

Properties of the Alumino-Silicate Geopolymer using Mine Tailing and Granulated Slag

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In this study, the physical characteristics of alumino-silicate geopolymer and the role of mine tailings in alumino-silicate geopolymer were investigated using mine tailings, coal fly ash, granulated blast furnace slag and alkali activator solution. The reaction products of alumino-silicate geopolymer using mine tailings are amorphous aluminosilicate gel and calcite, and are increased with decreasing the addition of mine tailings. The compressive strength of MRG-2 specimen is the highest as 142.2 MPa. The compressive strength of specimen adding mine tailings is decreased, as curing days are increased. When curing days are same, the compressive strength is decreased, as mine tailings is added more. The compressive strength of alumino-silicate geopolymer manufactured by adding mine tailings is higher than that of portland cement mortar, when cured for 28 days. The leaching resistance of heavy metal ion in alumino-silicate geopolymer is lower than the toxic threshold of each ion. It is confirmed that heavy metals are stabilized and fixed in alumino-silicate geopolymer.

Key words: Alumino-silicate geopolymer, Mine tailing, Fly ash, Slag, Compressive strength.

Introduction

Alkali activated cement has been studied for a long time [1]. Davidovits *et al.* developed “geopolymer” which is hardened rapidly at low temperature and has strong physical characteristics by polymerization. The geopolymer has received attention as a new material which can replace cement [2-3].

Geopolymer has similar characteristics to zeolite and is in non-crystal, not crystal. Generally, geopolymer is composed with silica and alumina. Silica and alumina leached out under alkaline condition are polycondensed. As a result, poly (silate) of geopolymer is yielded as forming three dimensional polymer chain and ring structure of Si-O-Al-O bond. Poly (silate) is amorphous as a ring polymer based on repeated units of SiO₄ and AlO₄ tetrahedra [3]. In M_n(-SiO₂)_z-AlO₂)_nwH₂O, M is alkali elements, such as K, Mg and Ca, or cations. Geopolymerisation process involves a chemical reaction between various aluminosilicate oxides (Si₂O₅ and Al₂O₅) and silicates under highly alkaline conditions, yielding Si-O-Al bonds.

Ikeda reported that geopolymer is composed with non-active filler, active filler and activ-ator [4]. Non-active filler includes silica or granite which are not easily leached out when exposed to acid and alkaline

solution. Active filler is easily activated, and leached out because bonds are easily broken in alkaline solution. Activator makes metal ions leached out as reacting with active filler, and supplies alkaline earth metal cations, such as Na⁺, K⁺, Ca²⁺ and Mg²⁺, which are used in polycondensation. In these days, geopolymer depends on starting materials, and can be applied in fixing heavy metals and developing lightweight building materials [5-9]. Especially, it has been studied through various methods to fix heavy metals. Zhang Yunsheng *et al* [6]. reported that when heavy metal leaching was tested after adding Cu and Pb ion into geopolymer which is composed with slag and metakaolin, the fixation rate of heavy metals was 98.5%. Fernando *et al* [7]. reported the characteristics of geopolymer using sludge of tungsten mine waste. Deventer *et al* [8]. studied the fixation of Cr, Cd and Pd ion in geopolymer, and showed to be stabilized as producing Pb₃SiO₅.

In this study, it was studied whether mine tailings can be used in alumino-silicate geopolymer. Also, the physical characteristics of alumino-silicate geopolymer and the role of mine tailings in alumino-silicate geopolymer were studied after making alumino-silicate geopolymer, using mine tailings as starting material.

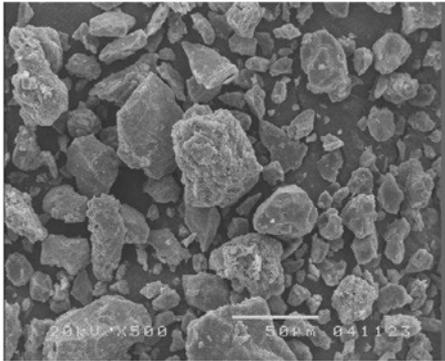
Experimental

Mine tailings obtained in a region near to Youngwol (Korea) were used as non-active filler, and granulated blast furnace slag and coal fly ash (Geo-Polymer

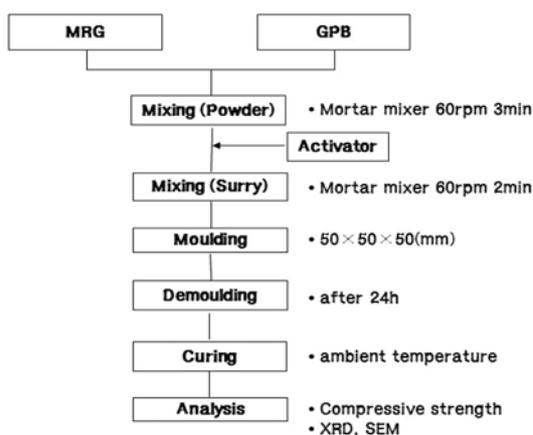
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Table 1. Chemical compositions of mine tailing analyzed with XRF and ICP-AES.

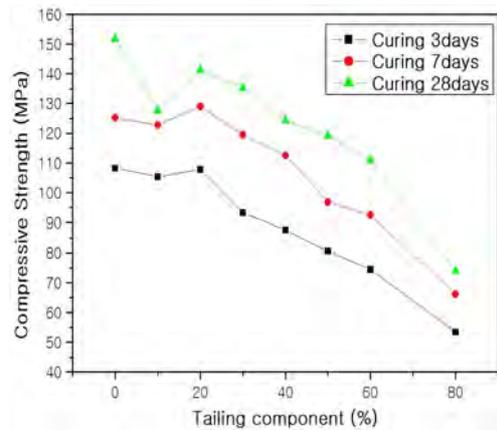
Compound	SiO ₂	Fe ₂ O ₃	SO ₃	CaO	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O
Amount (wt%)	56.3	13.3	1.03	13.3	9.24	1.88	2.12	0.24
Element	Zn	Cu	Cd	Pb	As			
Tailing (ppm)	0.006	ND	ND	ND	0.030			

**Fig. 1.** SEM micrographs of mine tailing red material.**Table 2.** Mixture proportions of alumino-silicate geopolymer (unit: wt%).

Specimen No.	GPB* (Slag + FA)	Mine Tailing	Liquid/Solid Ratio
MRG-0	100	0	0.45
MRG-1	90	10	0.43
MRG-2	80	20	0.40
MRG-3	70	30	0.38
MRG-4	60	40	0.32
MRG-5	50	50	0.30
MRG-6	40	60	0.30
MRG-7	20	80	0.30

**Fig. 2.** Experimental procedure of alumino-silicate geopolymer.

Binder; GPB*) as active filler. Active filler was used, adjusting the mol ratio of SiO₂ to Al₂O₃ to 2.18, using slag and fly ash. Activator, (Na₂O + K₂O)/SiO₂ of 0.52 weight ratio and pH 13.5, was prepared, using KOH, NaOH and sodium silicate solution (Na₂O/SiO₂

**Fig. 3.** Compressive strength of alumino-silicate geopolymer with the amount of mine tailing after curing 3, 7, and 28 days.

of 0.23 mol ratio and pH 11.5). The chemical composition and morphological characteristics of raw materials were examined by SEM, XRF and ICP-AES analysis, are shown in Table 1 and Fig. 1, respectively.

The condition to manufacture alumino-silicate geopolymer and the manufacturing process are shown in Table 2 and Fig. 2. Each material was measured and dry mixed in mortar bowl (5 L) at 60 rpm/min for 2 minutes according to conditions. Activator was added to mixed powder according to the ratio of L/S (Liquid/Solid), as shown in Table 2. Mixed slurry was manufactured, vibrating in a cubic mold (50 mm × 50 mm × 50 mm) for 1 minute. Specimens were hardened for 8 hours at 50 °C at 90% or more of humidity and then the compressive strength was measured after curing for 3, 7, 28 days.

The physical and chemical characteristics of alumino-silicate geopolymer were investigated by UTM, X-ray diffraction (XRD), X-ray fluorescence (XRF), Scanning electron microscopy (SEM). Cubic specimens of 50 × 50 × 50 mm were used to investigate the compressive strength of alumino-silicate geopolymer and leaching rate of heavy metal ions. The compressive strength was measured after curing for 3, 7 and 28 days, using UTM according to KSL 4201 method [10]. Heavy metal ion of mine tailings, were analyzed, using ICP-AES after pre-treating with microwave digestion system to investigate the content of harmful heavy metal ion. For XRD analysis, specimen was immersed in alcohol for 3 days to suppress the polymerization of alumino-silicate geopolymer and then ground. The leaching rate of Cu, Zn, Pb, As and Cd ion, the major components of mine tailings, were measured, using ICP-AES after curing for 28 days and then leaching according to Korea Standard Leaching Test (KSLT).

Results and Discussion

Fig. 3 shows the compressive strength of specimen. The compressive strength of alumino-silicate geopolymer is

decreased as mine tailings was added more. When cured for 3 days, the compressive strength of alumino-silicate geopolymer is decreased slowly, as mine tailings is added more. The compressive strength of MRG-2 is high as 107.8 MPa, and that of MRG-7 is the lowest as 53.5 MPa. When cured for 7 days, the compressive strength of MRG-2 is high as 129.0 MPa, but that of MRG-7 which 85% of mine tailings was added is low as 66.2 MPa. When cured for 28 days, the compressive strength of MRG-2 is the highest as 142.2 MPa and high in 20 wt% mine tailing. The compressive strength of specimen adding mine tailings is increased, as curing days are increased. When curing days are same, the compressive strength is decreased, as mine tailings is added more.

The reason may be why the self cohesion of the mixture of slag and fly ash (Geo-Polymer Binder; GPB), which were added as active filler, is very high. When 10 and 20 wt.% of mine tailings were added, it is thought that compressive strength is high, because

mine tailings acts as filler. But if mine tailings is added too much, it is thought that compressive strength is decreased, because the amount of mixture of slag and fly ash is decreased, of which the reactivity is high. Even though mine tailings is added up to 80 wt%, the compressive strength of alumino-silicate geopolymer manufactured by adding mine tailings is higher than that of portland cement mortar which is 60 MPa, when cured for 28 days [5].

X-ray diffractometry analysis of alumino-silicate geopolymer cured for 28 days is shown in Fig. 4. It is confirmed that the peak intensity of muscovite phase is decreased, as mine tailings is added more. But 20 ~ 35 ° (2θ) of halo pattern appears, as mine tailings is added less. The reason may be why bonding strength between non-active filler of mine tailing and active filler of slag and fly ash is increased and structure is changed into dense structure. Son *et al* [11]. reported that as fly ash is added, the amorphous phase of halo pattern is observed at 20 ~ 35 ° (2θ), and when alkaline alumino-silicate gel is produced by fly ash activated, compressive strength is high. Also, because the alumino-silicate gel of alumino-silicate geopolymer, halo pattern is observed at 20 ~ 35 ° (2θ), it is consistent well with above result [11-14]. Calcite peak is observed at 29 ° (2θ). It is thought that calcite is formed, when CaO, which is much in slag, fly ash and mine tailings, is leached out in alkaline solution under high alkaline condition, and reacts with CO₂ in air [15].

Generally, portland cement is hardened, when clinker mineral in portland cement reacts with water to form

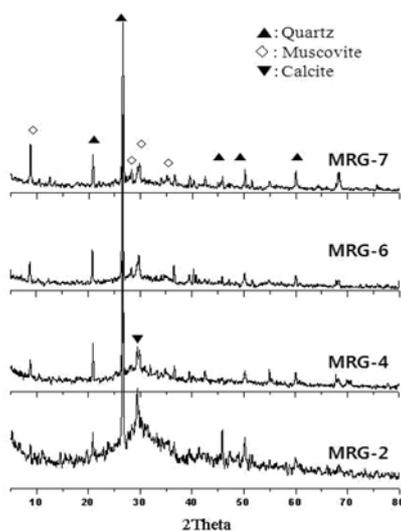


Fig. 4. X-ray diffraction patterns of alumino-silicate geopolymer with 20 wt%(MRG-2), 40 wt%(MRG-4), 60 wt% (MRG-6), and 80 wt%(MRG-7) mine tailing cured for 28 days.

Table 3. Leaching results of specimen by KSLT method (unit: ppm).

Specimen	Element			
	Cu	Zn	Pb	As
MRG-0	0.001	0.005	0.003	0.022
MRG-2	0.005	0.015	0.012	0.021
MRG-4	ND	ND	0.016	0.076
MRG-6	0.008	0.008	0.004	0.136

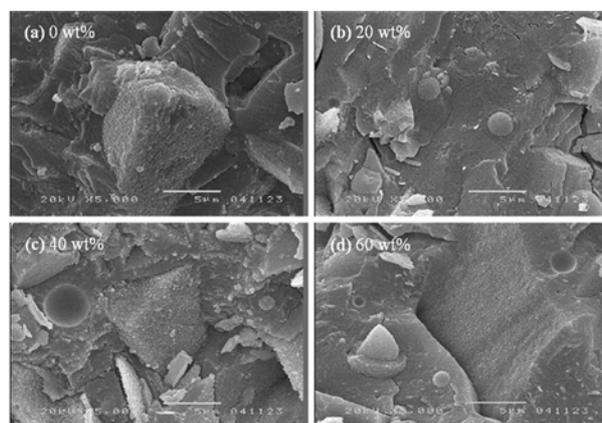


Fig. 5. Scanning electron microscopy photographs of alumino-silicate geopolymer with (a) 0 wt%, (b) 20 wt%, (c) 40 wt% and (d) 60 wt% mine tailings cured for 28 days.

portlandite ($\text{Ca}(\text{OH})_2$), and then portlandite forms C-S-H. Dense structure is formed by strong bonding among particles. Calcium silicate hydrate and calcium aluminum hydrate are produced primarily. But in alumino-silicate geopolymer, amorphous alumino-silicate gel and calcite are.

The microstructure of alumino-silicate geopolymer cured for 28 days is shown in Fig. 5, and is transformed into different shapes according to mine tailings content. The microstructure of MRG-2 in which mine tailings content is low is smooth, but that of MRG-7 in which mine tailings content is high shows that small particles are on surface. In MRG-2 and MRG-4 in which mine tailings content is low, there are sphere shape of fly ash particles, and there are new reaction products in MRG-4. But these reaction products are not observed in MRG-7. Therefore, the high compressive strength of alumino-silicate geopolymer is due to dense structure by these reaction products. Also, it is thought that these reaction products are amorphous alumino-silicate and calcite

The leaching resistance of Zn, Cu, Pb, Cd and As ion in alumino-silicate geopolymer is shown in Table 3. Cd ion is not detected in all specimens. Also, Pb, Cu, As and Zn ion are detected, but leaching is significantly less than the toxic threshold of each ion; 3.0 mg/L in Pb, 1.0 mg/L in Cu and 3.0 mg/L in Zn [16]. The stability of alumino-silicate geopolymer containing much amount of mine tailing is confirmed by these results [17].

Conclusions

1. The compressive strength of alumino-silicate geopolymer which uses mine tailing as non-active filler and slag and fly ash as active filler depends on the addition of mine tailing, and is the highest as 142.2 MPa in 20 wt% mine tailing.

2. The reaction products of alumino-silicate geopolymer using mine tailings are amorphous alumino-silicate gel and calcite, and are increased with

decreasing the addition of mine tailing.

3. The compressive strength of specimen adding mine tailing is increased, as curing days are increased. When curing days are same, the compressive strength is decreased, as mine tailing is added more. The compressive strength of alumino-silicate geopolymer manufactured by adding mine tailing is higher than that of portland cement mortar which is 60 MPa, when cured for 28 days.

4. The leaching resistance of heavy metal ion in alumino-silicate geopolymer is lower than the toxic threshold of each ion. It is confirmed that heavy metals are stabilized and fixed in alumino-silicate geopolymer.

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