

# Synthesis and heavy metal immobilization behaviors of slag based geopolymer

Zhang Yunsheng\*, Sun Wei, Chen Qianli, Chen Lin

*School of Materials Science and Engineering, Southeast University, Nanjing 210096, PR China*

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## Abstract

In this paper, two aspects of studies are carried out: (1) synthesis of geopolymer by using slag and metakaolin; (2) immobilization behaviors of slag based geopolymer in a presence of Pb and Cu ions. As for the synthesis of slag based geopolymer, four different slag content (10%, 30%, 50%, 70%) and three types of curing regimes (standard curing, steam curing and autoclave curing) are investigated to obtain the optimum synthesis condition based on the compressive and flexural strength. The testing results showed that geopolymer mortar containing 50% slag that is synthesized at steam curing (80 °C for 8 h), exhibits higher mechanical strengths. The compressive and flexural strengths of slag based geopolymer mortar are 75.2 MPa and 10.1 MPa, respectively. Additionally, Infrared (IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques are used to characterize the microstructure of the slag based geopolymer paste. IR spectra show that the absorptive band at 1086 cm<sup>-1</sup> shifts to lower wave number around 1007 cm<sup>-1</sup>, and some six-coordinated Al<sup>3+</sup> transforms into four-coordination during the synthesis of slag based geopolymer paste. The resulting slag based geopolymeric products are X-ray amorphous materials. SEM observation shows that it is possible to have geopolymeric gel and calcium silicate hydrate (C–S–H) gel forming simultaneously within slag based geopolymer paste. As for immobilization of heavy metals, the leaching tests are employed to investigate the immobilization behaviors of the slag based geopolymer mortar synthesized under the above optimum condition. The leaching tests show that slag based geopolymer mortar can effectively immobilize Cu and Pb heavy metal ions, and the immobilization efficiency reach 98.5% greater when heavy metals are incorporated in the slag geopolymeric matrix in the range of 0.1–0.3%. The Pb exhibits better immobilization efficiency than the Cu in the case of large dosages of heavy metals.

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## 1. Introduction

Recent years have seen a great development in new type of inorganic cementitious materials—geopolymer around the world. Geopolymer is one type of CaO-free aluminosilicate gel binders, which was firstly introduced into the inorganic cementitious world by Davidovits in the later 1970s [1]. Geopolymer can be synthesized by mixing aluminosilicate reactive materials with little or no CaO component (such as metakaolin, dehydrated clay) and strongly alkaline solutions (such as NaOH or KOH), then curing at room temperature. Under a strongly alkaline solution, aluminosilicate reactive materials are rapidly dissolved into solution to form free SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedral units. With the development of reaction, mix water is gradually

split out and these SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedral units are linked alternatively to yield polymeric precursors (–SiO<sub>4</sub>–AlO<sub>4</sub>–, or –SiO<sub>4</sub>–AlO<sub>4</sub>–SiO<sub>4</sub>–, or –SiO<sub>4</sub>–AlO<sub>4</sub>–SiO<sub>4</sub>–SiO<sub>4</sub>–) by sharing all oxygen atoms between two tetrahedral units, and thereby forming monolithic like geopolymer products [2].

Geopolymer made with reasonable mix-design and formulation can exhibit superior properties [3–6]: The production of geopolymer requires much lower calcining temperature (600–800 °C) and emits 80–90% less CO<sub>2</sub> than Portland cement. Reasonable strength can be gained in a short period at room temperature. In most cases, 70% of the final compressive strength is developed in the first 12 h. Low permeability, comparable to natural granite, is another property of geopolymer. It is also reported that resistance to fire and acid attacks for geopolymer are substantially superior to those for Portland cement. Apart from the high early strength, low permeability and good fire and acid resistance, geopolymer also can attain higher unconfined compressive strength and shrink much less than Portland cement.

\* Corresponding author. Tel.: +86 2583795374.

E-mail address: [zhangys279@163.com](mailto:zhangys279@163.com) (Z. Yunsheng).

Table 1  
Chemical compositions and physical properties of raw materials

Types of raw materials	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	MnO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	LOI	Specific surface (m <sup>2</sup> /kg)
Metakaolin	62.97	26.91	2.62	0.60	–	1.24	0.01	0.18	0.74	–	4.44	350
Slag	34.20	14.20	0.43	41.70	6.70	1.07	0.3	–	–	1.47	1.02	490

Other documented properties include good resistance to freeze-thaw cycles as well as excellent solidification of heavy metal ions. These properties make geopolymer have great potentials in the fields of civil, bridge, pavement, waste treatment, hydraulic, underground and military engineering [7].

Blast furnace slag is formed in the processes of iron manufacture from iron ore, combustion residue of coke, and fluxes such as limestone or serpentine and other materials. If the molten slag is rapidly chilled by immersion in water, a vitreous Ca–Al–Mg silicate fine grain glass is formed with a highly cementitious nature. At present, most of the slag is utilized in fields of Portland cement industry or concrete production companies. Only in China, over 100 million tonnes of slag is generated annually. Slag contain much reactive SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and can be a good raw material for partially substituting metakaolin to synthesize high-value geopolymer, which can be utilized in heavy metal immobilization applications.

Each year, millions of tonnes of heavy metal containments such as mine tailings and electroplating sludge are generated across the worlds. These wastes are accumulated to such an extent that ‘giga-scale disposal’ is becoming a common phenomenon. In general, Cu and Pb are two prominent heavy metals in the wastes as compared to other types of heavy metals [8]. Thus studies on the immobilization of Cu and Pb are very important for testing a new type of heavy metal solidification materials.

The synthesis and heavy metal immobilization behaviors of geopolymer by using metakaolin alone [9–11] or slag alone [12–19] have been systematically studied. However, little research is done in the synthesis and immobilization behaviors of geopolymer by using both metakaolin and slag [20–25]. Our primary researches suggest that the addition of slag will greatly increase the mechanical strength and improve the pore structure of the hardened geopolymeric matrix [26]. Thus the geopolymer incorporated with slag will be expected to possess superior immobilization capacity to the pure geopolymer without any slag addition. In order to better understand the immobilization behaviors of the geopolymer incorporated with slag, two aspects of studies are conducted in this paper: (1) synthesis of geopolymer by using both slag and metakaolin; (2) immobilization behaviors of slag based geopolymer in a presence of Pb and Cu ions.

## 2. Experimental

### 2.1. Materials

Metakaolin used in this study is obtained by calcining pure kaolin at 700 °C for 12 h. Blast furnace slag is supplied by Jiangnan cement plant, Jiangsu province, PR China. Chemical grade

NaOH and sodium silicate solution with the molar ratio of SiO<sub>2</sub> to Na<sub>2</sub>O of 3.2 are used as alkaline reagents. River sand as fine aggregate is incorporated into slag based geopolymer paste to achieve reasonable strengths ( $\geq 30$  MPa) and limited shrinkage ratio ( $\leq 350 \times 10^{-6}$ ) in this study. The fineness modulus of river sand is 2.8. Analytical grade Cu(NO<sub>3</sub>)<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub> are used as heavy metal contained resource. All experiments are performed using the same batches of reagents and starting materials. Distilled water is used throughout the experiment. The chemical compositions and physical properties of raw materials are listed in Table 1. The particle size distribution of raw materials is also shown in Fig. 1.

### 2.2. Experimental program

#### 2.2.1. Synthesis of slag based geopolymer

In this part, a total of 10 batches of geopolymer with different compositions are made in this study. The details of experimental program are given in Table 2. Batch ‘‘PSS’’ to Batch ‘‘SL70PSS’’ are used to compare the influence of slag content on mechanical strength. Batch ‘‘SL50PSS-D3’’ to Batch ‘‘SL50PSS-T150-2h’’ is specifically designed to optimize the curing regime. In order to investigate the effect of the steam curing time, Batch ‘‘SL50PSS-T80-2h’’ to Batch ‘‘SL50PSS-T80-8h’’ are prepared. Through the above studies, the optimum slag content and curing regime can be determined.

It is important to point out that Batch ‘‘PSS’’ is served as a control sample which is synthesized only by metakaolin, no any addition of slag. The oxidants molar ratio of Batch ‘‘PSS’’ that is optimized and used in literature [27] is as follows: SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 4.5, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 0.8, H<sub>2</sub>O/Na<sub>2</sub>O = 6.4.

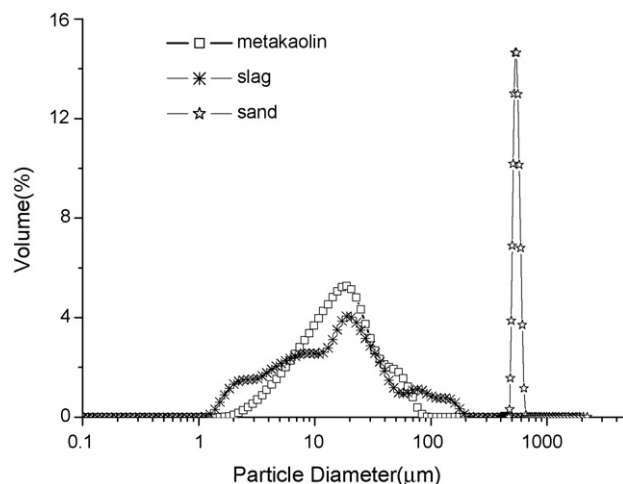


Fig. 1. Particle size distribution of raw materials.

Table 2  
Experimental program

Types of geopolymer	Binders		Binders:sand (by mass)	Curing regimes
	Metakaolin (%)	Slag (%)		
PSS	100	0	1:1	20 °C and RH 100% for 28 days
SL10PSS	90	10	1:1	20 °C and RH 100% for 28 days
SL30PSS	70	30	1:1	20 °C and RH 100% for 28 days
SL50PSS	50	50	1:1	20 °C and RH 100% for 28 days
SL70PSS	30	70	1:1	20 °C and RH 100% for 28 days
SL50PSS-D3	70	30	1:1	20 °C and RH 100% for 3 days
SL50PSS-T80-2h	70	30	1:1	80 °C and RH 100% for 2 h
SL50PSS-T80-4h	70	30	1:1	80 °C and RH 100% for 4 h
SL50PSS-T80-8h	70	30	1:1	80 °C and RH 100% for 8 h
SL50PSS-T150-2h	70	30	1:1	Autoclave curing at 150 °C for 2 h

Note. PSS represents pure geopolymer without any slag addition.

### 2.2.2. Immobilization behaviors of slag based geopolymer

In this part, geopolymer mortar synthesized under the optimum condition is used to investigate the immobilization behaviors of heavy metal ions. Two types of heavy metal ions— $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  in the format of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  are added to slag based geopolymer mixture during mixing as a solution of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  in water. Three different concentrations of 0.1%, 0.2% and 0.3% (accounting for the total mass of binders) are used for each type of heavy metal ions. Table 3 summarizes the compositions of slag based geopolymer under discussion.

Batch “SL50PSSCu1” to Batch “SL50PSSCu3” are used to investigate the influence of  $\text{Cu}^{2+}$  concentration on the immobilization behaviors of slag based geopolymer; Batch “SL50PSSPb1” to Batch “SL50PSSPb3” are used to study the influence of  $\text{Pb}^{2+}$  concentration on the immobilization behaviors.

### 2.3. Specimen preparation for mechanical test

Metakaolin and slag are firstly dry-mixed for 3 min in a Hobart-mixer. Then, NaOH, sodium polysilicate solution and water are mixed and cooled to room temperature. The cooled alkaline solution is added into pre-mixed slag plus metakaolin powders and mixed for another 3 min. After that, sand is placed into slag based geopolymer paste and mixed for 3 min. The fresh geopolymer mortar is poured into cubic steel moulds

with 40 mm × 40 mm × 40 mm for compressive strength and prismatic steel moulds 40 mm × 40 mm × 160 mm for flexural strength, then vibrated for 30 s. A plastic film is covered on the opening surface of moulds to prevent the evaporation of mixing water. After 24 h, the samples are demoulded and cured under scheduled regimes. Three samples are tested for each mechanical test. Herein it is important to point out that the pre-mix of NaOH and sodium silicate, rather than the direct addition of NaOH powder into geopolymer pastes is a key to ensure a enough long pot life to complete the above process.

### 2.4. Sample preparation for microanalysis

The slag based geopolymer paste without sand addition is specially prepared according to the procedure described in Section 2.3. The only difference in mixture proportions between geopolymer paste and geopolymer mortar is that geopolymer paste has not sand addition. Some of geopolymer paste samples are used to conduct ESEM-EDXA analysis. The others are further finely crushed, and then immersed in an ethanol for 3 days to stop the further geopolymerization reaction of geopolymeric cement, subsequently oven-dried at 60 °C for 6 h to remove the absorbed water. After that, these hardened geopolymeric cement paste fractions are further ground into very fine particles with agate mortar, and remove the coarse particles with the sieve of 80 μm in diameter. The fine powders are placed in desiccators for 24 h to conduct XRD, IR microanalysis.

Table 3  
Compositions of slag based geopolymer contained heavy metals

Types	Contaminant (%)	Binders		Binders:sand (by mass)	Water:binders (by mass)
		Metakaolin (%)	Slag (%)		
SL50PSSCu1	Cu 0.1			1:1	0.35
SL50PSSCu2	Cu 0.2	50	50	1:1	0.35
SL50PSSCu3	Cu 0.3	50	50	1:1	0.35
SL50PSSPb1	Pb 0.1	50	50	1:1	0.35
SL50PSSPb2	Pb 0.2	50	50	1:1	0.35
SL50PSSPb3	Pb 0.3	50	50	1:1	0.35

Note. SL50PSS represents slag based geopolymer synthesized under the optimum condition; Cu1 to Pb3 represents the types and amount of heavy metal ions.

## 2.5. Methods

### 2.5.1. Mechanical tests

Flexural strength and compressive strength are tested according to ASTM C39-96. Three samples of each batch are tested. The average value of three samples is served as the final compressive strength and flexural strength. A closed-loop servohydraulically controlled materials testing machine (Sintech 10/D MTS 810) is used to conduct flexural and compressive test.

### 2.5.2. Leaching tests

After mechanical tests, fragments of geopolymeric specimens are collected and used as the samples for leaching tests. A modified toxicity characteristic leaching procedure (TCLP) leaching test [28,29] is conducted to simulate an more aggressive leaching environment than normally used TCLP in this study for acquiring the necessary kinetic leaching data in a short time. The detailed procedure is as follows.

Samples collected from the compression test are firstly crushed and sieved into small particle size fractions. Particles of size fraction ranging from 0.6 mm to 2.5 mm are placed in an acetic acid solution buffered with sodium acetate at a pH of 3.3 for the leaching analysis. A solid:liquid ratio of 1:25 is used for the leaching tests and the temperature is maintained at 30 °C by a water bath. All samples are stirred at the mixing speed of 200 rpm by using the sealed magnetic stirring apparatus for 24 h, which allowed for leaching equilibrium to be attained in around 24 h the leachate solution is extracted by syringe at 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, 4.0 h, 8.0 h, 12.0 h and 24 h, respectively, and the total extracting volume never exceeded 10% of the fluid volume, thus creating an average error of 5%. The extracted solutions are centrifuged and filtered by using filter paper. The filtrate is diluted 20 times with 5% volume concentration of nitric acid and the concentrations of all metals are determined using Perkin-Elmer Optima 2000 ICP-AES (Perkin-Elmer, Norwalk, CT, USA).

## 3. Results and discussion

### 3.1. Synthesis of slag based geopolymer

#### 3.1.1. Optimization of slag content

In order to study the influence of slag replacement percentage, 10%, 30%, 50% and 70% by mass of the total amount of metakaolin are substituted by slag (Batch SL10PSS to Batch SL70PSS). Batch PSS is served as a referee sample without any slag addition. The water to binders (metakaolin plus slag) mass ratios and binders to sand mass ratio of all batches are fixed at 0.35 and 1:1, respectively. The compressive and flexural strength of geopolymeric mortars with different amount of slag are shown in Figs. 2 and 3. As can be seen, addition of slag leads to a great increase in both compressive and flexural strength. It is especially obvious when the replacement percentage exceeds 30%. As compared to referee sample (Batch PSS), the compressive strength of geopolymeric mortars incorporated with slag is increased by 2.5–100%, flexural strength by 32.6–54.3%. It is

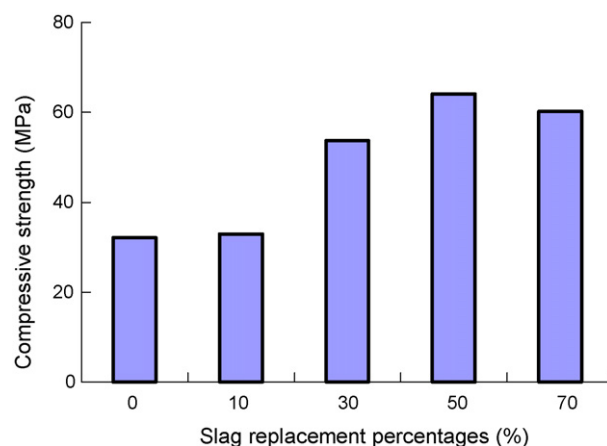


Fig. 2. Effect of slag replacement percentages on compressive strength.

worth pointing out that the mechanical properties of geopolymeric mortar with 50% slag are the highest among all slag based geopolymeric mortars whose compressive strength and flexural strengths are 64.1 MPa and 8.01 MPa, respectively. Based on the above analysis, 50% slag is selected as the optimum replacement percentage in the study.

#### 3.1.2. Selection of the optimum curing regime

Three types of curing regimes are employed in the study: (1) standard curing: 20 °C and RH 100% for 3 days; (2) steam curing: 80 °C and RH 100% for 2 h, 4 h and 8 h; (3) autoclave curing: 150 °C for 2 h.

The effects of three different types of curing regimes on the compressive and flexural strength of slag based geopolymer are shown in Fig. 4. It is found that curing regimes have great impact on mechanical strengths of slag based geopolymer. Slag based geopolymer under standard curing regime has the lowest strength. However, when steam curing is employed to slag based geopolymer, compressive and flexural strengths show an obvious increase. Only through 2-h steam curing, 9.4 MPa compressive strength is gained that is 19.14% higher than 3-day standard curing. As the time of steam curing increases, the enhancement of steam curing is more effectively exhibited. Four and 8 h steam curing can obtain 46.03% and 53.16% higher compressive strength than 3-day standard curing. Autoclave curing

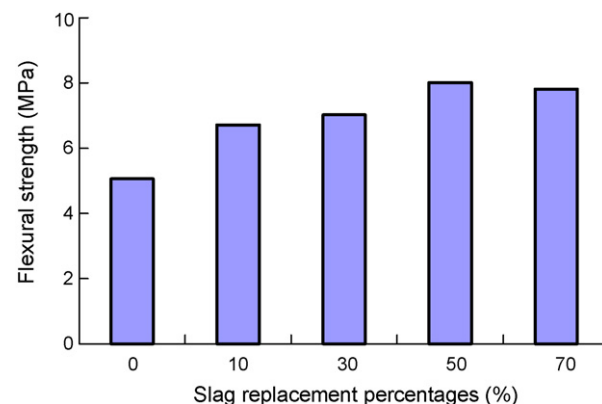


Fig. 3. Effect of slag replacement percentages on flexural strength.



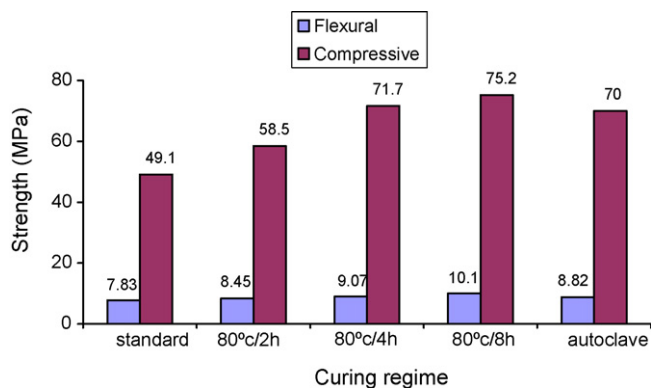


Fig. 4. Effect of curing regimes on mechanical strengths.

shows more attractive strength enhancement than steam curing. It is only through 2-h autoclave curing that 70.0 MPa compressive strength is achieved, which is 19.66% higher than 2-h steam curing. The above analysis indicates that elevating temperatures can significantly increase the reaction rate, accelerate the formation of products, resulting in high strength.

Fig. 4 also illustrates the effects of three different types of curing regimes on the flexural strength of slag based geopolymer. As can be seen from Fig. 4, the effects of curing regimes on flexural strength have a similar tendency as compressive strength, but the influencing extent is less for flexural strength than that for compressive strength. For instance, 8-h steam curing can only gain 28.99% higher flexural strength than 3-day standard curing, while 8-h steam curing can provide 53.16% higher compressive strength than 3-day standard curing.

Based on the above experimental results, it can be seen that autoclave curing is most effective in improving mechanical strength of slag based geopolymer among three types of curing regimes, but its high energy consumption and complex operation limit the curing regime widely to be applied in practices. Standard curing has such advantages as easy operation and lower energy consumption. However, mechanical strength of slag based geopolymer cannot be effectively developed under the curing condition in relatively short curing ages. Steam curing combines these merits of the other two curing regimes. As a result, 8-h steam curing is selected as the optimum curing regime in this study and adopted in all the following tests.

Based on the above selected optimum replacement percentage of slag and curing regime, SL50PSS-T80-8h is used as the final slag based geopolymeric matrix of heavy metal immobilization in the following study.

### 3.1.3. Microstructure of slag base geopolymer

**3.1.3.1. X-ray diffraction (XRD).** As can be seen from Fig. 5, slag based geopolymer have a large diffuse halo peak at about 20–40° ( $2\theta_{\max}$  Cu  $K\alpha$ ). This means that the slag based geopolymeric products are mainly X-ray amorphous materials. In addition, several sharp characteristic peaks (7.09 Å, 4.23 Å, 3.33 Å, 1.81 Å, 1.54 Å, 1.37 Å) are also seen from Fig. 5. According to the XRD pattern, these peaks are identified as quartz. With the respect to X-ray diffractogram of metakaolin, the quartz is

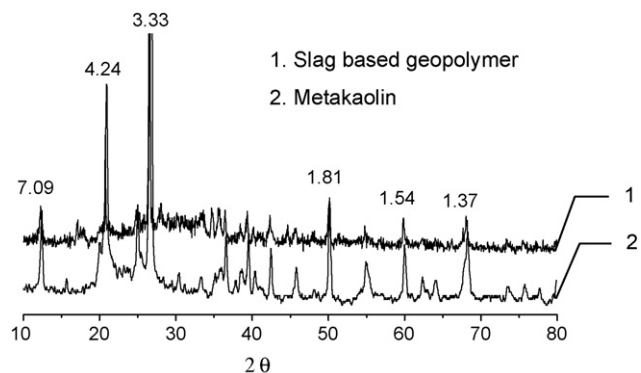


Fig. 5. X-ray diffractograms of metakaolin and slag based geopolymer.

induced by metakaolin, and these quartzes do not take part in the chemical reaction.

**3.1.3.2. Infrared analysis (IR).** The infrared spectra of metakaolin and slag based geopolymer are given in Fig. 6. The chemical shifts of main IR characteristic bands and corresponding species are also listed in Table 4.

Comparing IR spectra of metakaolin and slag base geopolymer, it can be observed that:

- (1) During geopolymerization, the prominent band at  $1086\text{ cm}^{-1}$  presented in IR spectrum of metakaolin shifts towards a lower wave number. The corresponding IR band of slag based geopolymer is  $1007\text{ cm}^{-1}$ . According to Table 4,  $1086\text{ cm}^{-1}$  band is caused by symmetrical vibration of Si–O bond, while  $1007\text{ cm}^{-1}$  band by asymmetrical vibration of Si–O bond. The shift toward the low wave number may be attributed to the partial replacement of  $\text{SiO}_4$  tetrahedron by  $\text{AlO}_4$  tetrahedron, resulting in a change in the local chemical environment of Si–O bond.
- (2) A  $914\text{ cm}^{-1}$  and  $798\text{ cm}^{-1}$  bands in IR spectrum of metakaolin cause by six-coordinated Al–OH stretching vibration and six-coordinated Al–O stretching vibration, respectively, become very weak in IR spectrum of slag based geopolymer. This means that six-coordinated Al

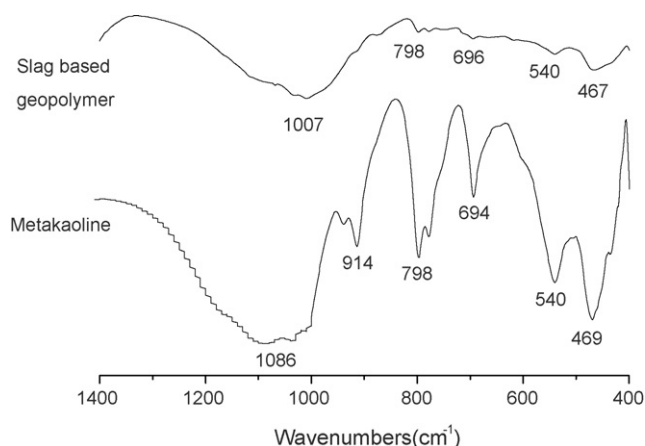


Fig. 6. IR spectra of metakaolin and slag based geopolymer.

Table 4  
IR bands and corresponding species of metakaolin and slag based geopolymer

Types of species	Metakaolin	Slag based geopolymer
Si–O	1086 cm <sup>-1</sup> (symmetrical vibration)	1007 cm <sup>-1</sup> (asymmetrical vibration)
Al–OH	914 cm <sup>-1</sup> (six-coordinated Al–OH stretching vibration)	Neglectable
Al–O	798 cm <sup>-1</sup> (six-coordinated Al–O stretching vibration)	Very weak
Si–O	694 cm <sup>-1</sup> (symmetrically stretching vibration)	Very weak
Si–O–Al	540 cm <sup>-1</sup> (bending vibration)	540 cm <sup>-1</sup> (bending vibration)
Si–O	469 cm <sup>-1</sup> (in-plane bending vibration)	467(in-plane bending vibration)

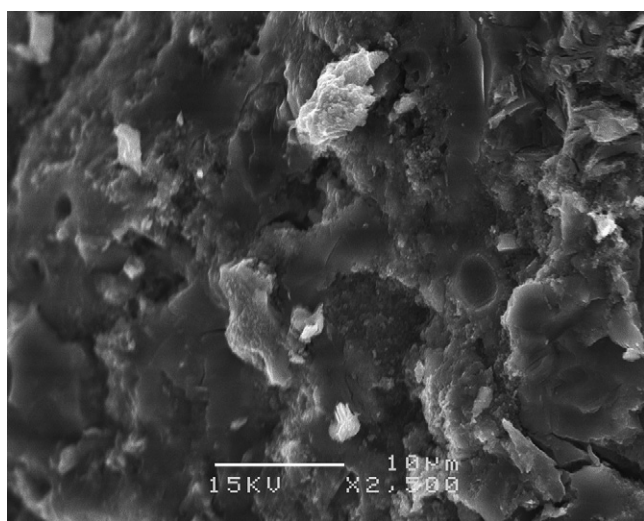


Fig. 7. SEM micrograph of pure geopolymeric matrix without slag addition.

will transform into other coordination in the process of hydration reaction.

**3.1.3.3. Scanning electron microscopy (SEM).** A JEOL-6300 scanning electron microscope with an energy dispersive X-ray analysis (SEM-EDXA) system is utilized to examine the micrographics of geopolymeric matrices. Figs. 7 and 8 are the typical SEM micrographics of pure geopolymeric matrix without slag addition, and geopolymeric matrix containing 50% by mass of

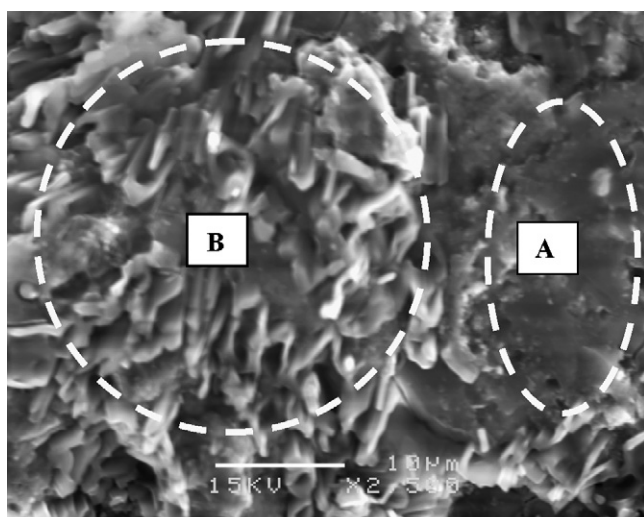


Fig. 8. SEM micrograph of slag based geopolymeric matrix.

slag. As can be seen in Figs. 7 and 8, the microstructure of the pure geopolymeric matrix is quite different from that of the slag based geopolymeric matrix. Only one homogeneous phase is observed in the pure geopolymeric matrix. Comparatively two separate phases (phases A and B) are clearly seen in the slag based geopolymeric matrix. EDXA analysis is conducted on the two sample and the results are listed in Table 5. It was found that the elemental composition of phase A was dominated by Si, Al and Na as well as very little Ca, while the elemental composition of phase B is dominated by Si, and Ca with some Na and little Al. This indicates that phases A and B are totally different in terms of their elemental composition. According to the chemical compositions and Si:Al:Na (=2.18:1.0:1.15), it is suggested that phase A might be a geopolymeric binder, which has similar characteristics to the PSS type of geopolymeric binder formed in the absence of slag as shown in Fig. 7. This observation is also consistent with previous observations by Yip et al. [20,21]. Considering that Si, and Ca are the main elements in the phase B, while Na and Al are of low concentrations, it is suggested that phase B might be some form of C–S–H (calcium silicate hydrate). However, it is believed that this C–S–H is not the normal gel products produced during the hydration process of Portland cement because of the low the much lower Ca/Si ratio (0.98). It should belong to the amorphous calcium silicate generated during the hydration process of alkali slag cement, the Ca/Si ratio of whose gel products is approximately 1.1. The Al presented within phase B may be due to some Si substitution by Al. Consequently, the Na in phase B is used to play a charge-balancing role for Si substitute by Al.

### 3.2. Immobilization behavior of slag based geopolymer

#### 3.2.1. Mechanical strength

The mechanical strengths of slag based geopolymer (SL50PSS) contained different types and amount of heavy metals are tested and listed in Table 6. It can be seen that the inclusion

Table 5  
The average elemental compositions of pure geopolymer matrix and slag based geopolymer matrix (%)

Types of geopolymers	Silicon (Si)	Aluminum (Al)	Sodium (Na)	Calcium (Ca)
Pure geopolymer	49.76	24.39	25.43	0.42
Slag based geopolymer				
Phase A	48.66	22.29	25.68	3.36
Phase B	38.39	9.30	14.57	37.74

Table 6

Mechanical strengths of slag based geopolymer contained different types and amount of heavy metals (MPa)

Gepolymeric matrix	Containment (%)	Mechanical strength (MPa)	
		Compressive	Flexural
SL50PSS	0	75.20	10.10
	Cu 0.1	73.52	9.60
	Cu 0.2	70.68	9.38
	Cu 0.3	66.81	9.44
	Pb 0.1	72.65	9.57
	Pb 0.2	72.93	8.23
	Pb 0.3	70.28	8.85

of heavy metals have certain influence on the mechanical properties of slag based geopolymer in terms of compressive and flexural strengths. A slight reduction in mechanical strength is observed when 0.2% or less heavy metal is incorporated into the slag based geopolymeric matrix. However, a further increase in heavy metal dosage will result in an obvious strength drop. This indicates that slag based geopolymeric matrix has a limited capacity for the amount of heavy metals that its structure can tolerate before structural integrity is destroyed. Exceeding the tolerant limit will result in a dramatic strength reduction and rapid heavy ion leaching out.

### 3.2.2. Leaching behaviors

Leaching test is a very powerful tool to determine the immobilization efficiencies of different system and concentrations of heavy metals in complex system. Kinetic leaching tests are conducted with sampling done specified in this experimental program until leaching equilibrium (about 24 h) is reached. Batch “SL50PSSCu1” to Batch “SL50PSSCu3”, Batch “SL50PSSPb1” to Batch “SL50PSSPb3” contained the same type, but different concentrations of heavy metal ions, therefore leaching results can determine the influence of concentration of heavy metal ions on immobilization behaviors. SL50PSSCu1 and SL50PSSPb1, SL50PSSCu2 and SL50PSSPb2, SL50PSSCu3 and SL50PSSPb3 contain the identical amounts, but different types of heavy metals, therefore leaching results can be used to distinguish the influence of types of heavy ions on immobilization behaviors on the same basis. Fig. 9 shows the kinetic leaching curves for SL50PSSCu1 to

Table 7

Immobilization efficiencies of slag based geopolymeric matrix (SL50PSS) contained different types and amount of heavy metals

Matrix	Containment (%)	Immobilization efficiency (%)
SL50PSS	Cu 0.1	99.66
	Cu 0.2	99.52
	Cu 0.3	98.67
	Pb 0.1	99.27
	Pb 0.2	99.28
	Pb 0.3	98.84

SL50PSSPb2. The corresponding immobilization efficiencies are also calculated and listed in Table 7 in terms of the equilibrium values obtained in Fig. 9.

As can be seen in Fig. 9, heavy metals are rapidly leached out from the hardened slag based geopolymeric matrix with an increase in leaching time, especially in the initial hours. After that, the leached rate starts to become very slow and the leaching curves gradually level off. The leaching equilibrium can be reached at approximately 4 h in this study. In addition, the leaching behaviors of heavy metals are also influenced by the amount of heavy metals. When less heavy metal is added to the geopolymeric matrix, such as 0.2% or less, the amount of the leached heavy metals is almost ignorable. As a result, the final immobilization efficiency reaches 99% or greater, as shown in Table 7. However, too much heavy metal is introduced, the immobilization capacity will rapidly reduced, which can be clearly seen in Fig. 9 and Table 7. This tendency seems to be consistent with the mechanical strengths, as shown in Table 6. Although an increase in the heavy metal amount will lead to a reduction in the immobilization efficiency, over 98.5% heavy metals incorporated can be still immobilized in the slag based geopolymeric matrix after 24 h leaching test. It is important to note that for slag based geopolymeric matrix, the Pb ion seems to leach slightly less than the Cu in the case of large dosages of heavy metals, regardless of the leaching time, as shown in Fig. 9. This fact could be partially attributed to the differences in ionic radius between Pb (0.12 Å) and Cu (0.72 Å) or the chemical interaction with the slag based geopolymeric matrix forming components during synthesis resulting in different roles played by Cu and Pb in the final product.

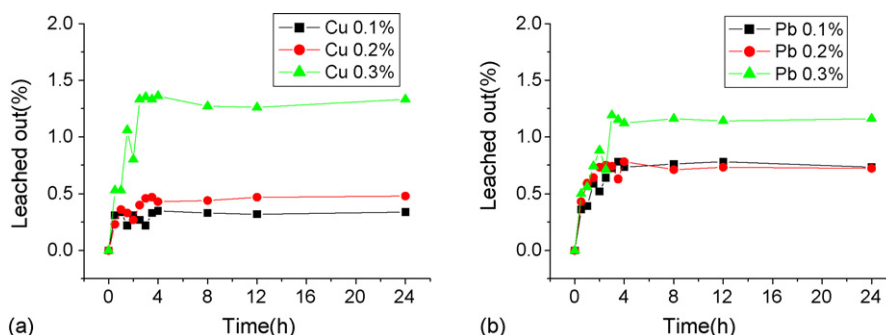


Fig. 9. Kinetic leaching curve of slag based geopolymeric matrix (SL50PSS) contained different types and amount of heavy metals: (a) leaching of Cu; (b) leaching of Pb.

#### 4. Conclusion

In this paper, two aspects of studies are conducted: (1) synthesis of geopolymer manufactured by slag and metakaolin; (2) immobilization behaviors of slag based geopolymer in a presence of Pb and Cu. Through the study, it is concluded that geopolymer containing 50% slag that is synthesized at steam curing (80 °C for 8 h), exhibited higher mechanical strength. The compressive and flexural strengths of slag based geopolymer reach 75.2 MPa and 10.1 MPa, respectively. Leaching tests shows that slag based geopolymer synthesized under the above optimum condition can effectively immobilize Cu and Pb heavy metals, and the immobilization efficiency exceeds 98.5% when the amount of heavy metals contained in slag based geopolymeric matrix is in the range of 0.1–0.3% by mass of binders. It is worth noting that Pb shows better immobilization efficiency than the Cu in the case of large dosages of heavy metals.

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#### References

- [1] J. Davidovits, Geopolymers and geopolymeric new materials, *J. Therm. Anal.* 35 (2) (1989) 429–441.
- [2] J. Davidovits, M. Davidovits, Geopolymer: ultrahigh-temperature tooling material for the manufacture of advanced composites, in: R. Adsit, F. Gordaninejad (Eds.), *Proceedings of the 36th Annual SAMPE Symposium and Exhibition*, vol. 36, pt 2, Covina, CA, USA, 1991, pp. 1939–1949.
- [3] J. Davidovits, Geopolymer cement to minimize carbon-dioxide greenhouse-warming, in: M. Moukwa, S.L. Sarkar, K. Luke, M.W. Grutzeck (Eds.), *Cement-Based Materials: Present, Future, and Environmental Aspects*, vol. 37, American Ceramic Society, Ceramic Transactions, Westerville, America, 1993, pp. 165–182.
- [4] J. Davidovits, Properties of geopolymer cement, in: F. Škvára (Ed.), *Proceedings of the First International Conference on Alkaline Cements and Concretes*, Scientific Research Institute on Binders and Materials, Kiev State Technical University, Kiev Ukraine, 1994, pp. 131–149.
- [5] R.E. Lyon, A. Foden, P.N. Balaguru, M. Davidovits, J. Davidovits, Fire-resistant aluminosilicate composites, *J. Fire Mater.* 21 (2) (1997) 67–73.
- [6] J. Davidovits, High alkali cements for 21st century concretes, in: P.K. Mehta (Ed.), *Concrete Technology, Past, Present and Future*, vol. SP-144, American Concrete Institute, Detroit, 1994, pp. 383–397.
- [7] J. Davidovits, Geopolymer chemistry and properties, in: J. Davidovits, J. Orlinl (Eds.), *Proceedings of the First European Conference on Soft Mineralogy*, vol. 1, The Geopolymer Institute, Compiègne, France, 1988, pp. 25–48.
- [8] J.W. Phaira, J.S.J. Van Deventer, J.D. Smith, Effect of Al source and alkali activation on Pb and Cu immobilization in fly-ash based geopolymers, *Appl. Geochem.* 19 (3) (2004) 423–434.
- [9] J. Davidovits, Method for obtaining a geopolymer binder allowing to stabilize, solidify and consolidate toxic or waste materials, International Patent Application, PCT/FR91/00689WO92/04298, 1992.
- [10] J. Davidovits, D.C. Comrie, J.H. Paterson, D.J. Ritcey, Geopolymeric concretes for environmental protection, *Concrete Int. Des. Constr.* 12 (7) (1990) 30–40.
- [11] D.C. Comrie, J. Davidovits, Waste containment technology for management of uranium mill tailings, in: *Proceedings of the 117th Annual Meeting of the Society of Mining Engineers*, Phoenix, AZ, USA, January 25, 1988.
- [12] S. Wang, X. Pu, K.L. Scrivener, P.L. Pratt, Alkali-activated slag cement and concrete: a review of properties and problems, *Adv. Cement Res.* 7 (27) (1995) 93–102.
- [13] D. Wang, S. Yan, Mechanism of solidified Cs<sup>+</sup> in simulated high level radioactive waste by alkali activated slag cement, *J. Chinese Ceram. Soc.* 32 (1) (2004) 90–94.
- [14] F.G. Collins, Workability and mechanical properties of alkali activated slag concrete, *Cement Concrete Res.* 29 (3) (1999) 455–458.
- [15] E. Douglas, A. Bilodeau, J. Brandstet, V.M. Malhotra, Alkali activated ground granulated blast-furnace slag concrete. Preliminary investigation, *Cement Concrete Res.* 21 (1) (1991) 101–108.
- [16] T. Bakharev, J.G. Sanjayan, C. Yibing, Alkali activation of Australian slag cements, *Cement Concrete Res.* 29 (1) (1999) 113–120.
- [17] G. Qian, D.D. Sun, J.H. Tay, Immobilization of mercury and zinc in an alkali-activated slag matrix, *J. Hazard. Mater.* 101 (1) (2003) 65–77.
- [18] D. Jan, Immobilization of Cr<sup>6+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> in alkali-activated slag binders, *Cement Concrete Res.* 32 (12) (2002) 1971–1979.
- [19] S. Caijun, L.D. Robert, *Alkali-Slag Cements for the Immobilization of Radioactive Wastes*, vol. 1240, ASTM Special Technical Publication, 1996, pp. 163–173.
- [20] C.K. Yip, G.C. Lukey, J.S.J. Van Deventer, The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation, *Cement Concrete Res.* 35 (9) (2005) 1688–1697.
- [21] C.K. Yip, J.S.J. Van Deventer, Microanalysis of calcium silicate hydrate gel formed within a geopolymeric binder, *J. Mater. Sci.* 38 (18) (2003) 3851–3860.
- [22] I. Lecomte, M. Liegeois, A. Rulmont, R. Cloots, F. Maseri, Synthesis and characterization of new inorganic polymeric composites based on kaolin or white clay and on ground-granulated blast furnace slag, *J. Mater. Res.* 18 (11) (2003) 2571–2579.
- [23] C.K. Yip, G.C. Lukey, J.S.J. Van Deventer, Effect of blast furnace slag addition on microstructure and properties of metakaolin geopolymeric materials, *Proceedings of the Advances in Ceramics Matrix Composites IX*, Ceramic Transactions, vol. 153, 2004, pp. 187–209.
- [24] Y.H. Ahmed, N.R. Buenfeld, Investigation of ground granulated blastfurnace slag as a toxic waste solidification/stabilization reagent, *Environ. Eng. Sci.* 14 (2) (1997) 113–132.
- [25] G. Qian, Y. Li, F. Yi, R. Shi, Improvement of metakaolin on radioactive Sr and Cs immobilization of alkali-activated slag matrix, *J. Hazard. Mater.* 92 (3) (2002) 289–300.
- [26] Z. Yunsheng, Research on Structure Formation Mechanism and Properties of High Performance Geopolymer Concrete, Ph.D. Thesis, Southeast University, Nanjing, PR China, 2004.
- [27] Z. Yunsheng, Impact Behavior and Microstructural Characteristics of PVA Fiber Reinforced Fly Ash-Geopolymer Boards Prepared by Extrusion Technique, vol. 41, no. 10, 2006, pp. 2787–2794.
- [28] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, Factors affecting the immobilization of metals in geopolymerised fly ash, *Metall. Mater. Trans. B* 29 (1) (1998) 283–291.
- [29] US Government, Toxicity characteristic leaching procedure (TCLP), Federal Register 55, 1990, 11798–11877.