surfactants	-	-	67	-	Surfactants ensure that GO remain dispersed in the alkaline cement environment.	[79]
Paste	0.07	GO	7/28	-	200/85.7	31.3/21.9	SEM showed that Go makes the hydrated crystal more regular and finally agglomerates into dense structure.	[58]
Paste	0.05	GO	3/28	-	86.1/90.5	52.4/40.4	GO can arrange crystals in an orderly manner and improve the compactness of cement slurry.	[65]
Mortar	0.05	GO	3/28	-	69.4/70.5	43.2/24.4		
Mortar	0.03	GO	28	-	55.8	31.9	XRD and EDS indicated that GO can regulate cement hydration products into regular shaped hydrated crystals through the template effect.	[72]
		GO/P(AA-AM)	28	-	83.7	72.3		

ture, which captures chloride ions and reduces the penetration depth effectively improves the anti-permeability of chloride ions. The study also showed that GO can also improve the carbonization resistance and frost resistance of cement-based composites. Studies by Lv *et al.* [83] and Tong *et al.* [77] also mentioned that the incorporation of GO contributes to the improvement of mortar's carbonization resistance and frost resistance. In summary, the incorporation of a suitable amount of GO can improve or improve the microstructure, mechanics, and durability of the sand. There are few studies on the effect of GO concrete durability in the existing studies. Du *et al.* [84] studied the water and chloride ion erosion resistance of graphene nanoplates (GNP) on concrete, and the results showed that GNP improved the chloride ion and water percolation resistance of concrete. The refinement is related to the improvement of torsion resistance. Mohammed *et al.* [85] investigated the effect of GO incorporation into ordinary and high-strength concrete at 800°C. The results showed that graphene oxide significantly improved the mechanical strength of the test piece, and proved that the thermal deformation of the sample was compatible with graphene oxide, and there was no early negative expansion. Gao *et al.* [86] showed that graphene oxide/multi-walled carbon nanotubes were distributed in a network in the slurry, which enhanced the pore structure of the slurry and improved the impermeability.

The durability of cement-based composites determines the service life of concrete structures. The above studies have verified the improvement effect of graphene-based nanomaterials on the cement-based durability, and also explained from a micro perspective, so that people have a certain understanding of the action mechanism of GO cement-based composites. However, there is not much research in this area, and there is no conclusion on the optimal amount of GO. This is the focus of future research.

3 Research progress of graphene modified geopolymer

As mentioned earlier, geopolymers have received widespread attention as substitutes for cement. Because of its excellent performance and energy saving, it has been widely used in many fields. Such as pavement repair [87], 3D printing [88], anticorrosive coatings [89], curing pollutants [90, 91], etc. Despite many advantages, geopolymers have similar disadvantages to cement-based materials, namely poor toughness and relatively low flexural strength [92]. Therefore, many researchers have studied the performance of the composite use of nanomaterials and geopolymers. These attempts include the addition of single-walled carbon nanotubes [93], multi-walled carbon nanotubes [94], nano-SiO_2 [95], nano-TiO_2 [96], nanofibers [97], and GO [98] into geopolymer, and the comprehensive performance studies of these composite materials. The rapid development of graphene cemented composites is based on the relatively mature research of carbon-based nanomaterials such as carbon nanotubes [11]. Compared with carbon nanotubes, graphene has better dispersibility and is easier to mass-produce [99]. This makes graphene materials more advantageous in the construction field. However, at present, the research of graphene geopolymer is much less than that of graphene cement-based materials, which may be due to the late start of the research on these two new materials.

Zhong *et al.* [100] studied the 3D printing of extruded geopolymer/graphene oxide (GOGP) nanocomposites, and found that the addition of graphene oxide can significantly change the rheology of the geopolymer precursor. The GOGP structure has higher mechanical properties, making 3D printing of geopolymers possible. Yang *et al.* [101] studied the effect of GO on the fluidity, mechanical properties, and microstructure of AAS slurry in alkaline activated slag (AAS) mortar. It was observed that the flexural strength of GO for 7 days of AAS mortar was increased by 20%, and the fluidity was also improved. The optimal content of GO was 0.01 wt% of the weight of slag. In addition, the study of the microstructure of the AAS slurry found that layered double hydroxides (LDHs) was produced in the GO-AAS system. Saafi *et al.* [102] studied the effect of geopolymers containing reduced graphene oxide (RGO) under different loads. The test results showed that RGO with 0.35 wt% produced the highest flexural strength, Young's modulus, and flexural toughness, which increased by 134%, 376%, and 56%, respectively. They believe that the improvement of the mechanical properties of the geopolymer and the decrease of the overall porosity are due to the interaction between GO and the alkaline solution to produce highly reduced and crosslinked GO flakes. Ranjbar *et al.* [103] studied the microstructure and mechanical properties of graphene nanoflake (GNPs) fly ash base polymer composites. The results showed that the compressive strength and flexural strength of geopolymers increased by 1.44 times and 2.16 times, respectively, after adding 1% GNPs. Yan *et al.* have conducted a number of graphene-related experimental studies [104–106]. In the study of the performance of GO geopolymers at different times, it was found that within 0 to 24 hours, RGO binds well to the geopolymer matrix. As the reaction time increases, the degree of densification increases and the amorphousness of the material

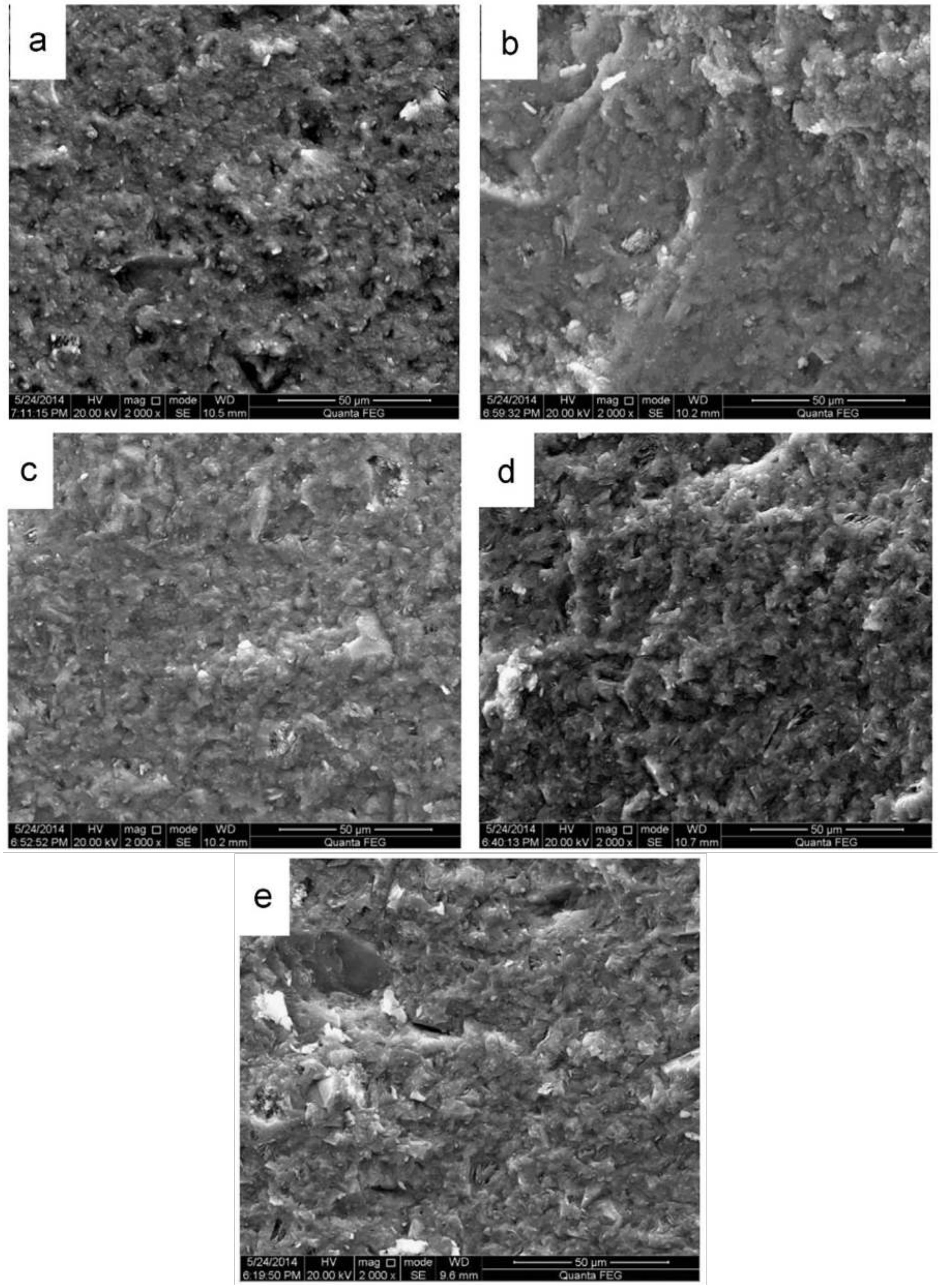

Figure 6: Typical fracture surface microstructure of rGO/GP composites with different rGO contents: (a) rGO/GP0; (b) rGO/GP0.5; (c) rGO/GP1; (d) rGO/GP3; (e) rGO/GP5 [105]

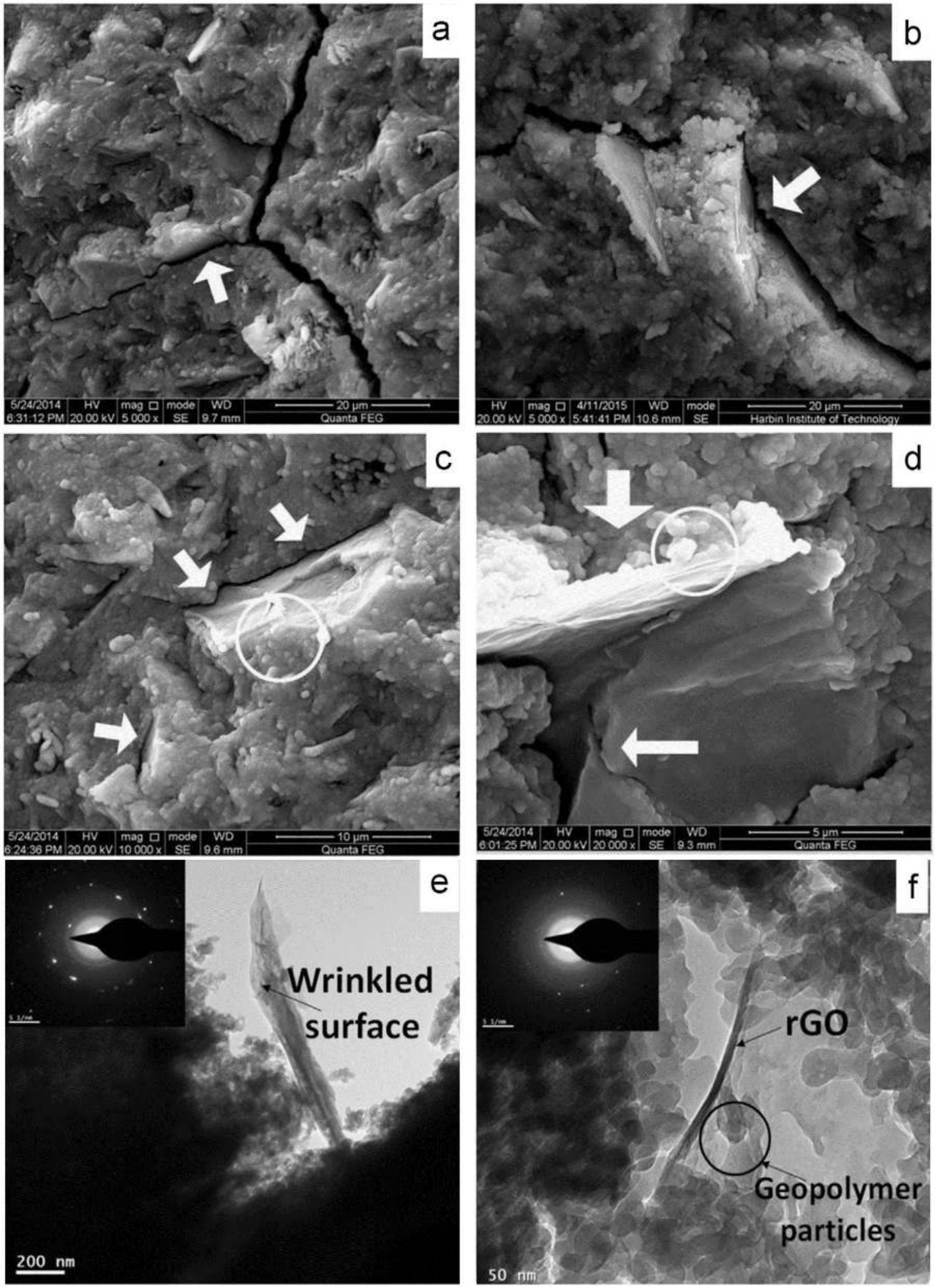

Figure 7: Detailed observation of interface microstructure of the rGO/GP5 composites: (a)–(d) SEM images; (e), (f) TEM images; insets display selected electronic diffraction patterns [105]

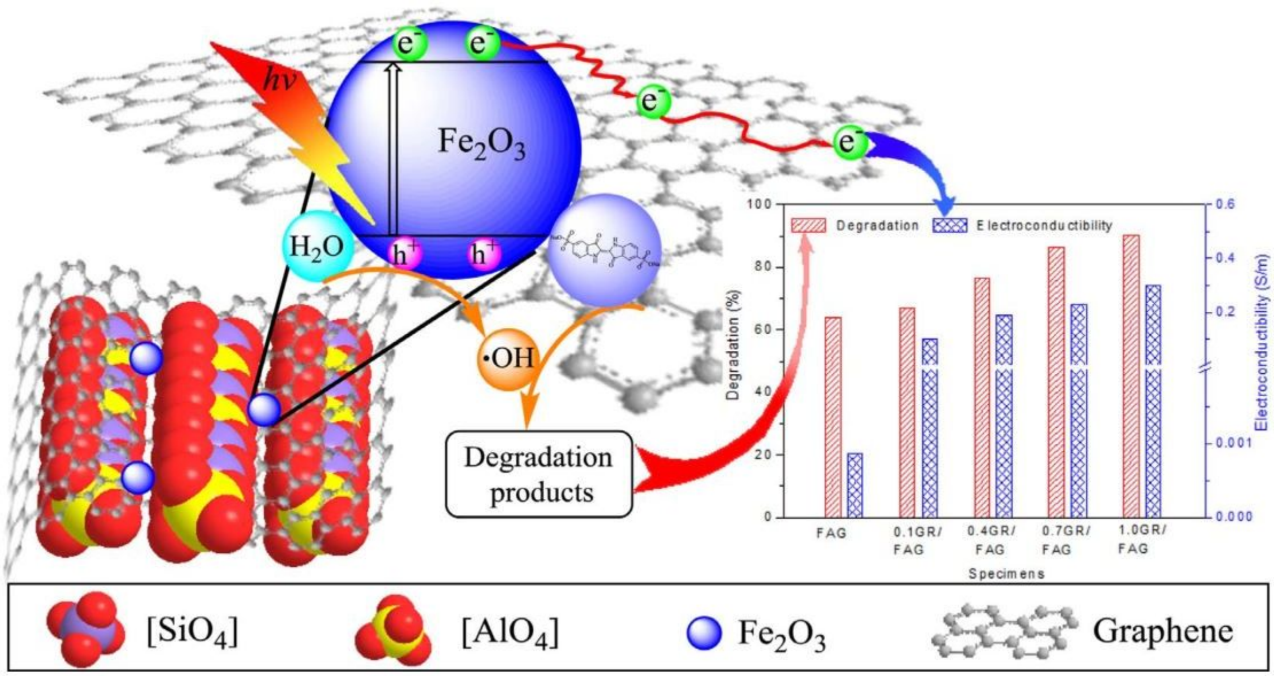

Figure 8: Schematic mechanism of the photocatalytic degradation of indigo carmine over an electroconductive GR/FAG composite [110]

decreases [104]. In another study [105] reported the effect of reduced GO content on graphene-geopolymer nanocomposites. It is pointed out that under the action of alkaline geopolymer solution, GO is reduced to RGO in a short time. The flexural strength of RGO/GP reaches a maximum value of 17.9 MPa as the RGO content increases to 0.3 wt%. The fracture toughness value increased by 61.5% as the RGO content increased to 0.5 wt%, reaching 0.21 MPa $m^{1/2}$. The authors explain that the improvement in performance is due to the pull-out, wrapping, and anchoring effects of RGO. The interface between RGO and the substrate is well combined, and under the effect of external stress, it will hinder the propagation of cracks and enhance the fracture toughness and bending strength of the material (Figure 6, Figure 7). The effects of crystallization kinetics and isothermal infusion time on the microstructure evolution and mechanical properties of RGO/leucite after high temperature treatment were also reported [106]. The results show that the activation energy of RGO/leucite is lower than that of pure geopolymers, and the isothermal immersion time has a significant effect on the mechanical properties of RGO/leucite. Xu *et al.* studied the effect of GO on the properties of fly ash base polymers [107, 108]. The results show that the addition of 0.02wt% GO (by fly ash weight) significantly improves the mechanical properties and durability of the fly ash base polymer, and GO has the potential to improve the fixation of heavy metals in fly ash. Dimov *et al.* [109] found that when water-stabilized graphene dispersion was added to concrete, its mechanical strength and impermeability were greatly improved. Its compressive strength and flexural strength were increased by 146% and 79.5%, water permeability was reduced by nearly 400%, and electrical and thermal properties were also found to be enhanced. Zhang *et al.* [110] studied the effect of graphene on the conductivity of fly ash base polymer (FAG), and found that adding 1 wt% of graphene to the fly ash base polymer improved the conductivity by 348.8 times. The authors point out that graphene can quickly accept photo-generated electrons of Fe_2O_3 semiconductors in FAG, thereby promoting the effective separation of photo-generated electron-hole pairs and improving the ability of oxidative degradation (Figure 8). It is proved that graphene can be used as an electron acceptor to improve the conductivity of geopolymers.

The above experimental studies have proved that graphene-based nanomaterials can still exert effects in geopolymers. Graphene-based nanomaterials can be well combined with the geopolymer matrix due to their unique lamellar structure and rich surface functions, build a specific microstructure, and greatly improve the mechanical properties and durability of the geopolymer. These studies provide guidance for the application of graphene-based nanomaterials in geopolymers in the future. But there are still some disadvantages: (1) The research scope of geopolymers is still very limited. The current research objects are mostly more active aluminum-siliceous materials, such as slag and fly ash. The effects of graphene-based nanomaterials are still unclear in red mud, rice hull ash and silica fume which are Low active material; (2) The experimental results are very different. The optimal content and gain effect of graphene proposed by different researchers are very different. This may be caused by different experimental environments and different ways of treating graphene; (3) Studies on improving the durability of geopolymers by graphene are scarce. At present, more research is on the mechanical properties.

In summary, there are not many studies on graphene-based nanomaterials modified geopolymers, which need to be expanded in the future. New technologies and high-performance products for the preparation of geopolymer composites suitable for the structural characteristics of graphene sheets were explored.

4 Conclusion and prospect

Based on the review of previous studies, the following conclusions can be drawn.

1. Graphene-based nanomaterials can be well combined with cement-based materials due to their unique lamellar structure and excellent physical properties, forms a dense microstructure, reduces porosity, prevents the generation of nano-dimensional cracks, solves the shortcomings of high brittleness of cement-based materials, greatly improves mechanical properties and durability, and has great significance for the development of high-performance cement-based products.
2. At this stage, a reasonable model can be constructed for the mechanism of GO's influence on the performance of cement-based composite materials. Understand the influence of GO content ratio on the mechanical properties of cement-based composite materials, and obtain a preliminary micro-cognition of the action mechanism of GO cement-based materials. These studies are of great significance for the macro-control and interpretation of GO cement-based materials' performance.
3. The improvement effect of graphene-based nanomaterials in geopolymers is also surprising, providing a basis for expanding the application of geopolymers, and also providing guidance and reference for the research of other types of geopolymer materials.
4. Graphene-based nanomaterials have proven to have the opportunity to replace the current traditional fibers as a new generation of reinforcing materials, which has positive significance for the application of graphene and the preparation of high-performance building materials.

   Although graphene and its derivatives have shown great application value and potential at present, their application to practical engineering still faces the following challenges.
5. Negative effects: We noticed that some researchers have proposed the negative impact of graphene on the fluidity of cement slurry. This increases the difficulty of applying graphene to large-scale construction projects to a certain extent. But they also mentioned that adding water reducer or silica fume can improve this negative effect.
6. High cost: Another factor restricting graphene nanomaterials is its higher price. Of course, this is for all nanomaterials. At present, it is not very economical. But graphene prices have been a lot cheaper than it was initially, I believe that as the study of graphene will be more affordable.
7. Geopolymer performance is unstable: Geopolymers are made from industrial waste materials containing aluminum-silicon raw materials through appropriate processes, but because of their complex components and unstable performance, the use of graphene with geopolymers may be subject to more interference factors.

Cement-based materials are currently the most mainstream building materials, and its performance improvement is of great significance to the technological development and innovation in the construction field. According to the current research, graphene-based nanomaterials have an excellent improvement effect on cement-based materials. A small amount of graphene can greatly improve the mechanical properties, fire resistance and impermeability of cement-based materials, ensuring the long-term use of cement-based materials in various environments, with great development prospects. With further understanding of the strengthening mechanism in the future, it is believed that the effect of graphene-based nanomaterials in cement-based materials will be better.

Geopolymer, as a new type of sustainable gelling material, is a cement substitute favored by scientific researchers, and will inevitably play a more important role in the construction field in the future. Graphene-based nanomaterials can further enhance its performance and expand its applications. It is foreseeable that graphene geopolymer composites will have great prospects in the future.

In order to make full use of the advantages of graphene and produce higher performance building materials, we also need to solve the current challenges and problems, which requires more attempts and research. With the deepening of people's research on graphene, some existing problems have gradually been improved. It is believed that in the near future, it will inevitably overcome the current difficulties and realize the widespread application of graphene in the construction industry.

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