Immobilization of Heavy Metals by Fly Ash-Based Geopolymer

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Abstract

This work was focused on immobilization of several types of heavy metal included Ni, Cd and Zn by geopolymer. Effect of each heavy metal on compressive strength was also reported in this work. Initial concentrations of each heavy metal in geopolymer were varied as 1, 7 and 10% by weight. It was found that compressive strengths of heavy metal-contaminated geopolymer were decreased when the initial concent rations of heavy metal increased. Among investigated heavy metal, Ni provided the least adverse affect on compressive strength (168.6 ksc. with 10% by weight of Ni initial concentration) while Zn exerted the most negative affect on compressive strength (80 ksc. with 10% by weight of Zn initial concentration). From TCLP test, the leaching value of nickel from geopolymer was lowest as the leaching value was less than 10 mg/l. In contrast, the leaching value of Cd and Zn were approximately 400 mg/l. In overall consideration, the synthesized geopolymer can be used in immobili-zation of heavy metal.

Keywords: Geopolymer, Leaching, Heavy Metals, Cadmium, Nikel, Zinc, Compressive Strength

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Introduction

The reaction of solid aluminosilicate with a highly concentrated aqueous alkali hydroxide of silicate solution produces a synthetic alkali aluminosilicate material generically called a 'geopolymer' (Davidovits, 1984; Duxson et al., 2007). It can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fire resistance and low thermal conductivity. According to cement production, one ton of cement product can release one ton of CO_2 to the atmosphere. CO_2 is one of the major gas among several greenhouse gases causing global warming. From its excellent mechanical property and environmental friendly production, geopolymer was considered as 'cement in the future'. Nowaday, geopolymer concretes are widely used in various types of infrastructure construction. Recently, geopolymers were introduced to be use for immobilization and stabilization of low-level radioactive waste of pure or contaminated (mixed waste) forms as well as heavy metals (Phair et al., 2007). It was found that toxic heavy metals tends to be immobilized by geopolymer with excellent long-term structure, chemical and microbial stability, satisfying high standards contaminant retention (Shimaoka et al., 2007). However, few works have been done to explore leachability of heavy metals from geopolymer matrix. This research were aimed to investigate microstructure of geopolymer with different heavy metals, compressive strength of geopolymer and leachability of three heavy metals (Ni, Cd and Zn) from fly ash based geopolymer using TCLP method (US.EPA).

Materials and Method

Materials

Fly ash was obtained from Mae Moh Electricity Generating Authority in Thailand. The chemical composition was shown in Table 1. NiO, CdO and ZnO were used as heavy metal contained resources. Sodium silicate (Na_2SiO_3), sodium hydroxide (NaOH) and distilled water were used throughout all experiments. All chemicals in this work were lab grade and used without purified.

Table 1. Chemical composition of original fly ash

composition	% by weight
SiO_2	30.50
Al_2O_3	17.90
Fe_2O_3	17.30
CaO	21.40
MgO	1.80
Na_2O	3.58
K_2O	1.92
SO_3	3.79
LOI	1.81

Synthesis

Each type of heavy metal with initial concentrations as 1% 7% and 10% by weight was individually added to fly ash. A solution of NaOH 10 M was mixed with fly ash. Meanwhile, solution containing sand was added slowly. Consequently, sodium silicate, with weight ratio of SiO_2/Na_2O as 3.0, and distilled water were added to the mixer. Plastic molds (5 mm∅ x 10 mm H) were used in specimen casting.

Geopolymer characterization

The micrograph of the specimen was obtained from XL 30 Phillip with accelerating voltage of 12 kV, current 80 mA. The specimens were coated with gold-coated before observation. The technique was studied the morphology of specimen with and without contaminated heavy metal at the age of 40 days.

The data from X-ray diffractrometer was obtained using D8000 with CuK_α radiation generated at 40 mA and 40 kV. Specimens were scanned from 20^o to 70^o 2θ at 0.02^o step side at the rate of 0.1 sec per step. This data was used to provide fundamental information of geopolymer structure at the age of 40 days.

Compressive strength

Compressive strength was tested according to ASTM D1633. The sample was submitted to tests at age 1, 3, 5, 7, 14, 28 and 40 days.

Toxicity characteristic leaching procedure

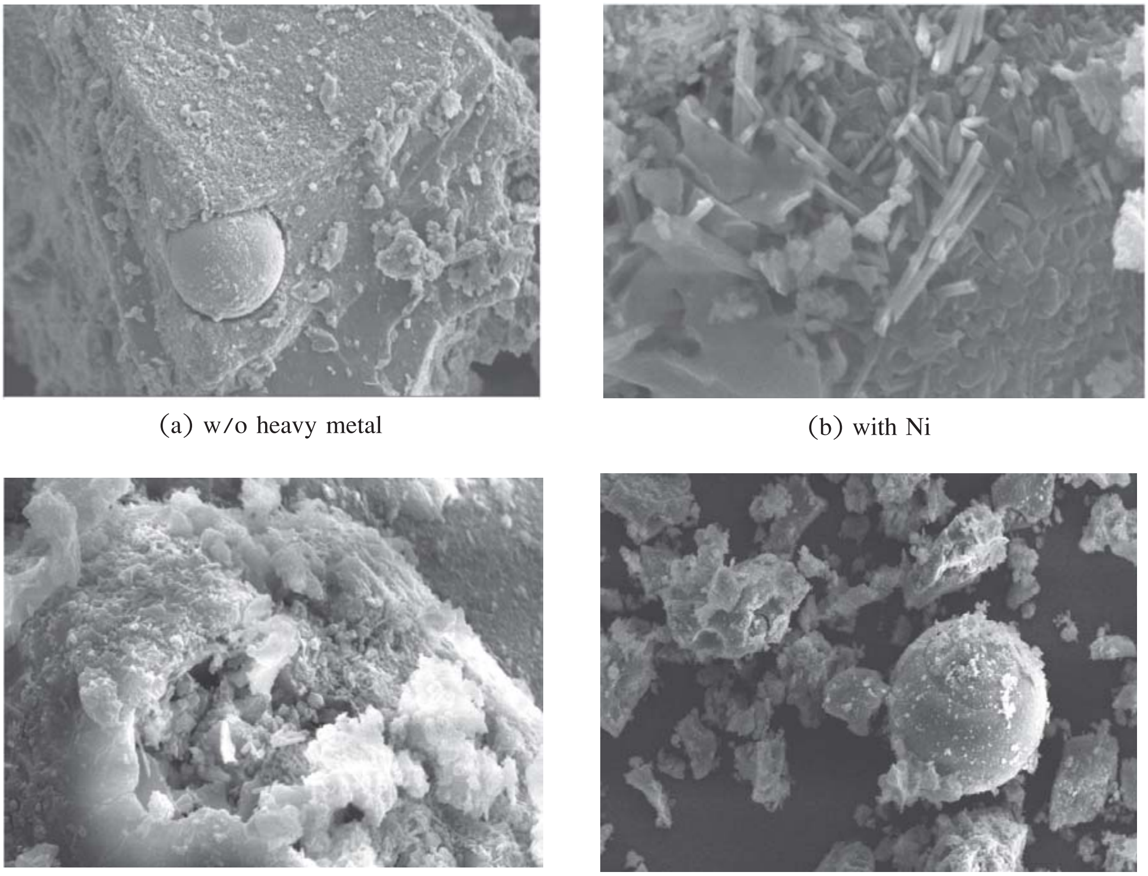
Nitric acid extraction at pH of 2.88 was used in this test. The solid/liquid ratio was kept at 1:20. The leaching tests were conducted by the rotating 360^o apparatus at 1.8 hr. The mixture was filtrated by using filter paper. The concentrations of heavy metal were determined using an ICP-AES.

Results and Discussion

Effect of heavy metal on geopolymer matrix

Different morphologies of contaminated geopolymers as measured by SEM are shown in Figure 1. As seen from the morphology of geopolymer without heavy metal in Figure 1(a), a spherical fly ash was inserted into the geopolymer matrix causing a dense structure. In contrast with other samples, all heavy metals were incorporated in geopolymer with the loose structure comparing to the dense structure of the control sample (Figure 1(a)). For the geopolymer with Ni-contamination (Figure 1(b)), the Ni compound was detected as a bar shape among other compositions. It was obvious to somewhat dense structure. On the other hand, geopolymer contaminated-Cd (Figure 1(c)), exhibited a sponge shape which indicated the loose structure. The morphology of geopolymer contaminated with Zn (Figure 1(d)), was found as a brittle structure with several opening space on the surface. In all cases, the results of SEM were related with XRD pattern which illustrated in Figure 2(a-c). Major phases of geopolymer were silicon dioxide (SiO_2), sodium silicate (Na_2SiO_3), calcium oxide (CaO) and sodium hydroxide (NaOH) as shown by the designated peaks in XRD spectra (Swanepoel and Strydom, 2002; Lecomte et al.; Alvarez-ayuso et al., 2007). Besides showing the major phases of geopolymer, the new compounds of foreign ions obtained from the chemical reaction during geopolymer formation were also detected as shown in Table 2.

From XRD analysis for geopolymer contaminated with Ni (Figure 2(a)), it was found that Ni ions was mainly reacted with silicon and sodium and the resulted compounds are Ni_2SiO_4 and $Na(NiO_2)$. Whereas, the component of CdO was remain in geopolymer matrix that was shown in Figure 2(b). It was indicated that CdO was encapsulated in matrix and none reacted with alkali activated solution. For Zn-contaminated geopolymer (Figure 2(c)), the Zn ions was reacted with silicon as the detected result was $ZnSiO_4$. In addition, the excess ZnO also shown in the same spectra. From our work, it is anticipated that the injected heavy metals tend to react mainly with silicate ions during geopolymer formation. It was reported in previous work (Davidovit et al.,2008) that those new compounds occurring from the reaction between heavy metal and geopolymer precursors cause the reduction in stability of geopolymer matrix (Davidovit et al., 2008).



(a) w/o heavy metal

(b) with Ni

(c) with Cd

(d) with Zn

Figure 1. SEM pictures of geopolymer with different heavy

Table 2. New compounds of heavy metals in geopolymer as identified by XRD

Heavy Metals	New compounds
Nickel	Ni_2SiO_4, $Na(NiO_2)$
Cadmium	CdO, $Cd_5Si_2O_8(OH)_2$
Zinc	$ZnSiO_4$, ZnO

Effect of heavy metals on compressive strength

Effect of three heavy metals on the compressive strength of fly ash based geopolymer illustrates in Figure 3 and the values of compressive strength of geopolymer contaminated heavy metals with 1, 7 and 10% by weight at the age of 40 days are shown in Table 3. The geopolymer without any heavy metal provided the highest compressive strength as 260 ksc. Among geopolymer conta minated with heavy metal, the Ni-contaminated geopolymer provided the highest compressive strength

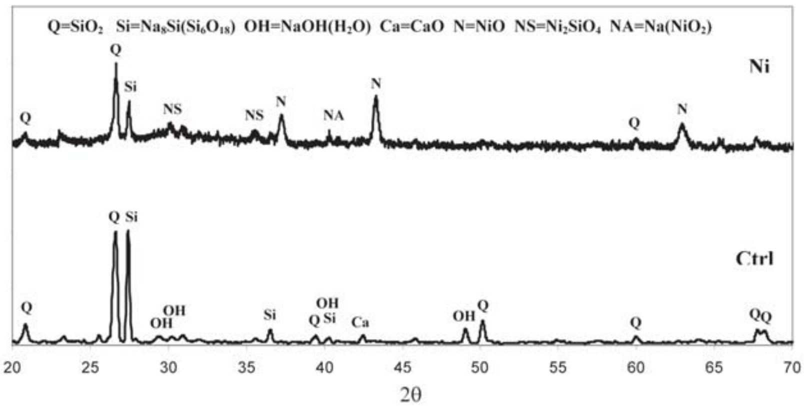
Table 3. Value of compressive strengths of contaminated geopolymer

% heavy metals	Compressive strength (ksc.)		
	Cd	Ni	Zn
0%	260 *(100%)*		
1%	239.2 *(92.0%)*	256.9 *(98.8%)*	222 *(85.4%)*
7%	184 *(70.7%)*	216.9 *(83.4%)*	90 *(34.6%)*
10%	152 *(58.5%)*	168.6 *(64.8%)*	80 *(30.8%)*

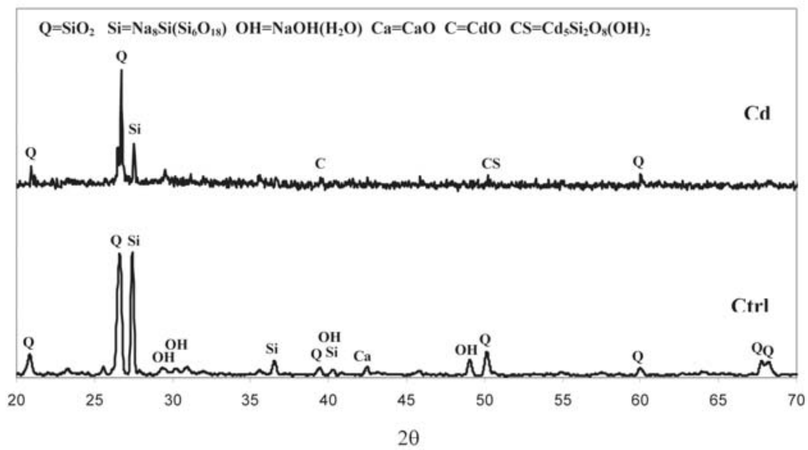
as 256.9, 216.9 and 168.6 ksc with 1, 7 and 10% by weight of Ni, respectively. In all cases, the compressive strength of geopolymer contaminated with heavy metals was decreased when initial concentrations of heavy metal increased. This finding is in a good agreement with previous work [Ref] in using geopolymer and cement based techniques for heavy metal stabilization, the low compressive strengths of the contaminated geompolymer with several types of heavy metal (Mn, Pb, Zn, Ni and Fe) from power plant sludge were obtained. It is anticipated that low compressive strength may be due to waste addition exerting the negative effect on the C-S-H hydration and setting time (Shefali et al., 2008). Apparently, Ni provided the least adverse affect on compressive strength while Zn exerted the most affect on compressive strength. Results of this part are well agreement with morphology of geopolymer as shown previously. This behavior can be explained by the loose structure of geopolymer contaminated with Zn as shown in SEM picture (Figure 1(d)), while geopolymer contaminated with Ni has dense structure than other types of investi-gated geopolymer. From XRD information, the heavy metals tend to react with silica and sodium from geoplymer precursors and form the new compound as described previously. From this work, silicon tends to react with all heavy metals yielding the reduction of strength and changing the geopolymer structure.

Leaching behavior of heavy metals from geopolymer

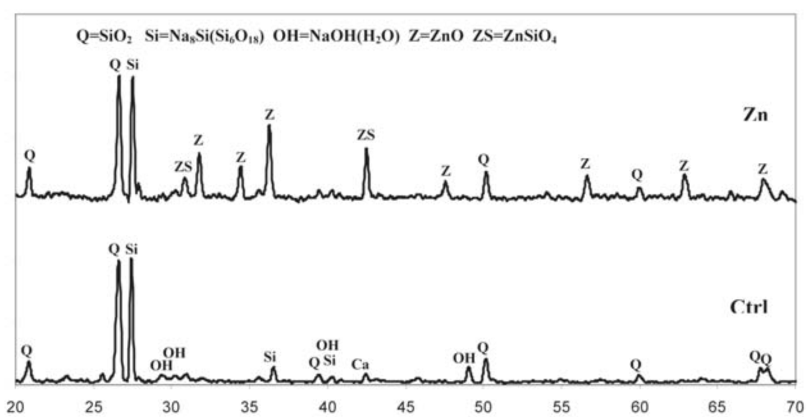
Results from TCLP test were presented in Figure 4. Comparatively, leaching concentration of Ni was minimal. The leached concentration of Ni slightly increased when the percentage concentration of Ni increased. The leaching concentration of Ni with 10% by weight was 5.34 mg/l. The results can be explained by XRD pattern, Ni ions reacted with both silicon (Si) and sodium (Na) (major element of geopoly-merization in geopolymer matrix resulting in the dense structure morphology as seen from SEM. Consequently, this solid structure immobilized Ni in the matrix of geopolymer and release small amount of Ni to environment. In contrast with the leaching behavior of Cd and Zn, the leaching concentrations of these heavy metals were substantially increased from 1 to 10% by weight of heavy metal. The highest leaching concentration of Cd was 420 mg/L with 10% by weight of Cd. The leaching behavior of this heavy metal can be explained by the loose structure of geopolymer that allowed Cd to be leached out from the matrix. For leaching behavior of Zn, the highest leaching concentration was 407 mg/l with 10% by weight of Zn. From XRD analysis, It was indicated that there are ZnO compound remaining in the geopolymer.



(a) XRD pattern of geopolymer contaminated-Ni



(b) XRD pattern of geopolymer contaminated-Cd



(c) XRD pattern of geopolymer contaminated-Zn

Figure 2. XRD pattern of geopolymer with different heavy metals

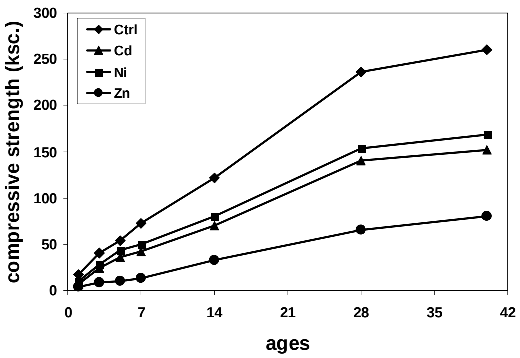


Figure 3. Compressive strengths of contaminated geopolymer (10% by weight of heavy metal)

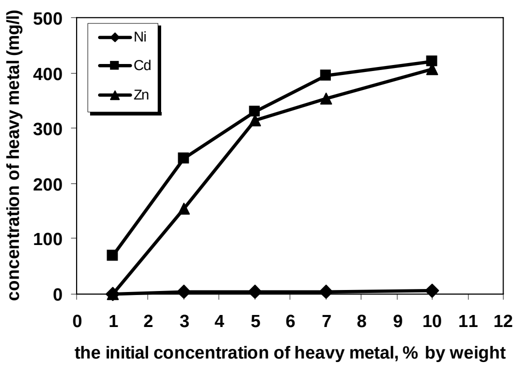


Figure 4. Leaching amount of heavy metals from Geopolymer

This composition can be easily leached out from geopolymer matrix. Consequently, the im mobilization of Zn and Cd using geopolymer in this work is not as effective as Ni. From TCLP test, leachability of heavy metals from geopolymer can be sequenced as : Cd≅Zn >> Ni. The leaching value of Ni was not exceed standard value (10 mg/l). Whereas leaching amount of cadmium was exceed standard value (1 mg/l). In overall consideration , geopolymer based fly ash was environmentally friendly material which can be immobilized the investigated heavy metals.

Conclusion

From this research, synthesized geopolymer can be used in immobilization of heavy metals. In part of effect of heavy metal on geopolymer matrix by SEM and XRD techniques, the morphology of geopolymer contaminated with Cd and Zn were loose structure, while structure of Ni-contaminated geopolymer was the dense structure. XRD sprectra exhibited the new compounds of heavy metal occurring during the reaction of heavy metals with alkali activated solution and geopolymer precursors such as silican and sodium resulting. These compounds exertes negative affect on strength and leaching behavior. Ni provided the least adverse affect on compressive strength while Zn exerted the most negative affect on compressive strength. From TCLP test, leachability of heavy metals from geopolymer can be sequenced as : Cd≅Zn >> Ni. The leaching value of Ni was not exceed standard value (10 mg/l). Whereas leaching amount of cadmium was exceed standard value (1 mg/l). In overall consideration , geopolymer based fly ash was environmentally friendly material which can be immobilized the investigated heavy metals.

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