The Effect of Pb Immobilization on Fly Ash Geopolymer Microstructure and Compressive Strength

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Abstract

Fly-ash based geopolymer was synthesized with the influence of immobilized Pb as a heavy metal on its polymer chain formation. In this research, lead immobilization was successfully applied to geopolymer specimens at various ratios of Pb weight against fly ash weight between 0 - 0.5 %wt. This was proven by using XRD analysis whose diffractogram shows hump peak around 28-30º. FTIR analysis results show that Al-O-Si bending vibration and Si-O-T asymmetric stretching mode are detected in geopolymers.

The highest compressive strength of lead-impregnated geopolymer was 69 MPa after 0.5%wt Pb immobilization in geopolymer. Pb was equally distributed to geopolymer surface after immobilization. Pb immobilization in geopolymer is recommended since the amount of Pb released to leachate after leaching was quite low.

Keywords: Geopolymer, immobilization, Pb ion, compressive strength, Pb distribution, leaching

Introduction

Nowadays heavy metal pollution is a serious environmental problem. Heavy metals in waste were mostly generated from metal processes in industry, such as battery manufacturing, electroplating and dye pigment production[1]. Lead as one of heavy metals in waste is toxic and non-biodegradable. The presence of lead could easily accumulate in the bodies of living things and cause some serious diseases, even in low concentration[2]. It is essential to perform further waste treatment in order to reduce the impact of lead pollution to aquatic ecosystem and living creatures around. Some methods used for lead waste treatment were performed at high temperature and pressure condition which include microbacterial degradation and high temperature combustion[3]. Such processes are not favorable since they are costly and consume a lot of energy.

Geopolymer as a high-performance material has a strong structure and thus is potential for heavy metals immobilization. Xu et al[4] stated that geopolymer is an aluminosilicate material with three-dimensional structure similar to cement and with amorphous structure could be utilized as stabilizer and waste encapsulation. The structure of polymer chain in geopolymer can be used to trap heavy metals. Cheng et al[5] in their experiments found that metakaolin-based geopolymer is good at adsorbing some heavy metal ions i.e. Pb^{2+}, Cu^{2+}, Cr^{3+} and Cd^{2+} while the best activity was observed at Pb^{2+} adsorption. Moreover, geopolymer synthesis through sol gel method at low temperature emits less carbondioxide gases than that of Portland cement concrete manufacturing.

In this study, geopolymer was synthesized by using fly ash as the aluminosilicate source with Si/Al ratio of 4:1[6]. The synthesis of geopolymer was then tested with a certain amount of lead to determine the immobilization capacity and was subsequently tested using compressive strength machine to determine its mechanical strength.

Material and Methods

Materials and Instrumentation: The materials used in this research were class-C fly ash from Paiton Power Plant as an aluminosilicate source, technical grade NaOH and Na_2SiO_3, distilled water, CH_3COOH and $Pb(NO_3)_2$. In order to determine a proper geopolymer mixture proportion, the composition of fly ash was measured using X-Ray Fluorescence (XRF) and it can be seen in table 1. The alkali activator solution was prepared by dissolving sodium hydroxide pellets into distilled water followed by cooling at room temperature and mixing with sodium silicate solution.

Geopolymer Synthesis: The synthesis of geopolymer was carried out according to the previous experiment conducted by Anggarini and Sukmana[6] with Si/Al ratio of 4. All mixing processes were performed at constant room temperature to eliminate side effects caused by temperature variations. The first mixing process between fly ash and the alkali activator solutions was carried out in a stirring machine for 5 minutes. Geopolymer paste was poured onto the cube mold and vibration treatment was performed for 10 seconds. The specimens were cured at room temperature for 28 days and the mechanical strength of geopolymer was measured by using compressive strength machine at Physical Laboratory of PT. Semen Indonesia.

Lead Metal Immobilization: The heavy metal used for immobilization, Pb^{2+}, was added into geopolymer matrix as $Pb(NO_3)_2$ solution. The geopolymer synthesis procedure was initially performed prior to immobilization. At the time geopolymer paste was produced, a certain amount of $Pb(NO_3)_2$ was added into geopolymer paste in various fly ash weight percentages of 0.1%, 0.2%, 0.3%, 0.4% and 0.5%. Since $Pb(NO_3)_2$ as a nitrate salt is difficult to dissolve in alkali activator solution, the homogenization of geopolymer paste decelerates. Lead-impregnated geopolymer was then cured at room temperature for 28 days prior to performing mechanical strength trial.

Lead Metal Leaching: Leaching procedure was conducted by adding 30 grams of geopolymer specimen containing lead into a leaching agent prepared from dilute acetic acid. Leached geopolymer specimens possessed highest compressive strengths after lead immobilization. Samples of leachate were taken after 4 and 24 hours of leaching and then analyzed by using ICP-AES to measure the amount of Pb therein.

Results and Discussion

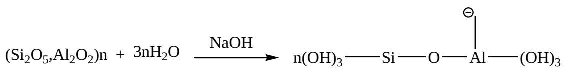
The crystal structure of synthesized geopolymers: Selected geopolymer samples containing immobilized lead were analyzed by using XRD to study the effect of lead immobilization on the structure of geopolymer. Figure 1 is a diffractogram presenting the structure comparison between lead-free geopolymer and 0.1% and 0.5%wt lead-impregnated geopolymers. It can be seen that all geopolymer structures were amorphous with several observable phases such as quartz and mullite. Guo et al[7] stated that both type of phases are the stable phases from fly ash resources. Among the hump peaks appearing at 28-30^o, the highest peak belongs to the 0.5%wt lead-impregnated geopolymer.

This result confirms that geopolymerization was successfully performed towards producing materials that possess high compressive strength. The synthesis of geopolymer through polycondensation of aluminosilicate precursor and alkali activator solution plays an important role to build a polymer structure that employs high mechanical strength. While the diffractogram of 0.5%wt lead-impregnated geopolymer has a peak at 29^o, which indicates the presence of Pb_3SiO_5, that of 0.1%wt lead-impregnated geopoplymer shows no peak at the same angle. The small amount of lead added was the main cause of Pb_3SiO_5 peak absence.

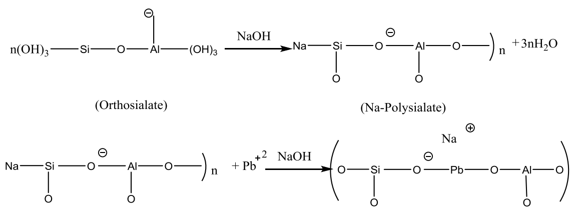
Nikoli et al[8] stated that Pb addition generates structure defects that lead to geopolymer compressive strength decrease. As can be seen in figure 3, the geopolymer mechanical strength did increase as more lead was immobilized to the specimens, except for 0.2%wt lead-impregnated geopolymer. Overlapping with mullite peak, the peak of sodium nitrate was detected between 28-30^o. Sodium nitrate was the product of reaction occurred between highly soluble lead nitrate and sodium contained in alkali activator solutions[8]. Zhang et al[9] declared that there was no negative effect of NO_3^- on geopolymer compressive strength. Pb was involved in the geopolymer polymeric chain formation prior to the structure conversion into amorphous phase[7].

Results of FTIR analysis of lead-impregnated geopolymers: The functional groups of geopolymers synthesized with and without lead immobilization were analyzed by using Fourier Transform Infrared Spectroscopy (FTIR). The results are shown in figure 2. Al-O-Si bending vibration and Si-O-T asymmetric stretching mode are detected at wavenumbers of 800 and 970 cm^{-1} respectively. These bands refer to the development of SiO_4 and AlO_4 tetrahedral structure that is coherently linked as polymeric precursors of either -SiO_4-AlO_4-, -SiO_4-AlO_4-SiO_4-, or -SiO_4-AlO_4-SiO_4-SiO_4- by employing shared oxygen atoms[10]. The anti-symmetrical stretching vibration of nitrate was observed at wavenumber of 1410 cm^{-1}.[11] The more Pb is added into geopolymer matrix, the higher is NO_3^- peak. The presence of this peak was a result from $NaNO_3$ formation after geopolymerization process.

The surface morphology of lead-impregnated geopolymers: The distribution of Pb atoms on geopolymer specimens was characterized by using SEM-EDX. Figure 3 shows that Pb atoms were distributed to almost every part of geopolymer surface while the red dots present the agglomerated ones. The color contrasts shown in the picture indicate different various chemical composition distribution. Among those are amorphous phases i.e. the unreacted parts of geopolymer raw materials. Uniformity of Pb distribution found within red dots proves that lead added into geopolymer was initially converted into amorphous phase, then equally distributed to all geopolymer chains through mechanisms explained by eqs. (1) and (2). This phenomena was due to the high solubility of $Pb(NO_3)_2$ and high reactivity between it and fly ash. Based on results shown in table 2, the amount of Pb detected in 0.5%wt lead-impregnated geopolymer is more than double than that of 0.1%wt one.



(1)



(2)

Effects of lead immobilization on geopolymer compressive strength: As can be seen in figure 3, the amount of Pb added into geopolymer matrix does affect its compressive strength. US Environmental Protection Agency[12] stated that the compressive strength of material used for disposal hazardous waste immobilization should be at least 0.35 MPa. The highest measured compressive strength of geopolymer in this research was 69 MPa after a 28-day curing at room temperature. This means that geopolymer is suitable for disposal hazardous waste immobilization.

Conclusively, the increase of geopolymer compressive strength was proportional to that of added lead amount except for 0.2%wt Pb. This indicates that geopolymer has a certain tolerance limit to heavy metal exposure. The higher is geopolymer mechanical strength, the stronger is its matrix which will lead to higher immobilization effectivity. The bond between Si-O-Si and Si-O-Al is the factor that determines geopolymer matrix strength[11]. The lowest amount of Pb leached to leachate was 0.0313 ppm. This value belongs to the 0.5%wt lead-impregnated geopolymer whose compressive strength was the highest (69 MPa). Guo et al[7] also found that Pb^{2+} addition does affect the geopolimeric compressive strength significantly.

Immobilization behavior of lead–impregnated geopolymer: Acetic acid was used to determine the erosion degree of geopolymer specimens in acid environment. The leaching procedure in this experiment was studied by using ICP-AES. The results in table 2 show that a small amount of lead was leached from geopolymer matrix. Palomo and Palacios[13] stated that Pb solidification inside geopolymer structure is a combination between encapsulation and chemical bonds. Geopolymer cementing system was able to stabilize lead inside geopolymer chain structure and control lead leaching by diffusion. Weast[14] found that the solubility of lead silicate is low. The formation of low soluble lead silicate leads to lesser concentration of Pb contained in leachate after leaching process. The Government Regulation of Republic of Indonesia number 82, in 2001 about water quality management and water polluting control states that the content of Pb in water should not exceed 1 ppm.

As seen in table 3, the amount of leached Pb measured in this study was quite low, i.e. between 0.0337 – 0.0313 ppm. This means that geopolymer has a good potential to immobilize heavy metals including Pb. Yunsheng et al[15] also proved that Pb has a good immobilization in high dosage within geopolymer specimen. The stabilization mechanism of heavy metal in geopolymer comprises following steps: metal ion impregnation into geopolymer framework, metal – geopolymer matrix chemical bond formation where the charge balancing takes place and lastly, heavy metal encapsulation[16].

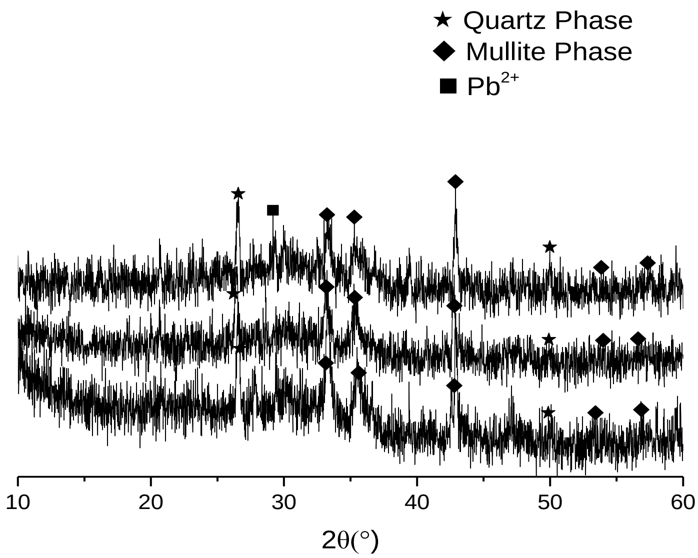


Figure 1: **The diffractogram of (a) lead-free geopolymer, (b) 0.1%wt lead-impregnated geopolymer and (c) 0.5%wt lead-impregnated geopolymer**

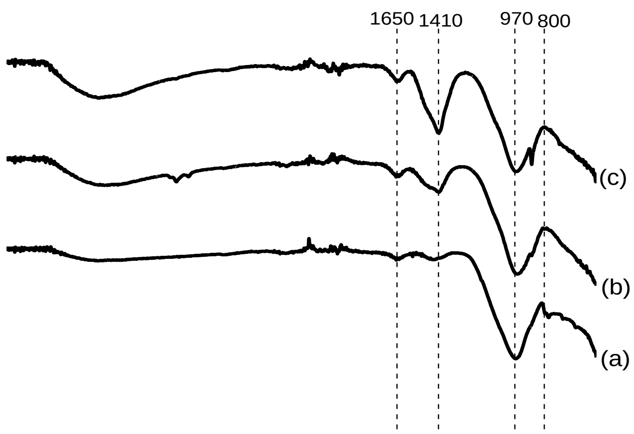


Figure 2: FTIR spectra of (a) geopolymer without heavy metal, (b) geopolymer matrix with the addition of 0.1%wt Pb, (c) geopolymer specimen with the addition of 0.5%wt of Pb

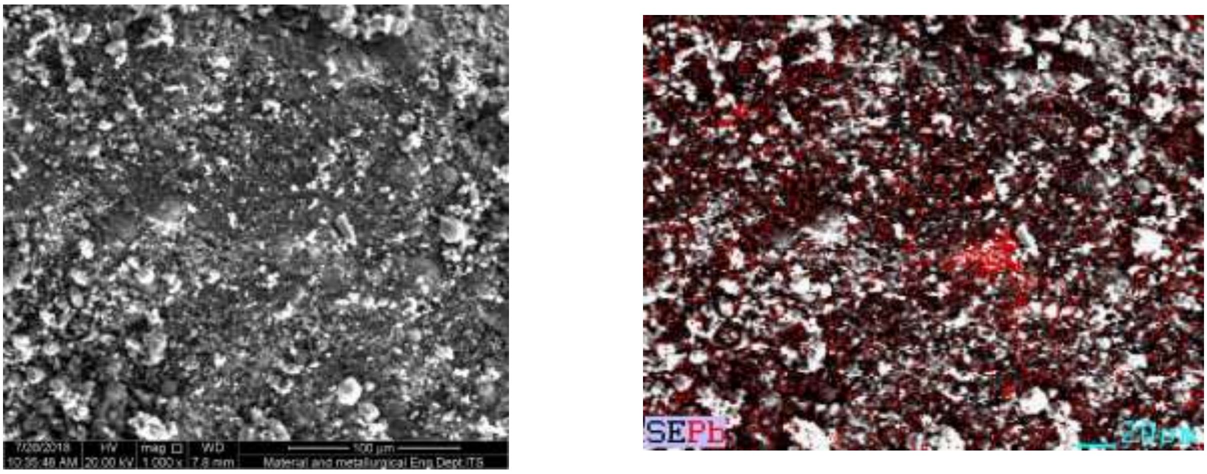


Figure 3a: SEM images and Pb metal distribution on the surface of 0.1%wt lead-impregnated geopolymer.

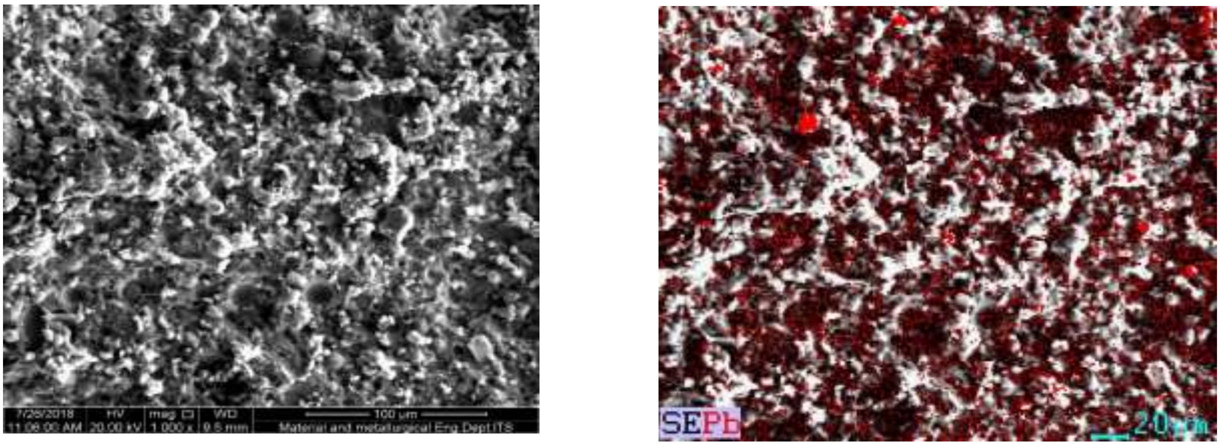


Figure 3b: SEM images and Pb metal distribution on the surface of 0.5%wt lead-impregnated geopolymer.

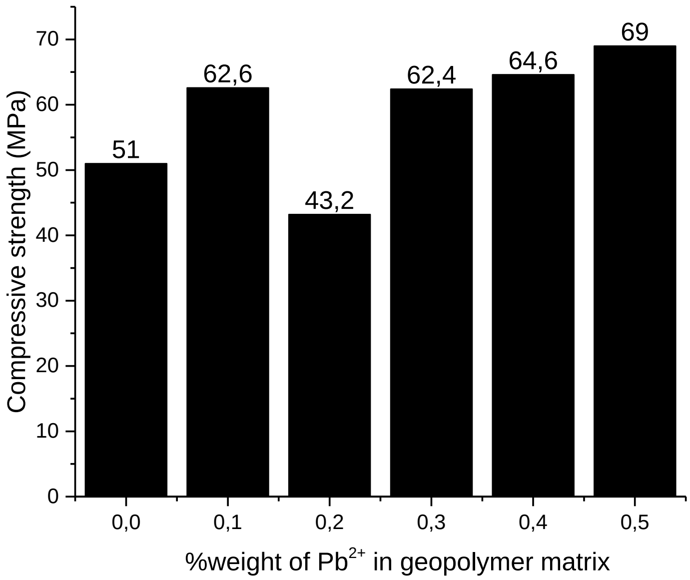


Figure 4: The compressive strength of geopolymer with various weight percentage of Pb^{2+}

Table 1
Chemical composition of fly ash as the aluminosilicate source for geopolymer synthesis

Oxide	**Al_2O_3**	**CaO**	**Fe_2O_3**	**SiO_2**	**K_2O**	**MgO**	**Na_2O**
Weight percentage (%)	27.11	9.07	6.18	46.93	1.49	3.18	0.59

Table 2
Elemental composition of synthesized geopolymers

Element	Weight percentage (%)		
	Lead-free geopolymer	0.1%wt lead-impregnated geopolymer	0.5%wt lead-impregnated geopolymer
C	3.23	5.60	4.44
O	29.91	35.22	42.90
Na	6.03	6.63	12.03
Mg	3.34	3.99	2.68
Al	6.78	6.87	4.30
Si	14.78	16.86	10.84
Pb	-	1.46	3.58
K	1.45	1.45	0.76
Ca	16.47	11.50	12.17
Fe	18.02	10.42	6.30

Table 3
Concentrations of leached Pb at various weight percentages of immobilized Pb

Weight percentage of Pb immobilization (%)	Weight of Pb before leaching (mg)	Concentration of leached Pb (ppm)
0%	0	0
0.1%	5940.6	0.0337
0.2%	11764.7	0.0336
0.3%	17475.7	0.033
0.4%	23076.9	0.0314
0.5%	28571.4	0.0313

Conclusion

The hump peak shown around 28-30º in XRD diffractogram indicates successful Pb immobilization on geopolymer. FTIR analysis results show that Al-O-Si bending vibration and Si-O-T asymmetric stretching mode are present in geopolymer at wavenumbers of 800 and 970 cm^{-1} respectively. The compressive strength of 0.5%wt lead-impregnated geopolymer improved from 51 MPa to 69 MPa after Pb immobilization. The distribution of Pb on geopolymer surface was uniform. The concentration of Pb released to leachate after leaching was between 0.3130 – 0.3370 ppm.

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