

# Research progress of geopolymer solidification / stabilization of heavy metal contaminated soil

Weifeng Yao \*

College of civil engineering, Henan Polytechnic University, Jiaozuo, China

\*Corresponding Author

## ABSTRACT

As a new type of green and environmentally friendly aluminosilicate gel material, geopolymer has attracted much attention from scholars for its good ability to immobilize heavy metals compared with traditional cement-based curing agents. Based on the research progress of geopolymer solidification of heavy metal contaminated soil at home and abroad in recent years, this paper introduces the process of geological polymerization reaction. The solidification mechanism of geopolymer on heavy metal contaminated soil and the influence of different factors on the solidification effect of geopolymer on heavy metal contaminated soil are described in detail. The leaching characteristics of heavy metals in geopolymer solidified heavy metal contaminated soil under freeze-thaw cycle, dry-wet cycle and carbonization were further discussed. Finally, the problems existing in the solidification of heavy metal contaminated soil by geopolymer are analyzed and the future research and development direction is prospected.

## KEYWORDS

Geopolymer; Solidification / stabilization; Heavy metal.

## 1. INTRODUCTION

With the continuous advancement of China's industrialization process, environmental pollution, ecological damage and other problems are becoming more and more serious. The discharge of industrial, domestic and hospital wastewater, the arbitrary stacking of industrial waste, and the excessive use of pesticides and fertilizers [1] have forced China's soil heavy metal pollution to become increasingly serious, causing serious harm to human health and sustainable development of ecosystems. The problem of contaminated soil treatment is imminent. According to the survey results of soil environmental quality in the latest China Ecological Environment Bulletin, the main pollutants affecting the soil environment of agricultural land are heavy metals, of which cadmium (Cd) is the primary pollutant [2]. Mercury (Hg), arsenic (As), lead (Pb), chromium (Cr), copper (Cu), zinc (Zn) and nickel (Ni) are also common heavy metals. These heavy metals are highly toxic and difficult to be degraded by microorganisms or natural degradation. Heavy metals are continuously enriched and concentrated in the human body through the food chain, which ultimately endangers human health and even has a fatal risk [3,4]. Therefore, the economic and effective treatment of heavy metal contaminated soil has become an urgent problem to be solved. Solidification/stabilization technology has been widely used in the remediation of heavy metal contaminated sites at home and abroad [5,6,7]. The principle is to fully mix heavy metal contaminated soil with curing agent. Due to the problems of common cement curing agents, such as high production cost, poor curing effect, excessive resource consumption and strong environmental pollution [8], geopolymer, as a new three-dimensional mesh inorganic gel material, has been favored by scholars for its advantages of high metal stabilization

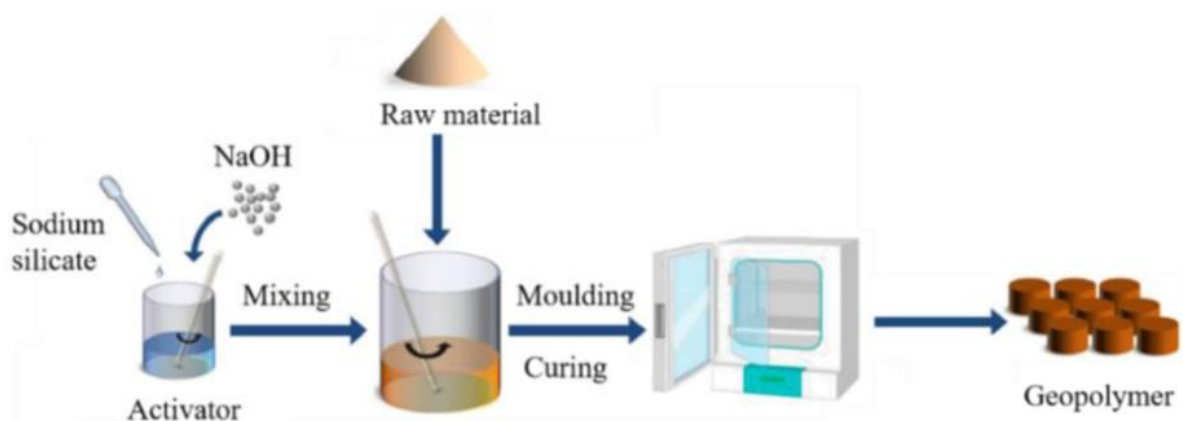
efficiency, low CO<sub>2</sub> emission, waste energy saving and so on [9]. However, the current research on geopolymer solidified soil mainly focuses on mechanical properties, while the leaching characteristics of heavy metal contaminated soil solidified by geopolymer are less studied. Based on the research content of scholars, the author systematically summarized the research on geopolymer solidified heavy metal contaminated soil from the aspects of reaction mechanism, stabilization mechanism, influencing factors and environmental degradation, etc., and summarized and analyzed the existing problems of geopolymer solidified heavy metal contaminated soil at the present stage and the future development direction.

## 2. GEOPOLYMER

In 1978, French professor Joseph · Davidovits used metakaolin and alkali activator or a certain amount of slag and lime mixed with water to prepare mortar, forming a new type of aluminosilicate material with a dense three-dimensional network structure at room temperature, commonly known as Geopolymer [10,11]. Geopolymer is formed by the staggered arrangement of silicon-oxygen tetrahedron [SiO<sub>4</sub>]<sup>4-</sup> and aluminum-oxygen tetrahedron [AlO<sub>4</sub>]<sup>5-</sup> [12]. Its dense three-dimensional network structure has excellent physical and chemical properties. Among them, the characteristics of fixing toxic and harmful wastes are widely used in the treatment of heavy metal contaminated soil [13]. The geological polymerization reaction generates aluminosilicate gel to make the connection between soil particles denser, and physically encapsulates and chemically bonds the heavy metal ions in the contaminated soil to retain them inside the geopolymer, so as to achieve the purpose of immobilizing heavy metals.

Geopolymer is a new type of three-dimensional network silicon, which is formed by the staggered arrangement of [SiO<sub>4</sub>]<sup>4-</sup> and [AlO<sub>4</sub>]<sup>5-</sup> tetrahedrons in the four stages of dissolution, diffusion, condensation and hardening under the action of alkali activator, using amorphous aluminum silicon compound industrial waste as precursor.

The formation of geopolymer involves the dissolution of aluminum and silicon minerals on the surface of aluminosilicate, the formation of aluminosilicate gel phase by dehydration polymerization, and the final polycondensation reaction to harden the gel to form a polyaluminosilicate hardened body [14,15]. The reaction mechanism is as follows [16]:



**Figure 1.** Geological polymerization process[25]

## 3. MECHANISM OF STABILIZATION OF HEAVY METAL IONS BY GEOPOLYMER SECTION HEADINGS

In the process of geological polymerization, the formation of geopolymer gel plays a decisive role in the stabilization of heavy metal ions. The main mechanisms for the stabilization of heavy metal ions

by geopolymers include physical encapsulation and chemical bonding [17]. It has been found that metal cations are fixed by a combination of chemical and physical encapsulation [18], and the stabilization mechanism of heavy metal ions is shown in Fig.2.

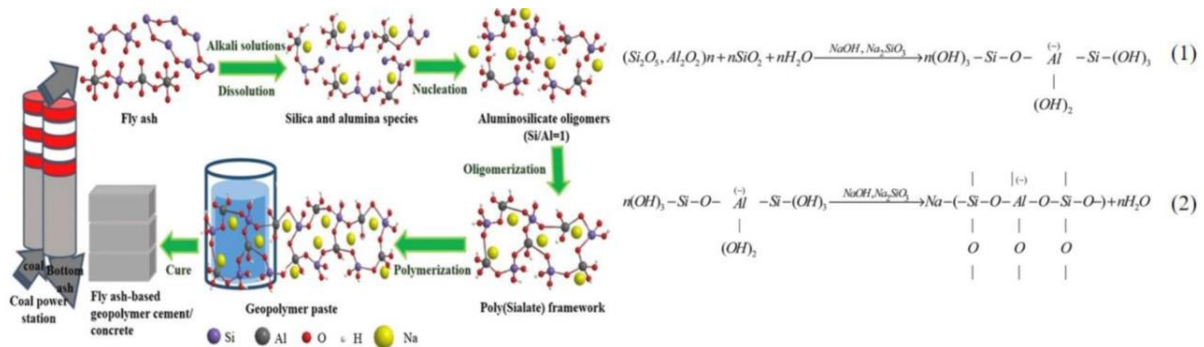


Figure 2. Alkali-excited geopolymerization process[25]

### 3.1. Physically stable

Liu [19] found that with the increase of  $Pb^{2+}$  content, the diffraction peak did not change basically, and no Pb-rich phase was detected. According to this, it was revealed that  $Pb^{2+}$  did not participate in the reaction of the new phase, and was mainly stabilized in the form of physical encapsulation inside the geopolymer structure. Wang et al [20] studied the stabilization effect of geopolymer on zinc tailings. The study revealed that ZnO did not react in geopolymer, but dissolved in acidic solution to  $Zn^{2+}$ , which was physically encapsulated and adsorbed in geopolymer by gel produced by geopolymer reaction. With the increase of geopolymer content, the leaching concentration of  $Zn^{2+}$  gradually decreased. Meng et al [21] found that the geological polymerization reaction products C-S-H and ettringite AFt can make the soil structure more compact, which is conducive to the physical encapsulation of heavy metal copper and cadmium through the microscopic study of solidified composite heavy metal copper and cadmium sediment. Therefore, it is known that the production of hydrated gels such as C-A-S-H gel, N-A-S-H gel and N-(C)-A-S-H gel provides an important structural basis for the physical encapsulation of geopolymers. The physical stabilization of heavy metal ions by geopolymer is mainly through the geological polymerization reaction of aluminosilicate to form a three-dimensional network structure of geopolymer gel. The geopolymer with dense structure hinders the leaching of heavy metal ions, so that heavy metal ions are retained in the network structure of geopolymer to achieve the effect of stabilizing heavy metals.

### 3.2. Chemical stabilization

Wang [22] studied the stabilization of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$  and  $Cr^{3+}$  by fly ash-based geopolymers and found that heavy metal ions can directly participate in the reaction and chemically bond with-Si-O-bond and-Al-O-bond, and then be fixed into geopolymers. Huang [23] pointed out that  $[SiO_4]^{4-}$  and  $[AlO_4]^{5-}$  constitute the amorphous structure of geopolymers, and the bond energy of Si-O and Al-O in each tetrahedral structure is uniform.  $Al^{3+}$  is connected to the four oxygen atoms in  $[AlO_4]^{5-}$ , which makes it negatively charged in the geopolymer, while  $Cr^{3+}$  can directly balance the charge in the reaction and replace the  $Ca^{2+}$  and  $Na^+$  sites, so they are effectively fixed in the solidified body. Heavy metal ions can produce strong covalent bonds in the structure by replacing the alkali metal ions in the geopolymer structure and are fixed in the geopolymer by chemical adsorption. The chemical bonds of heavy metals in geopolymers are mainly based on the fact that the tetrahedral aluminum in geopolymers has a negative charge, and the position of the negative charge is replaced by the alkali metal cation, thereby balancing the negatively charged Al tetrahedron and being fixed by geopolymers. [24,25] In addition, heavy metal ions can also form compounds such as hydroxides and

carbonates with extremely low solubility through chemical reactions; gels such as silicates and aluminates can also be formed and fixed in geopolymers.

Based on this stabilization mechanism, the author comprehensively reviewed the stabilization mechanism of geopolymer on different ion types in combination with the research on geopolymer stabilization of heavy metal contaminated soil in recent years ( Fig.3 ).

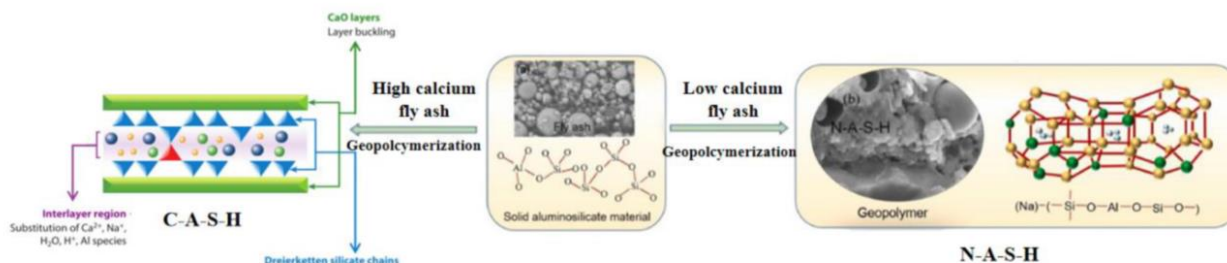


Figure 3. Hydration products of the geopolymerization reaction

## 4. INFLUENCING FACTORS OF HEAVY METAL SOLIDIFICATION BY GEOPOLYMER

### 4.1. Ion species

Different types of heavy metal ions have different curing effects on geopolymers due to their different ionic radius, ion morphology and their own properties. EI-Eswed et al studied the stabilization effect of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Th^{4+}$  and  $U^{6+}$  in metakaolin-based geopolymer, and found that the efficiency of metal increased with the increase of ion radius. This can be explained by the ion pair theory. Metal ions with large radius form weak ion pairs with small silicate oligomers, which helps to form large aluminosilicate oligomers, in which the negatively charged  $[AlO_4]^-$  tetrahedron tends to combine with it to lead to more effective stabilization effect. Guo et al found that PbS had the best solidification effect by using fly ash based geopolymer to solidify  $PbO$ ,  $PbSO_4$  and  $PbS$ , and concluded that the pollution form in geopolymer matrix was very important to the solidification effect. Zhang et al found that the reduction of  $Cr^{6+}$  to  $Cr^{3+}$  can play an active role in the curing process and improve the curing efficiency of chromium ions when using geopolymer to solidify  $Cr^{6+}$ . By studying the reduction and immobilization of  $Cr^{6+}$  in metakaolin-based geopolymers, Chen et al found that the partial reduction of  $Cr^{3+}$  by  $Cr^{6+}$  in  $FeSO_4 \cdot 4H_2O$  solution first, and then fixed in the geological polymerization system, can achieve better fixed efficiency and higher fixed amount.

### 4.2. Additives

In the process of geopolymer solidification of heavy metal contaminated soil, not all ions have good solidification effect. For example, the leaching rate of fixed  $Cr^{6+}$  in most cases seriously exceeds the national soil environmental quality standard. However, some scholars can play a synergistic role in the solidification of heavy metals in contaminated soil by adding some reducing additives, and fully improve the solidification effect. Li Jiangshan et al found that  $Fe^{2+}$  reduced  $Cr^{6+}$  to  $Cr^{3+}$  by studying the form of chromium in  $FeSO_4$ -stabilized chromium-contaminated soil, thus changing the occurrence form of chromium in stable soil and promoting the weak acid extractable state of chromium to be reducible and oxidizable, thereby improving the fixation effect of  $Cr^{6+}$ . Tian [32] studied the solidification mechanism of geopolymer by adding  $CaO$ ,  $MgO$  and  $FeSO_4 \cdot 7H_2O$  additives respectively through the problem of low efficiency of  $Cr^{6+}$  solidification by geopolymer. The results show that  $CaO$  or  $Fe^{2+}$  salt has a certain inhibitory effect on  $Cr$  leaching. The leaching amount of  $Cr^{6+}$  can be reduced to less than 10% under the action of  $MgO$ , and it is found that  $CaO$ ,  $MgO$  and  $Fe^{2+}$  salt have a certain synergistic effect on the leaching of  $Cr^{6+}$  in the solidified body.

### 4.3. Types and dosage of alkali activator

Alkali activator plays a vital role in the process of geopolymer materials. Researchers usually use  $\text{Na}_2\text{SiO}_3$  combined with NaOH to activate alkali. Some researchers have expanded the types of alkali activators and found that NaOH and KOH solutions can be combined with each other to obtain a good curing effect. However, most scholars believe that aluminosilicate minerals are easily dissolved in NaOH solution rather than KOH solution, but the geopolymer produced by aluminosilicate minerals under KOH alkali excitation is more stable. The Na / Al molar ratio determines the amount of alkali activator in the process of geological polymerization. Under the condition of low Na/Al ratio, the insufficient alkali activator cannot carry out the polymerization reaction smoothly. However, the excessive alkali activator with high Na/Al ratio will increase the alkalinity of the solidified body, which will lead to the dissolution of the gel and reduce the curing effect.

### 4.4. Si / Al ratio

The Si/Al molar ratio of geopolymer is one of the most important factors that determine the structure and properties of the final geopolymer, including chemical stability, mechanical strength, fire resistance and durability. Therefore, the study of the immobilization efficiency of geopolymers with different Si : Al molar ratios is considered to be highly correlated.

Tian by studying the immobilization effect of selenium and arsenic oxygen anions in geopolymers with different Si/Al molar ratios (2,3,4and5), it was found that the leaching rate of selenium and arsenic increased with the increase of Si/Al ratio. The reason is that the geopolymer with high Si/Al ratio has a relatively low specific surface area and pore volume, showing a high leaching amount. Therefore, the number and distribution of aluminum-oxygen tetrahedrons play a key role in the stability of these oxygen anions in the geopolymer structure. Kranzlein et al prepared geopolymers with Si/Al ratio between 2.0 and 3.0 to immobilize Pb and Zn. The structure showed that the sample with Si/Al ratio of 2.0 was the most stable under hydrochloric acid erosion, and the leaching rate was the lowest. The leaching rates of Pb with Si/Al ratios of 2.2, 2.4, 2.8 and 3.0 are as high as 100%, and the amorphous matrix is completely destroyed, which confirms that the effectiveness of geopolymer immobilization of heavy metals depends on the ratio of silicon to aluminum. Therefore, it is of great significance to find the optimal silicon-aluminum ratio in the test of geopolymer solidification of heavy metals.

### 4.5. Maintenance conditions

Curing conditions play an important role in solidifying heavy metals. When the curing temperature is low, the slow rate of geopolymerization reaction may lead to the failure to generate a dense and complete geopolymer, resulting in poor curing effect. Appropriately increasing the curing temperature has a positive effect on the solidification of heavy metals by geopolymers, because it can accelerate the reaction rate and degree of geopolymers. When the temperature is high, it may lead to micropores and cracks in the dense structure, which also affects the solidification effect. Nikolic et al studied the lead leaching of geopolymers with 4 % lead. The results showed that the lead fixation efficiency of geopolymers solidified at 20 °C for 28 days was 99.99 % .High temperature solidification leads to more obvious defects in geopolymer matrix, thus reducing the effectiveness of lead fixation.

Curing time also has a positive effect on the stabilization of heavy metal ions by geopolymers. Du found that the leaching concentration of heavy metals in contaminated soil decreased gradually with the extension of curing time by studying the stability of heavy metal contaminated clay solidified by new hydroxyapatite. It shows that with the increase of curing time, the curing products increase, thus improving the stabilization effect on heavy metals.

## 5. ENVIRONMENTAL FACTORS AFFECTING THE STABILIZATION EFFECT OF HEAVY METAL CONTAMINATED SOIL

In the practical engineering application of geopolymer solidified contaminated soil, the natural environment has an important external force on the mechanical properties and leaching characteristics of geopolymer solidified heavy metal contaminated soil. Therefore, it is of great significance to consider the influence of external environmental factors in the process of repairing heavy metal contaminated soil.

### 5.1. Freeze-thaw cycles

The freeze-thaw resistance of geopolymer mainly depends on the void ratio of solidified soil. Li Jiangshan et al. carried out freeze-thaw cycle tests with different compaction degrees (90%, 96% to explore the influence of freeze-thaw cycles on the engineering properties of lead-contaminated soil solidified bodies. The results show that with the increase of freeze-thaw cycles, the leaching concentration of Pb in the 90% compaction degree sample increases continuously, while the leaching concentration of the 96% compaction degree sample decreases continuously. The reason is that the freeze-thaw cycle has little effect on the high-pressure solid solidified body. The deterioration effect of soil frost heave on the solidified body is worse than the cementation effect of hydration products. In order to explore the effect of freeze-thaw on the long-term stability of Pb, Zn and Cd heavy metal contaminated soil, it was found that the freeze-thaw cycle promoted the soil pore to become larger and the structure to be loose, which destroyed the internal structure of the soil. The solidified heavy metals have the risk of increasing the leaching rate after entering the freeze-thaw cycle. Wang et al. found that with the increase of freeze-thaw cycles (FT<5), the freezing front gradually moved to the interior of the soil until the soil was completely frozen by the freeze-thaw effect of active MgO alkali-activated fly ash stabilized lead-contaminated soil. During this period, the water in the sample was redistributed, which promoted the hydration reaction of some curing agents with complete reaction, and the generated M-S-H and other gel encapsulated soil particles.

In summary, the freeze-thaw cycle will destroy the internal structure of the soil, increase the pores of the solidified soil, agglomerate the particles in the sample, and the large pores between the agglomerates account for the main proportion, which is the root cause of the deterioration of the engineering characteristics of the solidified soil of low-pressure solid lead contaminated soil. Therefore, when the heavy metal pollutants in the seasonal frozen soil area are repaired, the soil should be properly compacted and solidified to improve its frost resistance and increase the long-term effectiveness of the solid stability repair.

### 5.2. Dry-wet cycle

The stability of geopolymer solidified heavy metal contaminated soil under dry-wet cycle caused by rainfall-evaporation process still needs further evaluation.

In order to explore the effect of dry-wet cycle on the leaching characteristics of solidified body, Zhao Sanqing found that the integrity of the solid structure destroyed by dry-wet cycle and the increased pores of solidified soil by pressure pump test. Therefore, the contact area between heavy metal Pb and leaching solution is increased, which increases the risk of Pb leaching. Du Yanjun studied the leaching characteristics of a new type of steel slag-based stabilized nickel and zinc composite contaminated clay by improved dry-wet cycle test. The results show that with the increase of the number of dry-wet cycles, the leaching concentration of heavy metals in solidified soil decreases first and then increases. The high temperature and wetting conditions of drying-wetting cycles further promote the formation of hydrated calcium silicate (C-S-H), ettringite (AFt) and other gels and heavy metal hydroxide precipitation in solidified soil, thereby promoting the stability of heavy metals. With the increase of the number of dry-wet cycles, the clay mineral aggregates are disintegrated, the pores

of the soil increase, and the leaching concentration of heavy metals increases. Cha et al revealed that with the increase of dry-wet cycles, the concentration of heavy metal leaching solution of high calcium fly ash solidified contaminated soil showed a positive correlation when the concentration of heavy metal ions was low, and the concentration of heavy metal ions in the leaching solution remained basically unchanged when the concentration of heavy metals was high.

### **5.3. Carbonization**

Due to the influence of carbonization, the long-term properties of geopolymer solidified heavy metal contaminated soil in the actual environment have the risk of deterioration. In order to ensure the safety of secondary development and utilization of heavy metal solidified sites, it is of great significance to study the effect of carbonation on the chemical dissolution characteristics of solidified heavy metal contaminated soil.

Li found that heavy metals can be converted into water-insoluble oxides or hydroxides in an alkaline environment, and these products can be adsorbed by gel or physically encapsulated. Under the action of carbonization, heavy metal hydroxides will gradually react into carbonates. Therefore, carbonization is an important reason for changing the leaching concentration of heavy metals. Zhang et al studied the change of chemical dissolution characteristics of cement solidified heavy metal contaminated clay under carbonation. It was found that carbonation could affect the degree of acid/alkali buffering capacity of cement solidified soil, and the proportion of exchangeable state of lead in solidified contaminated soil increased, which verified the conclusion that the solubility of lead increased under carbonation.

## **6. SUMMARY**

As a new type of aluminosilicate inorganic polymer material with a three-dimensional network structure, geopolymer has been widely studied by scholars for its good solid heavy metal ability. The solidification mechanism of heavy metals mainly includes physical encapsulation, chemical bonding and adsorption. At present, geopolymer has made great progress in the field of solidification of heavy metal contaminated soil, but there are still some problems to be further studied.

(1) Due to the wide variety of geopolymers, alkali activators, soils in different regions and heavy metals, the effects of different types and contents of geopolymers on the stabilization of heavy metal contaminated soils are also different. Therefore, it is of great significance to carry out research on the reaction mechanism model of geopolymer and different contaminated soils. According to the types of heavy metals in contaminated soils and the properties of contaminated soils, considering the effects of silicon-aluminum ratio, curing temperature, types and contents of alkali activators and additives on the solidification of heavy metal ions, the most ideal geopolymer was developed.

(2) In recent years, scholars' research on geopolymer solidified contaminated soil is mostly limited to the laboratory research stage, and there are few studies applied to practical engineering practice. Therefore, the research field should gradually change to the direction of practical engineering application, so as to achieve market popularization.

(3) Based on the fact that the natural environment is an important external force affecting the effect of geopolymer on the stabilization of heavy metal contaminated soil, the research on the toxicity leaching of geopolymer solidified contaminated soil is mainly carried out under the single factors such as freeze-thaw cycle, dry-wet cycle and carbonization. However, in the actual process, the solidification of contaminated soil occurs under the coupling of many factors. Therefore, the study of geopolymer solidification of heavy metal contaminated soil under the coupling of various factors should be carried out according to the local natural environmental factors.

## CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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