Effect of Molarity of Potassium Hydroxide Solution on Heat Resistance of Fly Ash-Slag Based Geopolymer

Apriany Saludung, Takumu Azeyanagi, Yuko Ogawa, and Kenji Kawai

Abstract Designing a building material with high fire resistance is crucial for minimizing the impact of catastrophic fire. Geopolymer, a new type of binder synthesized by the reaction of aluminosilicate sources with an alkaline solution, has been extensively studied as it offers comparable or even high durability when compared to ordinary Portland cement (OPC). The concentration of the alkaline solution is one of the important factors that affect the durability; however, there is very little data on the heat resistance of geopolymer activated with potassium hydroxide. Thus, this study aims to investigate the effect of molarity of potassium hydroxide on the heat resistance of fly ash-slag blended geopolymer paste. The potassium hydroxide (10, 12, and 14 M) and sodium silicate solutions were prepared as activator solutions. The initial heat curing at 70 °C for 24 h was applied. In addition, an OPC specimen was also prepared for comparison. After curing for 28 days, some specimens were exposed to high temperatures (500, 750, and 950 °C). The compressive strength of unexposed and exposed geopolymer and OPC paste specimens was measured. The results showed that the increase of molarity of potassium hydroxide solution increased the heat resistance of geopolymer in terms of retained compressive strength. Moreover, the geopolymer specimens could maintain higher compressive strength than that of OPC paste when exposed to high temperatures up to 950 °C. This is attributed to the mineral composition of geopolymer, which is different from OPC paste, as studied by X-ray diffraction analysis.

Keywords Geopolymer · Potassium hydroxide · Molarity · Compressive strength · Heat resistance

A. Saludung · T. Azeyanagi
Department of Civil and Environmental Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashihiroshima City, Japan

Y. Ogawa · K. Kawai (✉)
Civil and Environmental Engineering Program, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashihiroshima City, Japan
e-mail: kkawai@hiroshima-u.ac.jp

1   Introduction

Geopolymer material produced by the reaction of aluminosilicate sources with alkaline solutions has emerged as an alternative binder to ordinary Portland cement (OPC), essentially because of low energy consumption and low carbon dioxide emission when using industrial by-products in its production. The by-products used in the synthesis are mainly fly ash and ground granulated blast furnace slag (GGBS). Geopolymer produced from only fly ash is associated with a very long setting time and low compressive strength; therefore, the addition of slag is crucial to improve these properties [15]. The reaction mechanism of geopolymerization has been explained by some authors. The geopolymerization process starts with the dissolution of the solid aluminosilicate source by alkaline hydrolysis that releases $[SiO_4]^-$ and $[AlO_4]^-$ tetrahedral units. These tetrahedral units are linked with each other by sharing oxygen atoms to form polymeric bonds. The last process involves the polycondensation, where the geopolymer gel sets and forms a three-dimensional aluminosilicate network [4, 6, 18]. In fly ash/slag blends, the C-S-H phase and aluminosilicate gel co-exist in the system, which contributes to strength improvement [15].

On the other hand, designing buildings with good fire resistance is required in many sectors due to the experiences of fire disasters. Even though many buildings have been constructed with non-combustible materials such as brick, concrete, and steel, they cannot completely prevent the outbreak of fire and the building from collapsing. Some buildings are equipped or covered with heat-insulating materials, which can be very expensive. Geopolymer materials possess the potential as a fire-retardant due to their ceramic-like properties [3]. As shown by several previous studies, geopolymer material can maintain high compressive strength after exposure to high temperatures compared to OPC [8, 17, 20]. For instance, Kong and Sanjayan [8] compared the compressive strength of OPC paste with fly ash geopolymer paste after exposure to various temperatures. They found that OPC paste almost totally lost its compressive strength after being heated at 400 °C, while geopolymer paste exhibited high compressive strength after exposure to a temperature of 800 °C, which was 5.4% higher than its initial strength at room temperature. Another study by Zhang et al. [20] also compared the compressive strength of OPC and geopolymer pastes. They found that OPC paste completely lost its compressive strength after exposure to 800 °C, while geopolymer still maintained its compressive strength after exposure to this temperature. The reason behind this is because of the re-crystallization of geopolymer at a very high temperature which leads to the formation of the analogies to natural minerals having extremely high fire resistance [5]. Moreover, some studies also claimed that geopolymer could maintain its strength at high temperatures due to the sintering effect [7, 10].

The fire resistance of geopolymer is affected by several factors, such as the type of raw materials [9, 14, 20], curing conditions [1], and alkali cation types [1, 11]. The combination of sodium silicate and sodium hydroxide is the most common activator solution used in geopolymer production. Although many studies have been conducted on the heat resistance of geopolymers, there is very little data on the heat

resistance of geopolymer activated with potassium hydroxide (KOH). In addition, the molarity of alkali hydroxide solution can significantly affect the properties of geopolymer [2, 15]. Thus, this study aims to investigate the effect of the molarity of KOH solution on the heat resistance of fly ash-slag blended geopolymer paste. As a comparison, a heat resistance test on OPC paste was also conducted.

2 Materials and Method

2.1 Materials and Specimen Preparation

This study utilized fly ash (Blaine fineness = 3,550 cm^2/g, density = 2.24 g/cm^3) which conforms to JIS A 6201, GGBS (Blaine fineness = 4,170 cm^2/g, density = 2.91 g/cm^3) which conforms to JIS A 6206, and OPC (Blaine fineness = 3,340 cm^2/g, density = 3.16 g/cm^3). Their chemical compositions are shown in Table 1. Sodium silicate solution consisting of 13.4 mass% Na_2O, 27.3 mass% SiO_2, and 59.3 mass% H_2O, and potassium hydroxide solution were utilized as alkaline solutions. The potassium hydroxide solutions were prepared in 10, 12, and 14 M by dissolving the potassium hydroxide pellets in water to form one liter solution. These solutions were prepared one day before mixing. The ratio of alkaline liquid to binder (l/b) and the ratio of sodium silicate to potassium hydroxide (SS/KH) were maintained constant at 0.52 and 1.35 by mass, respectively. The detail of the mix proportion is shown in Table 2.

The geopolymer paste was synthesized as follows: fly ash and GGBS were first dry-mixed together in a pan mixer for 3 min. Alkaline solutions were added to the dry materials and mixed rapidly and continuously for another 3 min. Subsequently, the fresh geopolymer paste was cast into cylindrical plastic molds ($\Phi50 \times 100$ mm).

Table 1 Chemical composition of raw materials. LOI is loss of ignition at 1000 °C

Component (mass%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	MgO	Na_2O	SO_3	LOI
Fly ash	64.44	20.65	4.18	2.25	1.53	1.19	0.58	N/A	N/A	2.9
GGBS	35.45	14.06	0.27	43.78	0.23	0.56	5.84	0.24	0.62	0.05
OPC	19.89	5.19	3.07	64.79	0.36	N/A	1.26	0.31	1.95	2.65

Table 2 Mix proportion

Sample ID	Fly ash (g)	GGBS (g)	OPC (g)	Alkali solution/binder ratio	Na_2SiO_3/KOH	Water/cement ratio	Na_2SiO_3 solution (g)	KOH solution (g)	Water (g)
Geo-10 M	385	315	0	0.52	1.35	–	210	156	–
Geo-12 M	385	315	0	0.52	1.35	–	210	156	–
Geo-14 M	385	315	0	0.52	1.35	–	210	156	–
OPC paste	0	0	700	–	–	0.45	0	0	315

On the other hand, OPC paste was prepared with a water to cement ratio of 0.45 in accordance with the above mixing procedure. Just after casting, both OPC and geopolymer specimens were cured in an oven at 70 °C for 24 h under sealed condition. After oven curing, the specimens were stored at ambient temperature (approximately 20°C), demolded after aging for three days, and stored in a sealed plastic bag to prevent alkalinity loss or carbonation before the tests.

2.2 Heat Resistance Test

After curing for 28 days, specimens were exposed to high temperatures at 500, 750, and 950 °C by placing them into an electric furnace with a heating rate of 20 °C/min. When the targeted temperature was reached, it was maintained for 1 h. Afterward, the furnace was turned off and let it cool down to room temperature. Some specimens were left unexposed for comparison.

2.3 Characterization and Measurement

The compressive strength of unexposed and exposed geopolymer paste and OPC paste specimens at the age of 28 days was evaluated following JIS R 5201. It was conducted using a universal testing machine with a compression capacity of 250 kN and a loading rate of 0.2 mm/min. The test was repeated for three specimens for each mixture, and an average was taken.

The phase of geopolymer and OPC product was characterized by X-ray diffraction (XRD). It was conducted using an X-ray diffractometer in the 2-theta range of 10–65° with a Cu Kα X-ray source.

The microstructure of unexposed and exposed geopolymer specimens was examined using scanning electron microscopy (SEM). It was conducted at 15 kV of accelerated voltage. The samples were coated with platinum.

3 Results and Discussion

3.1 Compressive Strength

The compressive strength of the specimens unexposed and exposed to high temperatures was measured and compared. Figure 1(a) shows that the increase of KOH molarity leads to the increase of initial compressive strength. The improvement is attributed to the fact that the increase in molarity increases the dissolution rate of the aluminosilicate precursors due to the high pH of high concentration of alkali solution
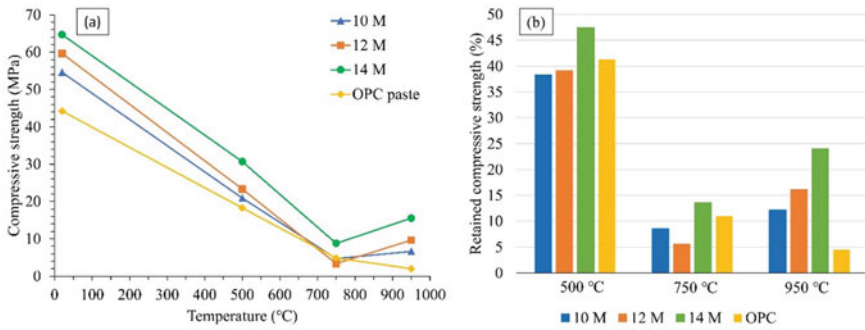
Fig. 1 Compressive strength of geopolymer paste as a function of temperature **a** and retained compressive strength after heat exposure **b**

[4, 12], resulting in more gel formation and denser microstructure. In addition, it can be seen that the compressive strength of all the geopolymer specimens is higher than that of OPC paste.

After exposure to high temperatures, all the specimens exhibited a significant loss of compressive strength due to the decomposition of C-(A)-S-H gel. Similar to C-S-H in OPC paste, C-(A)-S-H in geopolymer is the main source of compressive strength development, and therefore, the decomposition of C-(A)-S-H in geopolymer and C-S-H in OPC paste will lead to a significant loss of compressive strength. Further heating at a higher temperature, all the specimens continuously lost their strength; however, when geopolymer specimens were heated up to 950 °C, the compressive strength slightly increased and became higher than the retained compressive strength of specimens after exposure to 750 °C.

Increasing the molarity improves the heat resistance of geopolymer. Figure 1(b) shows the percentage of retained compressive strength of geopolymer and OPC paste. Although the three series of geopolymer present a similar tendency of strength loss, the geopolymer with 14 M KOH shows the highest retained compressive strength corresponding to approximately 24% of its initial strength after heating at 950 °C. In contrast, the OPC specimen retains only 4.5% of its initial compressive strength after heating at 950 °C.

3.2 Phase Changes

Figure 2 represents the XRD patterns of unexposed and exposed OPC paste and geopolymer paste. Only the XRD pattern of geopolymer activated with 14 M KOH was shown since all the geopolymer specimens present similar phase changes after exposure to high temperatures. It can be seen in Fig. 2(a) that OPC paste mainly consists of portlandite, with some low-intensity peaks of C_2S (belite), C_3S (alite), ettringite, and calcite. At 500 °C, the portlandite peak was still observable, and it
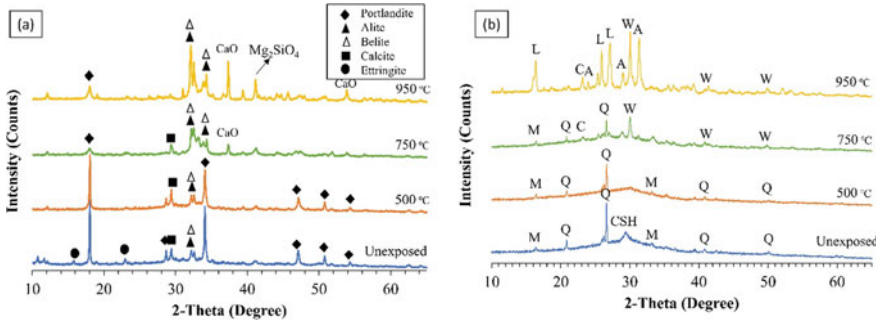
Fig. 2 XRD patterns of unexposed and exposed OPC pastes **a**, and geopolymer paste activated with 14 M KOH **b**. (Q = quartz, M = mullite, C = cristobalite, W = wollastonite, A = akermanite, L = leucite)

started to decrease considerably at 750 °C. At 750 °C, a CaO peak was formed, and considerable amounts of C_2S and C_3S were observed. Calcite peak disappeared at 950 °C, which indicates a complete decomposition of calcite at a temperature between 750 and 950 °C. The peak intensity of CaO and C_3S increased considerably with the increase of exposure temperature at 950 °C. This is attributed to the further decomposition of portlandite, calcite, and C-S-H.

Figure 2(b) represents the XRD pattern of geopolymer paste (14 M). In the unexposed specimen, the mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2) peaks are originally from fly ash [16]. After exposure to 500 °C, these peaks remain, while the C-(A)-S-H peak almost vanished due to dehydroxylation. Unlike the OPC specimen, further heating at 750 °C, new crystalline peaks such as wollastonite ($CaSiO_3$) and cristobalite (SiO_2) were observed in geopolymer, proving the re-crystallization of this material into secondary mineral phases. Moreover, at 950 °C, other new crystalline phases such as leucite ($KAlSi_2O_6$) and akermanite ($Ca_2Mg[Si_2O_7]$) were observed. The presence of these two major phases is believed to contribute to the slight increase in the compressive strength after exposure to 950 °C. The effect of molarity on phase change was insignificant because all the geopolymer specimens present similar phase changes at high temperatures; however, increasing the molarity increases the potassium content in the paste, and therefore, the amount of leucite formed after heating at 950 °C probably increased.

3.3 Microstructure

The geopolymer specimen showing the highest retained compressive strength after exposure to high temperatures was also characterized by SEM, and the result is shown in Fig. 3. In the unexposed specimen, it was evident that geopolymeric gel was found to co-exist with the calcium aluminate silicate gel (C-(A)-S-H), resulting in a compact microstructure.
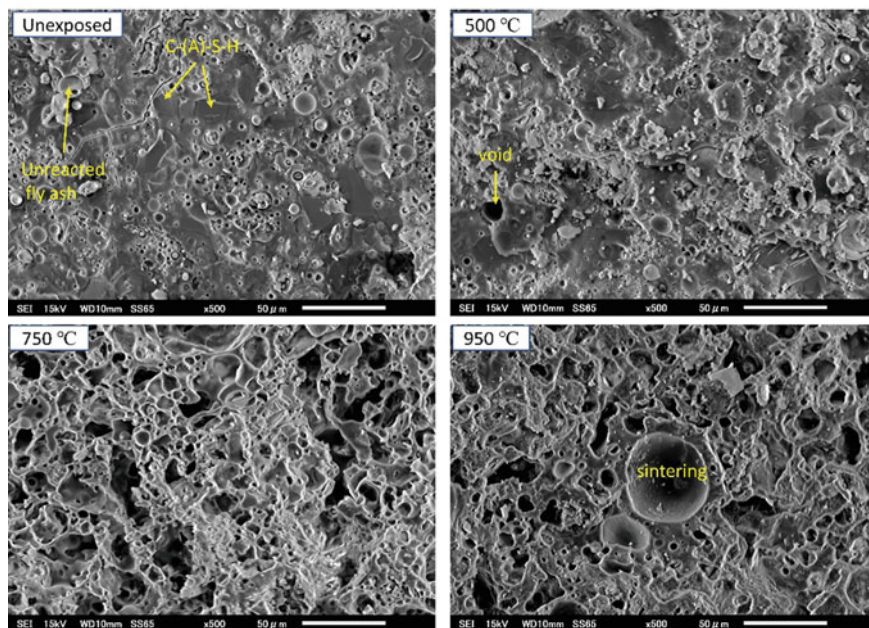
Fig. 3 SEM images of unexposed and exposed geopolymer paste activated with 14 M KOH

After heating at 500 °C, the deterioration occurs due to the impact of dehydration and decomposition of the gels, resulting in a coarser microstructure compared to the unexposed sample. According to previous studies, the dehydration of the C-S-H in hardened OPC commences at approximately 110 °C and becomes completely decomposed at a temperature range of 600–800 °C [13, 19]. The dehydration of C-(A)-S-H in geopolymer is estimated to occur at a temperature similar to C-S-H in OPC. Further heating at 750 °C, the microstructure becomes highly porous, resulting in very low compressive strength. However, after heating at 950 °C, there was evidence of sintering. This could be the reason for slightly increasing the compressive strength from 750 to 950 °C of exposure temperature.

4 Conclusion

In this study, the effect of KOH molarity on the heat resistance of geopolymer exposed to 500, 750, and 950 °C was investigated. The following conclusions can be drawn from the experimental results.

1. The increase of molarity of KOH solution increases the initial compressive strength of geopolymer pastes.

After exposure to high temperature, 14 M KOH solution performed the highest retained compressive strength, followed by 12 and 10 M. The compressive strength of all the geopolymer samples exposed to 950 °C was higher than that exposed to 750 °C, which is attributed to the sintering effect and formation of new crystalline phases.

2. In comparison with the OPC paste, geopolymer pastes showed better heat resistance in terms of compressive strength loss. Unlike geopolymer which re-crystallized at high temperature, OPC paste presents an increase in the amount of C_2S and C_3S and the formation of CaO as the result of the thermal decomposition of C-S-H and calcium hydroxide.

Geopolymer made from fly ash and GGBS, activated with sodium silicate and potassium hydroxide solutions has been proven to have better performance than OPC paste when exposed to high temperatures, thus promising the use of geopolymer as an alternative material to OPC.

References

1. Bakharev T (2006) Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing. Cem Concr Res 36:1134–1147
2. Budh CD, Warhade NR (2014) Effect of molarity on compressive strength of geopolymer mortar. Int J Civ Eng Res 5:2278–3652
3. Davidovits J (2017) Geopolymers: ceramic-like inorganic polymers. J Ceram Sci Technol 8:335–350
4. Duxson P, Fernández-Jiménez A, Provis JL, Lukey GC, Palomo A, Van Deventer JSJ (2007) Geopolymer technology: the current state of art. J Mater Sci 42:2917–2933
5. Duxson P, Lukey GC, Van Deventer JSJ (2006) Evolution of gel structure during thermal processing of Na-geopolymer gels. Langmuir 22:8750–8757
6. Hajimohammadi A, Provis JL, Van Deventer JSJ (2010) Effect of alumina release rate on the mechanism of geopolymer gel formation. Chem Mater 22:5199–5208
7. Jaya NA, Al Bakri Abdullah MM, Ghazali CMR, Hussain M, Hussin K, Ahmad R (2016) Kaolin Geopolymer as precursor to ceramic formation. In: MATEC Web Conference
8. Kong DLY, Sanjayan JG (2010) Effect of elevated temperatures on geopolymer paste, mortar and concrete. Cem Concr Res 40:334–339
9. Kong DLY, Sanjayan JG, Sagoe-Crentsil K (2007) Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures. Cem Concr Res 37:1583–1589
10. Kuenzel C, Grover LM, Vandeperre L, Boccaccini AR, Cheeseman CR (2013) Production of nepheline/quartz ceramics from geopolymer mortars. J Eur Ceram Soc 33:251–258
11. Lahoti M, Wong KK, Tan KH, Yang EH (2018) Effect of alkali cation type on strength endurance of fly ash geopolymers subject to high temperature exposure. Mater Des 154:8–19
12. Nath SK, Kumar S (2019) Role of alkali concentration on reaction kinetics of fly ash geopolymerization. J Non Cryst Solids 505:241–251
13. Peng GF, Huang ZS (2008) Change in microstructure of hardened cement paste subjected to elevated temperatures. Constr Build Mater 22:593–599
14. Rickard WDA, Temuujin J, Van Riessen A (2012) Thermal analysis of geopolymer pastes synthesised from five fly ashes of variable composition. J Non Cryst Solids 358:1830–1839
15. Saha S, Rajasekaran C (2017) Enhancement of the properties of fly ash based geopolymer paste by incorporating ground granulated blast furnace slag. Constr Build Mater 146:615–620

16. Saludung A, Ogawa Y, Kawai K (2018) Microstructure and mechanical properties of FA/GGBS-based geopolymer. In: MATEC Web Conference. https://doi.org/10.1051/matecconf/201819501013
17. Saxena SK, Kumar M, Singh NB (2017) Fire resistant properties of alumino silicate geopolymer cement mortars. Mater Today Proc 4:5605–5612
18. Singh B, Ishwarya G, Gupta M, Bhattacharyya SK (2015) Geopolymer concrete: a review of some recent developments. Constr Build Mater 85:78–90
19. Tantawy MA (2017) Effect of high temperatures on the microstructure of cement paste. J Mater Sci Chem Eng 05:33–48
20. Zhang HY, Kodur V, Qi SL, Cao L, Wu B (2014) Development of metakaolin-fly ash based geopolymers for fire resistance applications. Constr Build Mater 55:38–45