I O U R N A L O F

Ceramic Processing Research

Fabrication of porous geopolymer using fused slag with silicon sludge

Yootaek Kim*, Seongyeol Kim and Changsub Jang

Department of the Materials Engineering, Kyonggi University, Suwon 443-760, Korea

Geopolymers release 80% less carbon dioxide than Portland cement and simultaneously provide sufficient mechanical strength for structural applications. Therefore, they were worth as cement substitutes and have attracted from eco-friendly construction industries. Spent silicon sludge is increasing as the demand of silicon wafer for the solar energy generation and semiconductor is steadily increasing. Silicon sludge is produced from the cutting and grinding process of silicon ingot for making silicon wafer. In this study, silicon sludge is used as bloating agent for making porous geopolymers with spent industrial wastes such as fused slags from IGCC (integrated gasification combined cycle) process or municipal waste treatment system. The compressive strength and density of porous geopolymers decreased with silicon sludge addition. Because high addition of silicon sludge to fused slags under the high alkaline atmosphere releases much of H_2 gas, highly porous geopolymers could be obtained in a short curing period. However, high silicon content also showed adversely effects on polymerization process. Geopolymers with specific gravity less than 0.4 was fabricated by using silicon sludge and fused slag; having compressive strength up to 1.3 MPa. In conclusion, very light and porous geopolymers having relatively higher compressive strength could be fabricated with fused slag and spent silicon sludge as a bloating agent.

Key words: Geopolymer, Silicon sludge, Recycling, Bloating agent, Fused slag.

Introduction

The rapid development of an industrial society lead to produce a lot of Portland cement. Production of Portland cement is responsible for almost 5% of total CO_2 emissions in the world [1]. However, alternatives to Portland cement are based on the development of geopolymer materials [2]. Geopolymers release 80% less carbon dioxide CO2 than Portland cement and simultaneously provide sufficient mechanical strength for structural applications. They were worth as cement substitutes and have attracted from eco-friendly construction industries. Inorganic geopolymers can be fabricated by alkali activator of materials rich in SiO₂ and Al₂O₃. Geopolymerization involves a heterogeneous chemical reaction between the dissolution of Al and Si at highly alkaline conditions and mild temperatures yielding amorphous to semicrystalline polymeric structures, which consist of Si-O-Al and Si-O-Si bonds [3]. The mechanical properties of the geopolymer depend on various parameter such as the moral ratio of Si and Al and alkali activator concentration [2]. In this study, waste fused slag as raw materials was used for making geopolymer. The materials contain high silica and alumina, hence is suitable as raw material for undergoing geopolymerization [4]. The slag was obtained by IGCC (integrated gasification combined cycle) process or municipal waste treatment system. IGCC is the type of power technology particularly favorable for plant

*Corresponding author:

retrofitting so that carbon dioxide can be removed at a convenient stage of the process [5]. Waste fused slag is an inorganic vitreous product which is produced as a result of the combustion process of electric power central stations by the combined cycle IGCC [6]. To fabricate porous geopolymer was required to use bloating agent such as Al powder, silica fume and silicon sludge. Spent silicon sludge is increasing as the demand of silicon wafer for the solar energy generation and semiconductor is steadily increasing. Silicon sludge is produced from the cutting and grinding process of silicon ingot for making silicon wafer [7].

The aim of this work was to synthesize porous geopolymer by using waste fused slag and silicon sludge as bloating agent. It also investigates the effect of increasing silicon sludge on physical properties and geopolymerization. The compressive strength and microstructure were characterized by compression tester (UTM-900NH Series Daekyung, Korea) and SEM (scanning electron microscopy, S-4800, Hitachi, Japan), respectively.

Experimental Procedures

This study suggests that high porous geopolymer was synthesized by silicon sludge as bloating agent. Raw material of the geopolymer are waste fused slag.

The slag was obtained by IGCC (integrated gasification combined cycle) process or municipal waste treatment system. Silicon sludge was produced from the cutting and grinding process of silicon ingot for making silicon wafer. Table 1 shows the chemical composition of waste fused slag and silicon sludge. Waste fused slag and silicon sludge were prepared from milling for respectively

Tel : +82-70-4024-9765

E-mail: ytkim@kyonggi.ac.kr

Waste 53.61 9.00 14.94 4.19 5.88 10.23 0.70 1.44 5.04	Materials	SiO ₂	Al_2O_3	CaO	MgO	Na ₂ O	Fe ₂ O ₃	K ₂ O	TiO ₂	P_2O_5	SO ₃	Si/Al
	Waste fused slag	53.61	9.00	14.94	4.19	5.88	10.23	0.70	1.44			5.04
Silicon sludge 97.78 1.97 0.017 0.006 0.003 0.19 0.022 -	Silicon sludge	97.78	1.97	0.017			0.006	0.003		0.19	0.022	-

Table 1. Chemical composition of waste fused slag and silicon sludge by XRF.



Fig. 1. XRD patterns of materials: (a) waste fused slag and (b) silicon sludge.

2 hour and 30minute with planetary ball mill (SFM-1 desk-top planetary ball mill, MTI, USA) and the particles passed a 106 μ m sieve (testing sieve, Chung Gye Industrial MFG, Co, Korea). Microstructure and phase analysis of materials were studied by SEM and XRD.

Fig. 1 shows XRD patterns of waste fused slag and silicon sludge. XRD patterns of waste fused slag were indicate amorphous peak. XRD patterns of silicon sludge shows the presence of high intensity 2θ (28, 47 and 56°) peak which indicated that silicon sludge consisted mainly of silicon peak.

Fig. 2 shows microstructure of waste fused slag and silicon sludge. Particle size of waste fused slag and silicon sludge ranged from 90-100 μ m and 1 ~ 2.5 μ m respectively. Alkali activatior solution was used sodium hydroxide pellets (above 97.0% of purity DAEJUNG, Korea).

The conditions for fabricating geopolymer are organized in Table 2. To synthesize geopolymer, geopolymer paste was fabricated based on the following steps: 1) Waste fused slag and silicon sludge were mixed in accordance to composition. 2) NaOH alkali activator was also added to the mixture for five minutes. The geopolymer paste was molded into a cube mold $(5 \times 5 \times 5 \text{ cm}^3)$ and sealed to prevent water loss, which was cured for 24 hours at 70 °C, 100% humidity. After processing through three days of the aging stage, compressive strength and unit volume weight were measured.

Table 2. The conditions for fabricating geopolymers.

Silicon sludge (wt%)	Alkiali activator (M)	L/S ratio
10 to 100	18	0.41
3, 6, 9,12	9, 12, 15, 18	0.41
3	15	0.4 to 0.5

XRD analysis was performed on the sample with its compressive strength already measured, in order to perform crystalline analysis. X-ray diffraction (XRD, Rigaku MiniFlex2), operated at 40 kV, 40 mA and, CuK α radiation. The data was collected by using a nominal 2 θ step size of 0.01 °, count time of 0.5 s and 2 θ range of 5-90 °. The microstructure of geopolymer was observed using by scanning electron microscopy using secondary electrons. Specimens were coated with platinum prior to imaging in the SEM of accelerating voltage of 5 kV.

Results and Discussions

Effect of silicon sludge addition



Fig. 3. Physical properties on silicon sludge addition with alkali activator 18 M and L/S ratio 0.41: (a) compressive strength and (b) weight of unit volume.



Fig. 2. Microstructure of materials: (a) silicon sludge, (b) waste fused slag with silicon sludge and (c) waste fused slag.

Table 3. Minimisation of Gibbs free energy of geopolymer.

Experimental Ω (kJ/mol)	Comment
26 ± 3	b-eucryptite, NMnR/calorimetry
31 ± 8	Na-aluminosilicate glass, NMR
16 ± 2	Ca-aluminosilicate glass, NMR
39 ± 12	Synthetic anorthite, NMR/calorimetry
14 ± 4	Anorthite (minimum value), calorimetry
22.6	Na-aluminosilicate glass, calorimetry
9.2	Ca-aluminosilicate glass, calorimetry
25	Albite, NMR/calorimetry
34	Cordierite, NMR/calorimetry
Simulated/	
Calculated	Comment
U(KJ/IIIOI)	ALC: O (OILUD ² -view of initial matrices have
73 ± 2	Al ₂ Sl ₂ O ₄ (OH,H) ₈ ⁻ ring, ab initio, various basis sets
32	Anorthite, Monte Carlo simulation
34 ± 5	Kalsilite, ab initio total energy calculation
75	Al ₂ Si ₂ O ₄ (OH) ₈ ²⁻ ring, ab initio
162	Hydrated Al ₂ Si ₂ O ₄ (OH) ₈ ²⁻ ring, ab initio/MM
40	Cordierite, Monte Carlo simulation
40	Zeolite NaA, lattice energy calculation
43	Aluminosilicate cubic octamer (Q3,q3)8, semiempirical AM1 Hamiltonian
24	Ca-Tschermak's pyroxene, exchange across chains, lattice energy calculation

To observe the characteristics of geopolymer after adding the silicon sludge, compressive strength and unit volume weight were measured under various conditions. Fig. 3 shows the physical characteristics on addition of silicon sludge with alkali activator (18 M, L/S ratio 0.41).

As shown in Fig. 3, the sample without addition of silicon sludge showed the highest value (3.058 MPa). It is assessed that many pores created due to high Si/Al ratio of the waste fused slag are responsible for such low value at an initial stage. Depending on the amount of silicon sludge added, the compressive strength showed no insignificant difference from 10 wt% to 70 wt%, until it

heavily decreased after 80 wt%. This can be explained through complex reaction of geopolymer and reaction of silicon sludge. Initially, such influence is based on the difference of Gibbs free energy.

Table 3 shows minimization of Gibbs free energy at an amorphous aluminosilicate phase calculated based on John [8]. Eq. (1) represents reaction of the silicon sludge, and the Gibbs free energy on such reaction is -858.23 kJ/mol:

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$$
(1)

As shown in geopolymer and silicon sludge Gibbs free energy, a silicon sludge having very low Gibbs free energy reacts prior to geopolymerization, which ends up wasting a lot of Na^+ ions during the silicon sludge reaction. Therefore, due to the dominant reaction of silicon sludge, Na^+ to be used during geopolymerization is used during silicon sludge reaction instead, and ends up decreasing the compressive strength.

Secondly, addition of silicon sludge forms a large volume of pores. Especially, for the silicon sludge reaction having low Gibbs free energy, adding only 10 wt% silicon sludge causes discharge of fair amount of H₂ gas, forming a large volume of pores. Therefore, such pores formed through silicon sludge reaction weaken the matrix system of geopolymer, and decreases compressive strength. While observing unit volume weight, it decreased rapidly when more than 10 wt% silicon sludge was added, which means it's responsible for the formation of a large volume of pores due to the silicon sludge reaction. Thirdly, Si redox reaction consumed a large amount of water from geopolymer matrix. Therefore, not enough water is used during geopolymer reaction, which ends up decreasing the strength. In addition, a high curing temperature (70 °C) accelerates Si reaction and evaporates water. Therefore not enough is used during the reaction, which ends up decreasing the strength as well [9]. Such phenomena can be observed through XRD pattern.

Fig. 4 shows the change in XRD pattern when silicon sludge was added. When no silicon sludge (0 wt%) was added, due to a high pH level (18 M Alkali activator), a



Fig. 4. XRD pattern on silicon sludge addition with alkali activator 18 M and L/S ratio 0.41.

well-developed zeolite crystal phase was observed. However, when 10 wt% was added, it showed amorphous peak, and started to gradually show silicon peak when more than 20 wt% was added. In addition, it was observed that the intensity of the silicon peak increased as the amount of silicon sludge being added increased. This proves that larger amount of silicon sludge being added allows a lot of Na⁺ to be used during silicon sludge reaction, which eventually decreases geopolymerization and increases the silicon sludge reaction.

Surface of geopolymer on silicon sludge addition and L/S ratio

Silicon sludge reaction discharges H₂ gas and forms a number of pores internally and on the surface. These pores formed decrease unit volume weight and decrease physical characteristics. The reaction becomes more intense as the amount of silicon sludge being added increases, and forms more pores. Fig. 5 shows change of surface morphology and SEM micrograph depending on the amount of silicon sludge being added. It was observed in the surface morphology that the size of pores increased in size as the amount of silicon sludge being added increased. As more silicon sludge is added, Si which reacts to H₂O increases in volume and discharges more H₂ gas. However, geopolymer paste at L/S ratio 0.41 becomes unable to randomly discharge H₂ gas due to high viscosity, which ends up increasing the pore size. In addition, silicon sludge reaction causes the exothermic reaction by having high Gibbs free energy. Due to such process, as more silicon sludge is added, the temperature rises and accelerates formation of H₂ gas. As for SEM micrograph, a particle of silicon sludge was observed



Fig. 6. Weight of unit volume on various L/S ratio with alkali activator 15 M and silicon sludge 3 wt% addition.

overall. This is due to the fact that geopolymerization gets controlled and silicon sludge reaction accelerates when more than 20wt% is added. Even through XRD analysis results, the main peak appeared to be the silicon peak. Therefore, it was confirmed that the geopolymerization was controlled. In addition, fibers started to increase and formed heterogeneous microstructures as the amount being added increased. This is because the geopolymerization decreased as the amount being added increased.

Fig. 6 and Fig. 7 show surface morphology and weight of unit volume depending on L/S ratio. Unit volume weight tended to decrease as L/S ratio increased. Viscosity decreases as L/S ratio increases, and this process allows smooth discharge of H_2 gas which then increases micropores and decreases unit volume weight. No significant difference was observed from the surface morphology shown in Fig. 7. However the internal pores are expected to be increasing since the unit volume weight is decreasing.

Influence of alkali activator concentration

Fig. 8 shows physical characteristics of the silicon sludge



Fig. 5. Surface morphology of geopolymer on silicon sludge addition.



L/S ratio: 0.46 L/S ratio: 0.48 L/S ratio: 0.5 Fig. 7. Surface morphology on various L/S ratio with alkali activator 15 M and silicon sludge 3 wt% addition.



Fig. 8. Physical properties on silicon sludge addition with various alkali activator and L/S ratio 0.41: (a) compressive strength and (b) weight of unit volume.



Fig. 9. XRD pattern on silicon sludge addition with various alkali activator and L/S ratio 0.41: (a) 9 M, (b) 12 M, (c) 15 M and (d) 18 M.

addition geopolymer depending on the concentration of alkali activator. When no silicon sludge (0 wt%) was added, the strength tended to increase as the moral concentration increased.

The highest compressive strength (4.234 MPa) was shown at 12 M. The strength (4.233 MPa) maintained at 15 M and tended to decrease at 18 M. Excessively high moral concentration creates excess hydroxide ion which accelerates the formation of aluminosilicate and decreases compressive strength [10]. The strength tended to decrease as more silicon sludge was added. However, when 3 wt% was added, the strength maintained and the unit volume weight tended to decrease at 12 M and 15 M. This is because at 12 M and 15 M, sufficient amount of Na⁺ is provided to be used during silicon sludge reaction geopolymerization. Accordingly, due to the pores formed during silicon sludge reaction, the unit volume weight decreased while the compressive strength maintained due to geopolymerization.

Fig. 9 shows XRD pattern of silicon sludge addition geopolymer depending on the concentration of Alkali activator. Similar to the tendency of compressive strength, Zeolite intensity tended to increase as the concentration increased when no silicon sludge (0 wt%) was added. This is due to an adequate geopolymerization along with smooth elution of Si and Al within the raw material as the concentration increased. At 18 M, zeolite was observed, but the intensity decreased. Similar to compressive strength, it is assessed to have a lower crystallizability compared to that at 15 M in which excess hydroxide ion rapidly produced aluminosilicate gel and reacted suitably. While adding silicon sludge, from 3 wt% to 9 wt%, amorphous peak was observed. However, the silicon peak became the main peak when 12 wt% was added. It is assessed that the silicon sludge reaction disturbed geopolymerization, which prevented the formation of zeolite crystal phase.

Conclusions

In this experiment, physical characteristics and crystal phases of the waste fused slag geopolymer depending on addition of silicon sludge were observed to confirm influence of silicon sludge on geopolymerization. The waste fused slag geopolymer formed a large amount of H_2 gas and formed a number of pores as more silicon sludge was added, and it was possible to gain a very low unit volume weight. However, due to very low Gibbs free energy, silicon sludge reaction uses up a lot of Na⁺ compared to geopolymerization. Na⁺ within geopolymerization maintains electro-neutrality as a positive ion, and also forms a strong bonding to increase strength. Silicon sludge reaction occurs prior to geopolymerization and uses a large volume of Na⁺ leaving only insufficient amount for geopolymerization

which eventually decreases the compressive strength. In addition, silicon sludge not only forms a number of pores and weakens the matrix of geopolymer, but it also uses a large amount of water which must be used in geopolymer reaction and weakens the matrix. Therefore, the moral concentration must be controlled in order to increase the strength of geopolymer and to gain low unit volume weight. As a research result from 9 M to 18 M, the strength maintained and the unit volume weight decreased at 12 M and 15 M when silicon sludge (3 wt%) was added. For the case of waste fused geopolymer, moral concentration which would supply sufficient amount of Na⁺ when the silicon sludge is being added in order to process geopolymerization came out to be either 12 M or 15 M. At 18 M, too much OH- rapidly produced aluminosilicate and decreased the strength. In conclusion, a moral concentration suitable for geopolymerization does exist. It was observed that a sufficient supply of Na⁺ along with adequate existence of OH- are the most important factors in processing silicon sludge reaction and geopolymerization. In addition, it was observed that very light and porous geopolymers having relatively higher compressive strength could be fabricated with fused slag and spend silicon sludge as a bloating agent.

Acknowledgments

This work was supported by the New & Renewable

Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. (No. 2015 3030050080)

References

- 1. B. Nematollahi, J. Sanjayan and F.U.A. Sahikh, Ceram Int. 41 (2015) 5696-5704.
- A. Autef, E. Joussein, G. Gasgnier and S. Rossignol, J. Non Cryst Solids 358 (2012) 2886-2893.
- M.M.A. Abdullah, K. Hussin, M. Bnhussain, K.N. Ismail and W.M.W. Ibrahim, Int. J. Pure Appl. Sci. Technol. 6[1] (2011) 35-44.
- 4. U. Rattanasak and P. Chindaprasirt, Miner. Eng. 22 (2009) 1073-1078.
- 5. C. Descamps, C. bouallou and M. Kanniche, Energy. 3 (2008) 874-881.
- A. ACosta, I. Iglesias, M. Aineto, M. Romero and J.M. Rincon, Waste Manage. 22 (2002) 887-891.
- D.S. Kil, H.D. Jang, K.S. Kang and H.J. Han, J. of Korean Inst. of Resources Recycling. 17[4] (2008) 66-76.
- J.L. Provis, "modelling the Formation of Geopolymer, Modelling the formation of geoplymer", The University of Melbourne (2006) 66-75.
- 9. V. Medri, E. Papa, J. Dedecek, H. Jirglova, P. Benito, A. Vaccari and E. Landi, Ceram Int. 39 (2013) 7657-7668.
- 10. K. Somna, C. Jaturapitakkul, P. Kajitvichyanukul and P. Chindaprasirt, Fuel. 90 (2011) 2118-2124.
- 11. J. Davidovis, "Geopolymer Chemistry and Application", Iinstitut Geopolymere (2008) 3-75.