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Fabrication and characterization of hardened bodies from Japanese volcanic ash using geopolymerization

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Abstract

Hardened bodies were fabricated from Japanese volcanic ash after mixing with an alkali solution, molding, and curing. The volcanic ash was composed of approximately 70% crystalline anorthite sodium [(Ca, Na) (Si, Al)$_4$O$_8$] phase and $\leq 30\%$ amorphous silicate phase. First, a starting mixture was prepared by mixing the ground volcanic ash with a sodium hydroxide solution. The mixture was placed in a plastic mold using a glass rod, and then cured at 50 °C and 80% relative humidity for 3 days. The compressive strength of the resulting hardened body increased with increasing concentration of sodium hydroxide solution. When a 13.5 mol/L sodium hydroxide solution was used, the average compressive strength of the hardened body reached 80.1 MPa. The hardening mechanism for the volcanic ash during curing is discussed.

Keywords: C. Mechanical properties; D. Silicate; E. Structural applications; Volcanic ash

1. Introduction

Generally, alkali-activated cements (geopolymers) are fabricated from a slurry consisting of metakaolin, which is obtained by heating the clay mineral kaolin at approximately 600–700 °C, or mixing fly ash exhaust from a coal-burning power plant with an alkali solution [1–9]. Usually, water glass (sodium silicate hydroxide) is also added to the starting slurry to support the solidification reaction as an active reactant. This solidification behavior is called geopolymerization, and the chemical reaction that forms the hardened bodies (geopolymers) can be written as follows [7]:

$$-\mathrm{Si}-\mathrm{OH}+\mathrm{HO}-\mathrm{Si}-+n\mathrm{M}^{m+} \rightarrow -[-\mathrm{Si}-\mathrm{O}-\mathrm{M}-\mathrm{O}-\mathrm{Si}-]-_{n}+{}_{n}\mathrm{H_2O}\uparrow \quad (1)$$

To date, geopolymers have been fabricated from various starting materials with amorphous aluminosilicate phases, such as sewage sludge [10] or ferronickel slag [11], not only from conventional metakaolin or fly ash. Although Palomo et. al reported that the amorphous/vitreous phase content in binders should be over 50 wt% [12], volcanic ash that contains only a small amount of active silicate glass phases is thought to be a potential raw material for fabrication of geopolymers. In fact, several reports concerning volcanic ash derived geopolymers have been published [13–15]. In Japan, there are many active volcanoes, and these emit a large amount of volcanic ash when they erupt. At present, most of this ash is collected and disposed of in landfills, and the establishment of an effective use for volcanic ash has long been desired in Japan.

This study employed a low energy consumption method for the fabrication of hardened bodies from Japanese volcanic ash without the need for sintering. Specifically, the geopolymerization reaction shown in (1) was used. First, the amount of amorphous silicate phase in the volcanic ash precursor was estimated using a reported extrapolation method [16]. An attempt was then made to fabricate a hardened body by mixing volcanic ash and an alkali solution. The effects of the NaOH solution concentration, the addition of water glass, and the curing time on the compressive strength of the resulting hardened bodies were investigated. Furthermore, in order to clarify the formation and hardening mechanism for geopolymers using this method, X-ray diffraction (XRD), Fourier

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transform infrared (FTIR) spectroscopy, and inductively coupled plasma (ICP) spectroscopy were carried out on the volcanic ash before and after alkali solution treatment.

2. Experimental procedure

Mt. Shinmoe, which is located in the southern part of Japan between Kagoshima and Miyazaki Prefectures, resumed eruption in January 2011 and remains active today. Fig. 1 shows SEM micrographs of volcanic ash from Mt. Shinmoe, and Table 1 shows its chemical composition and that of geopolymer samples. Some of the particles had porous surfaces, while others were dense. The crystal phases in the volcanic ash were analyzed by XRD (XD-D1: Shimadzu Co., Ltd., Japan). In order to estimate the relative content of each phase, an artificial anorthite crystal was prepared from a reagent-grade powder mixture of $CaCO_3$, Al_2O_3, and SiO_2, in proportions corresponding to stoichiometric anorthite. This mixture was heated at 1300 °C for 30 h in a platinum crucible. Following cooling, it was then ground into particles less than 500 μm in diameter with a sieve and this powder was reheated at 1300 °C for 30 h in the same crucible to form a single crystal phase of anorthite. This highly crystalline sample was used as a reference for extrapolating the crystalline anorthite content of the original volcanic ash by comparing the peak intensities at 2θ values of around 23.7°. The amount of glass phase in the volcanic ash could then be calculated as the remainder.

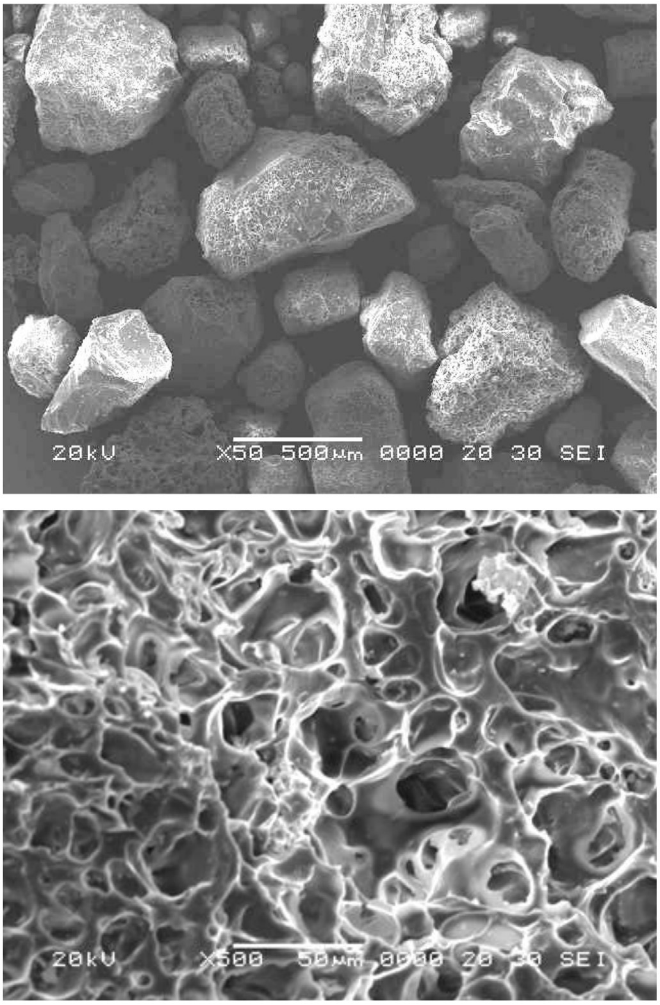

Fig. 1. SEM micrographs of volcanic ash from Mt. Shinmoe.

Ground volcanic ash (30 g) consisting of particles smaller than 200 μm was mixed with 10 ml of 1–16.5 mol/L NaOH solution and placed using a glass pushrod (∅6 mm) into a cylindrical acrylic pipe (∅15 mm × 30 mm in height) with one end sealed. In order to clarify the effect of water glass addition to the starting mixture, and to investigate the standard geopolymer fabrication method from fly ash or metakaolin, starting mixtures containing 30 g of volcanic ash, 4.5 ml of 8.5 mol/L NaOH (99%; Kishida Chemical Industries, Ltd., Japan) solution, and various amounts of sodium silicate water glass (SiO_2: 37%, Na_2O: 17.5%; Kishida Chemical Industries, Ltd., Japan) were also prepared. Hardened bodies were prepared by curing these mixtures in the acrylic mold at 50 °C and 80% relative humidity for 72 h. The compressive strength of the samples was measured using an Instron 5582 universal testing machine (Instron Co., Ltd., U.S.A.), with a crosshead speed of 10 mm/min. Three to five test pieces were prepared for each set of conditions. In order to confirm the formation of a geopolymer, FT-IR spectra were recorded using the KBr pellet method with a Spectrum 100 (PerkinElmer Inc., U.S.A.). In addition, to determine the solubility of Al, Si and Ca ions from the volcanic ash in a strongly alkali solution, 3 g of volcanic ash was soaked in 300 ml of a 10 mol/L NaOH solution so as to form a C–S–H gel by the pozzolanic reaction (not geopolymerization). After 0.5–3 days, the concentrations of Al^{3+}, Si^{4+} and Ca^{2+} in the solution were analyzed by ICP spectroscopy (ICPS-7000: Shimadzu Co., Ltd., Japan).

3. Results and discussion

3.1. Hardening behavior

Fig. 2 shows the compressive strength of hardened bodies formed with different concentrations of NaOH solution. The compressive strength is seen to increase with NaOH concentration, and has a value of 80.1 MPa for a 13.5 mol/L solution. This is relatively high compared to that for geopolymers fabricated from fly ash or kaolin [19–21]. It should be noted that when higher solution concentrations of 15.5 and 16.5 mol/L were used, the samples did not completely harden after curing for 72 h, so compressive strength tests were not carried out for these samples. It is believed that the results shown in Fig. 2 can be explained in terms of the amount of the sodium silicate phase that is formed in the samples. This phase is thought to be responsible for the increase in compressive strength. Since the amount of sodium silicate increased with NaOH solution concentration, so too did the compressive strength of the samples. It has been reported that for geopolymers under wet conditions, the compressive strength decreased by about 40% [14]. Therefore, for the samples in the present study with a high compressive strength, there is also a possibility of a decrease in compressive strength under wet conditions.

Table 1
Chemical composition of volcanic ash (from Mt. Shinmoe in Japan) and geopolymer samples used in this study.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	TiO	MnO	Total
Volcanic ash	54.93	16.44	10.89	8.79	2.84	3.30	1.72	0.75	0.21	99.87
With 1 mol/L	54.28	16.24	10.76	8.69	4.12	3.26	1.70	0.74	0.21	100
3.5 mol/L	52.55	15.73	10.42	8.41	7.18	3.16	1.65	0.72	0.20	100
6.5 mol/L	50.61	15.15	10.03	8.10	10.60	3.04	1.58	0.69	0.19	100
7.5 mol/L	50.00	14.96	9.91	8.00	11.69	3.00	1.57	0.68	0.19	100
8.5 mol/L	49.40	14.78	9.79	7.90	12.75	2.97	1.55	0.67	0.19	100
9.5 mol/L	48.81	14.61	9.68	7.81	13.78	2.93	1.53	0.67	0.19	100
10.5 mol/L	48.24	14.44	9.56	7.72	14.79	2.90	1.51	0.66	0.18	100
11.5 mol/L	47.68	14.27	9.45	7.63	15.78	2.86	1.49	0.65	0.18	100
12.5 mol/L	47.14	14.11	9.34	7.54	16.74	2.83	1.48	0.64	0.18	100
13.5 mol/L	46.60	13.95	9.24	7.46	17.68	2.80	1.46	0.64	0.18	100
15.5 mol/L	45.57	13.64	9.03	7.29	19.50	2.74	1.43	0.62	0.17	100
16.5 mol/L	45.07	13.49	8.94	7.21	20.38	2.71	1.41	0.62	0.17	100

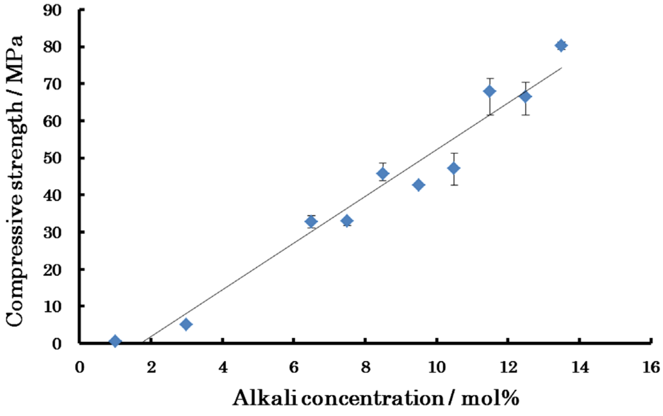

Fig. 2. Compressive strength of hardened bodies formed with various concentrations of NaOH solution.

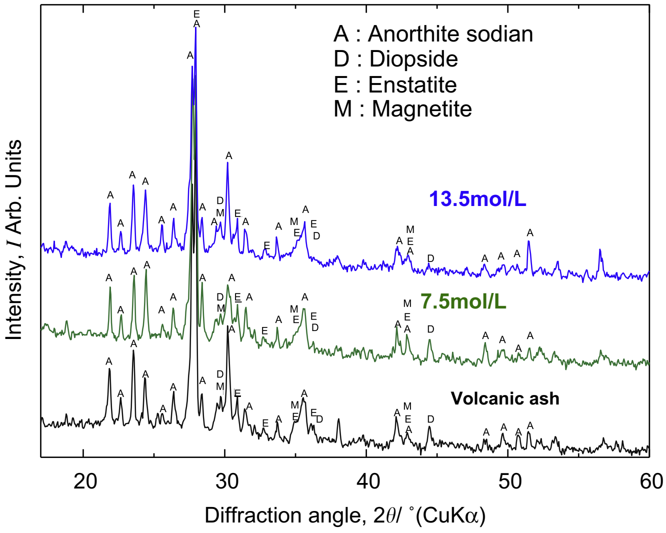

Fig. 3. XRD patterns for samples formed with 7.5, 11.5, and 13.5 mol/L NaOH solutions, and for the original volcanic ash.

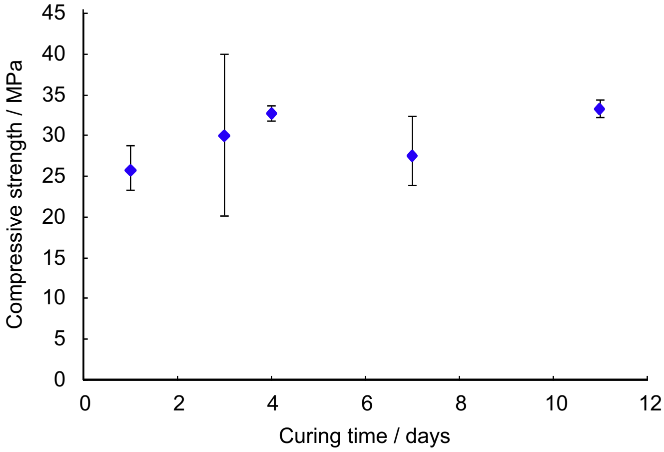

Fig. 4. Compressive strength of hardened bodies formed from 7.5 mol/L NaOH solution with various curing times.

Fig. 3 shows XRD patterns for samples after mixing with 7.5 and 13.5 mol/L NaOH solutions, and that for the original volcanic ash is included as a reference. It can be seen that the NaOH solution had no effect on the XRD pattern. Although the main crystal phase was anorthite sodium, (Ca,Na)(Si, $Al)_4O_8$, smaller amounts of diopside, enstatite and magnesite were also detected. No halo peaks with 2θ values between 20° and 30° and between 25° and 35°, corresponding to silicate glass and geopolymers, respectively, could be clearly detected for any of the samples, because their intensity was too low compared to that for the anorthite peaks [9].

3.2. Effects of curing time and addition of water glass

Fig. 4 shows the compressive strength of hardened bodies formed using a 7.5 mol/L NaOH solution and various curing times. Although a higher average compressive strength was obtained for a curing time of 3 days than for 1 day, further curing had little effect, with the compressive strength remaining at 30–35 MPa. This suggests that a curing time of 3 days yields a sufficient compressive strength, since the solidification reaction, or geopolymerization, seemed to be completed within that timeframe. However, the curing temperature of 50 °C should also be taken into account because water evaporation is fast at this temperature, and extended curing should be avoided.

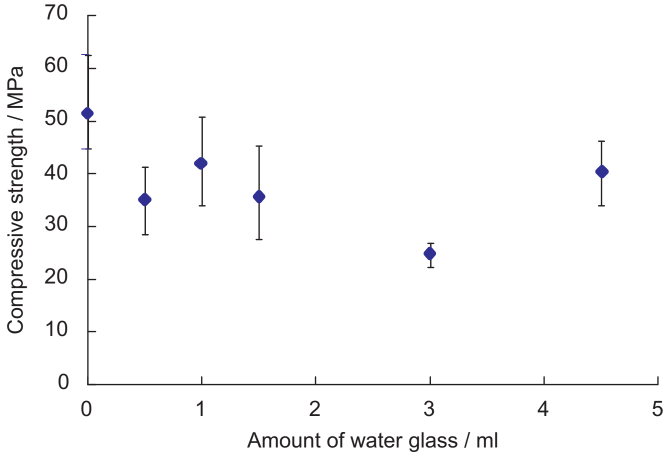

Fig. 5. Compressive strength of hardened bodies formed from 8.5 mol/L NaOH solution with various amounts of water glass added.

In order to clarify the effect of water glass addition on the hardening process, various amounts of water glass were added to a starting mixture containing volcanic ash and a 8.5 mol/L NaOH solution. Fig. 5 shows that although the addition of water glass causes a slight reduction in the compressive strength, there is very little dependence on the actual amount added. It is considered that the presence of water glass does not have an important influence on the hardening mechanism in this system, because the volcanic ash already contains a significant amount of SiO_2, unlike other raw materials such as fly ash or kaolinite, as shown in Table 1.

3.3. Geopolymerization

As previously stated, no strong halo peak due to the silicate glass phase could be detected in the XRD pattern in Fig. 3 for a 2θ value of around 26° [9]. Therefore, to estimate the silicate glass content, it was first necessary to determine the amount of anorthite phase based on extrapolation of accurately determined XRD peak intensities for a highly crystalline artificial anorthite sample [16]. Fig. 6 shows the results of this extrapolation for the volcanic ash of Mt. Shinmoe, which is found to contain 70 mass% of the crystalline anorthite phase. Since small amounts of diopside, enstatite and magnetite crystalline phases were also present in the volcanic ash, the silicate glass phase was estimated to be less than 30 mass%. It should be noted that when the artificial anorthite crystal was ground to a particle size of ≤200 μm and mixed with a 10 mol/L NaOH solution, the sample did not harden after a curing time of 72 h. This suggests that the presence of the silicate glass phase plays an important role in the hardening process.

Fig. 7 shows FT-IR spectra of the original volcanic ash and hardened bodies after mixing with NaOH solutions with concentrations ranging from 3.5 to 13.5 mol/L. Fly ash shows a typical adsorption band around 1085 cm^{-1}, which can be assigned to asymmetric stretching vibrations of T–O (T: Si, Al) [9]. For both fly ash and metakaolin, this band was found to shift to a lower frequency of about 990 cm^{-1} after reaction with an alkali solution [9]. This is probably due to the arrangement of Al^{3+} ions, namely the Al–O network structure formed in the silicate chain network due to geopolymerization, as expressed by reaction (1) [6]. In contrast, for the hardened bodies derived from volcanic ash, the adsorption band around 1000 cm^{-1} did not shift after alkali solution treatment, as seen in Fig. 7. However, it appears sharper after alkali solution treatment, possibly because of the formation of an Al–O network structure in the hardened body. The adsorption band in Fig. 7 at around 1450 cm^{-1} which becomes stronger with increasing solution concentration, corresponds to the adsorption band of CO_3^{2-} [11].

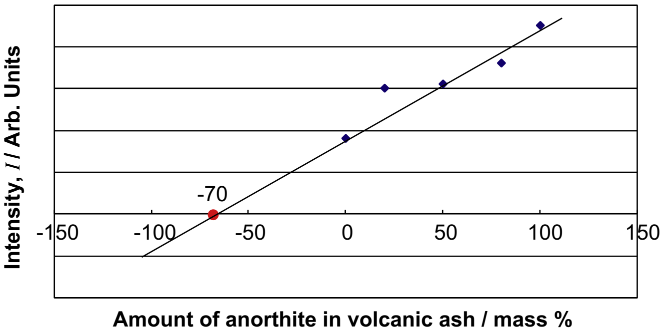

Fig. 6. Extrapolation line used to estimate the amount of crystalline anorthite phase in volcanic ash by comparison with an artificial highly crystalline anorthite sample.

Fig. 8 shows the cumulative amount of Si^{4+}, Al^{3+}, and Ca^{2+} eluted into a 10 mol/L sodium NaOH from the original volcanic ash over time. Both Si^{4+} and Al^{3+} ions dissolved into the solution, and the eluted amount saturated after 12 h. In contrast, Ca^{2+} ions did not dissolve into the solution, even after 3 days. Thus, the pozzolanic reaction involving Ca^{2+} and Si^{4+} ions seems not to occur in this system. The dissolved Si^{4+} and Al^{3+} ions can react with each other to form a geopolymer structure, as expressed by reaction (1), resulting in a hardened body.

3.4. Micromorphology

The strengthening of hardened bodies produced from volcanic ash after alkali treatment indicates a change in their micromorphology. Fig. 9(a) and (b) show the micromorphology of fractured surfaces of the hardened bodies formed with 3.5 and 13.5 mol/L NaOH solutions, respectively. In Fig. 9(a), particles smaller than 10 μm in diameter are observed. In contrast, in Fig. 9(b), these particles are surrounded by a newly precipitated phase, so that the individual particles cannot be distinguished. Furthermore, since the XRD data shown in Fig. 3 indicates that the alkali treatment did not cause a change in the crystal phases present, the large rectangular particles seen in Fig. 9(b) are thought to be anorthite sodium crystals. Although such particles could not be directly observed in the original volcanic ash, they are thought to have been present within the amorphous component, which was subsequently removed by dissolution into the concentrated alkali solution. This was followed by precipitation of an amorphous sodium silicate containing aluminosilicate phase (a geopolymer), which bonded strongly

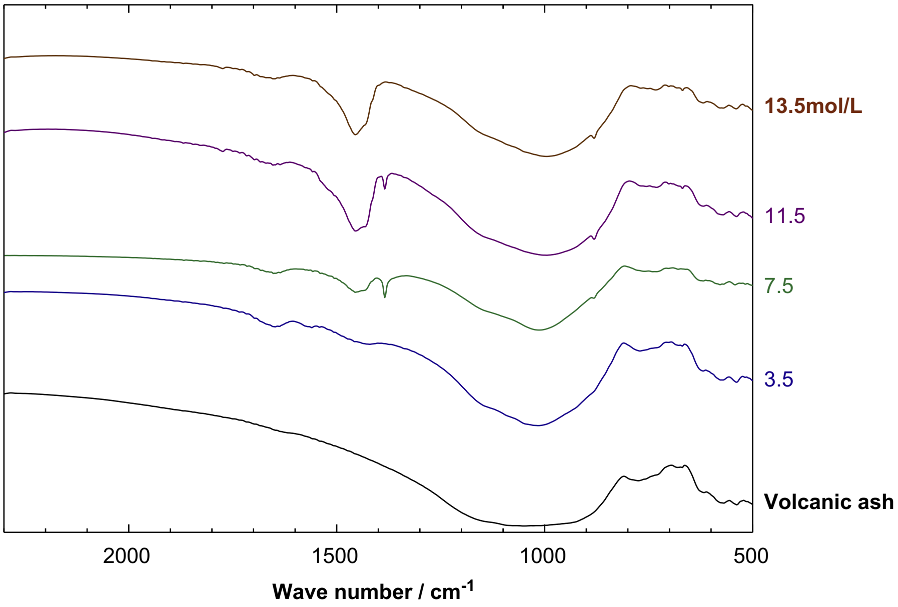

Fig. 7. FT-IR spectra of original volcanic ash and hardened bodies after mixing with NaOH solutions with concentrations from 3.5 to 13.5 mol/L.

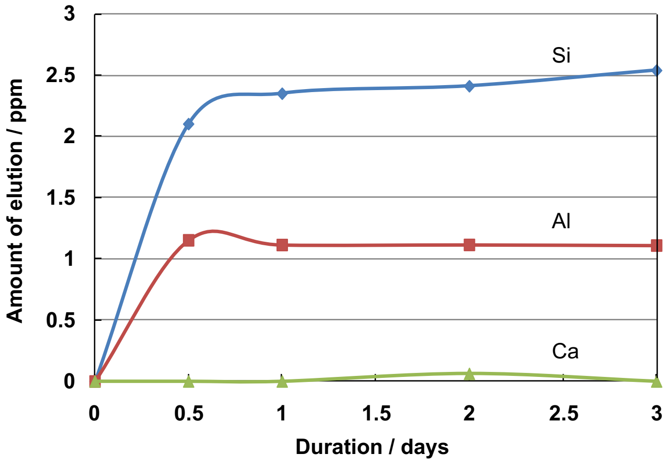

Fig. 8. Cumulative amount of Si^{4+}, Al^{3+}, and Ca^{2+} eluted over time into 10 mol/L NaOH solution from original volcanic ash.

with the rectangular anorthite sodium crystal particles, thus leading to an increase in the compressive strength of the material. In other words, the crystalline anorthite sodium phase is thought to act as an active filler material in the geopolymer, because hardened bodies derived from volcanic ash had higher strength than those derived from fly ash [17–19].

The above observations indicate that the polycondensation mechanism in volcanic ash is different to that in metakaolin or fly ash based geopolymers. From the ICP results, the volcanic ash contains a very low concentration of Al^{3+} ions, most of which remain within the aluminosilicate crystal structure and so do not become dissolved during geopolymerization. Hence, polycondensation may result from chemical reactions involving amorphous silica that produce (Na,Si) phases in sufficient quantities to form bridges between the various crystalline and microcrystalline phases. At least in the surface region, these

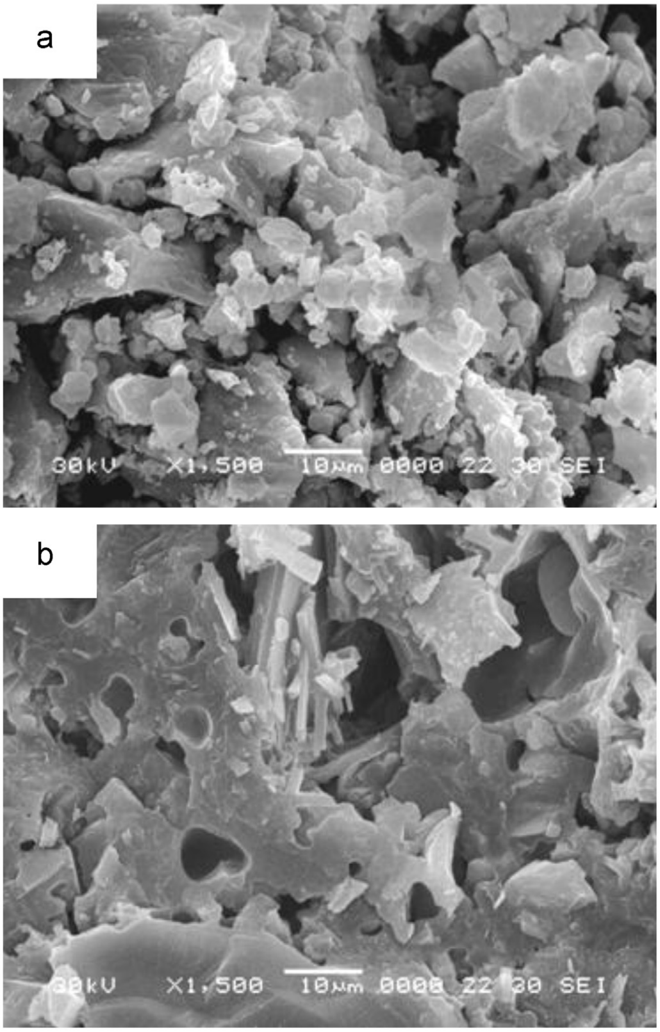

Fig. 9. Micromorphology of fractured surfaces of hardened bodies made with (a) 3.5 and (b) 13.5 mol/L of NaOH solution.

crystalline and microcrystalline phases become reactive in a highly alkaline medium. Although this is particularly true at a temperature of 50 °C, it was also shown to be the case at room temperature and to lead to very stable geopolymers [13].

4. Summary

Ground volcanic ash particles (30 g) from Mt. Shinmoe with diameters of $\leq 200\ \mu m$ were mixed with 10 ml of NaOH solutions with different concentrations. These mixtures were placed in an acrylic cylindrical pipe, and hardened bodies were formed after curing for 3 days at 50 °C and 80% relative humidity. The crystal phase present in the volcanic ash was found to be anorthite sodium, and the amorphous content was estimated to be ≤ 30 mass%. The maximum compressive strength of the hardened bodies was 80.1 MPa when a 13.5 mol/L NaOH solution was used. The addition of water glass had little influence on the compressive strength. Furthermore, a curing time of 3 days was determined to be sufficient, as the compressive strength did not increase after this.

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