- Technical Paper -

REACTION AND RESULTANT PHYSICAL PROPERTIES OF FA-BASED ALKALI ACTIVATED MATERIALS AND GEOPOLYMER CURED AT 80°C

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ABSTRACT

Fly ash based alkali-activated material and geopolymer were synthesized at 80°C to study the reaction system of alkali activated condition and the system with/without liquid glass. X-ray diffraction and ^{29}Si NMR were obtained to discuss the role of Si in those systems. Liquid glass always produced a reactant having a three-dimensional network. Physical properties are also obtained to discuss the applicability of those materials. As a result, fly ash based system containing the mixture of NaOH solution and liquid glass solution showed high potential for structural applications.

Keywords: geopolymer, alkali-activated materials, fly ash, microstructure, young's modulus

1. INTRODUCTION

1.1 Background

With the various environmental problems in recent years, efforts to build a sustainable society in all fields are required. Portland cement, which is commonly used as a building material, requires a burning process at the time of production, and it is inevitable to generate CO_2 due to energy combustion at that time. CO_2 is also generated by thermal decomposition of limestone, which is the main component for cement clinker. Energy efficiency in cement production in Japan is at the highest level in the world, and in order to further reduce CO_2, it is necessary to reduce CO_2 derived from raw materials. In addition, from the viewpoint of environmental conservation, effective utilization of fly ash (FA) caused by combustion of coal, which is mainly discharged at a coal-fired power plant, is required.

Research on the alternative binders that can substitute for cement using FA is underway as one of the methods to promote the reductions of CO_2 emissions by cement production and the effective utilization of FA. Among them, Alkali-Activated Materials (AAM) is known as a hardened paste formed by amorphous material originated from FA dissolved under high alkali condition [1]. And Geopolymer (GP) is known as another paste matrix composed of an amorphous substance having a three-dimensional (3D) network [2]. However, the hardening mechanism of AAM and GP has not been fully understood. Regarding the difference in alkaline solution based reaction products, it was shown by electron microscopy observation that a material synthesized using an alkali solution without adding silica has a microstructure of a nonreactive system and that a geopolymer is formed by adding silica [3].

In this paper, in order to elucidate the hardening mechanism of FA-based AAM and GP, parametric studies were performed. To evaluate the applicabilities of such mixtures to the engineering field, some physical properties were also obtained.

1.2 Hardening mechanism of GP

Firstly, we address the summary of existing research on the hardening mechanism of GP made of FA and liquid glass (Na_2SiO_3 aqueous solution).

As shown in Fig. 1, it is considered that GP using FA and liquid glass generates a polymer by condensation polymerization reaction of silicic acid monomer accompanied with dehydration and hardens. By mixing FA, which is an aluminosilicate material, with alkaline liquid glass, metal ions such as Al^{3+} and Si^{4+} are eluted from FA and act as a cross-linking metal ion, resulting in high molecular compound [4].

1.3 Preparation of cured zeolite

A technique for manufacturing a high strength zeolite matrix made of FA with NaOH solution or KOH solution has been reported in reference [5]. It has been confirmed that zeolite-type matrices are produced by using any aqueous solution and the produced zeolite species depend on the kind of aqueous solution and

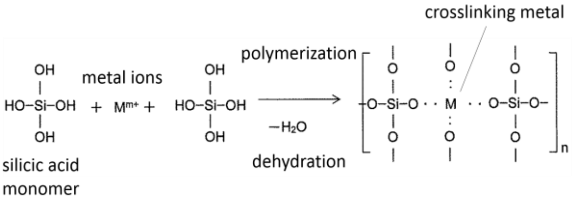

Fig. 1 Crosslinking and polycondensation [4]

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elevated temperature condition during hydrothermal synthesis.

1.4 Objectives of research

From the findings in References [4] [5], the hardened paste using FA and alkali solution can be classified into the following two types of systems. In one system, the matrix is composed of crystalline phases. In the other system, the matrix is composed of the amorphous phase. Since GP is composed of an amorphous phase, the phase of the matrix seems to be a key point in distinguishing GP from AAM.

The objectives of this research are then to answer the following two questions:

1) What is the key difference in the mixture for producing GP and AAM from FA?
2) Which mixture cured at relatively low temperature (say, 80°C) is promising in structural applications?

2. EXPERIMENTAL PROCEDURE

2.1 Materials and formulations

In this study, 3 systems are selected to quantify the mechanism of the hardening process of AAM and GP made from FA.

It has been reported that when FA is used as the binder, crystal phase is formed when an NaOH solution is used as an activator (NAXX in Table 1), while amorphous phase is formed when a Na_2SiO_3 solution (liquid glass) is used (LGXX in Table 1) [4] [5]. Consequently, in the case where both NaOH and Na_2SiO_3 are used (MIXXX in Table 1), it is expected that both crystal and amorphous phases are formed in the system.

In this study, the following 3 types of systems are examined: (1) a system in which a crystalline phase is mainly formed, (2) a system in which an amorphous phase is mainly formed, and (3) a system in which both crystalline and amorphous phases are expected to be formed. In each of these 3 systems, 3 types of solid mass to liquid ratios of 60, 50, and 40% were prepared, while both NaOH solution and Na_2SiO_3 solution are considered as the liquid phase. The parameters of the experiments are summarized in Table 1.

For the mixture proportion, the NaOH solution diluted to 7mol / L was used. For the Na_2SiO_3 solution, a sodium silicate solution (manufactured by Junsei Chemical Co., concentration: about 55%) was used. When used in the stock solution, the viscosity was high and it was difficult to mix. Therefore, it was diluted to a concentration of about 48.9%. Type II fly ash according to JIS classification was used.

2.2 Preparation of specimens

For mixture processing, a rotation/revolution mixer ARE-500 (manufactured by THINKY) was used. After mixture for 1 minute at 1000 rpm, the sample adhered to the inner side wall of the container was scraped off, and additional mixture with 1000 rpm for 1 minute was processed.

The sample was placed into a 3 × 13 × 135mm steel mold. After the placing, curing in air at 80°C was carried out. There are 2 different elevated curing conditions i.e. 6 hours and 24 hours. The test specimens after demolding were stored in a constant temperature chamber (20 ± 2°C) under a sealed condition.

Table 1 Formulation

Specimen name	L/S ratio (%)	Mass ratio (%)		
		FA	Na_2SiO_3	NaOH
NA60	60	62.5	0	37.5
NA50	50	66.67	0	33.33
NA40	40	71.43	0	28.57
LG60	60	62.5	37.5	0
LG50	50	66.67	33.33	0
LG40	40	71.43	28.57	0
MIX60	60	62.5	20.84	16.66
MIX50	50	66.67	18.52	14.81
MIX40	40	71.43	15.87	12.7

2.3 Powder X-ray diffraction and Rietveld analysis

In order to confirm the formation of crystalline and amorphous phases, powder X-ray diffraction (XRD) was performed on all the samples. The samples were pulverized and classified to 100μm or less. Measurement of XRD was conducted using a D8 ADVANCE X-ray diffractometer (Bruker AXS) under the following conditions: Cu-Kα X-ray source, 40kV tube voltage, 40mA tube current, $2\theta = 2\sim65°$ scanning range, 0.02° step width, and 0.5°/min scanning speed. The samples used for the measurement consisted of powder samples to which corundum (α-Al_2O_3) was admixed at the rate of 10wt% in terms of inner percentage as an internal standard.

Rietveld analysis was performed with TOPAS Ver4.2 (manufactured by Bruker AXS). The quantitative targets were Fe_2O_3 (Haematite), Fe_3O_4 (Magnetite), $3Al_2O_3 \cdot 2SiO_2$ (Mullite), SiO_2 (Quartz), $NaAlSi_3O_8$ (Albite), $|Na_6(H_2O)_8|[Si_6Al_6O_{24}]$ (Hydroxy Sodalite) , α-Al_2O_3. Calculation of amorphous substance was performed from the quantitative value of the internal standard substance α - Al_2O_3 by using the following equation [6].

$$\mathrm{A} = \frac{\{100 \times (S_R - S)\}}{\{S_R \times (100 - S)100\}} \tag{1}$$

where,
A: amorphous mass (%)
S: mixing ratio (%) of α-Al_2O_3
S_R: quantitative value (%) of α- Al_2O_3

2.4 NMR measurement

^{29}Si Dipolar Decoupling (DD) MAS NMR spectra were acquired using a Bruker Avance 300MHz spectrometer equipped with a 9.4T wide bore magnet. Samples were packed into 7mm ZrO_2 rotors and rotated at MAS rates up to 5kHz using a standard CP MAS probe. Generally, a recycle delay of 60s was used and the number of scans was 2000. All the spectra were recorded at room temperature and referenced using hexaclotrisiloxane peak at -9.55ppm relative to tetramethylsilane (run separately).

The chemical shift values of Q0, Q1, Q2 or Q4 (4Al), Q4(3Al) or Q3, A4(2Al), Q4(1Al), and Q4(0Al) were assumed to be -71.4, -79, -85 to -87, -92, -96, -103, -108 to -111ppm, respectively, based on the shifts reported by Fernandez et al. [7] , Brunet et al. [8] and Rawal et al. [9].

2.5 Indentation test

A Vickers indenter was attached to a compact tensile compression test apparatus and indentation test was carried out. For the pre-treatment, the specimen was subjected to double-side polishing. The load was applied until it reached 20N and then it was unloaded. Three indentation tests were performed for each test specimen.

The indentation depth during loading and unloading was monitored by the laser displacement meter (Keyence LK-G30, precision was 0.0001mm.). Young's modulus of the sample was calculated from the load-pushing depth curve (P - h curve) without direct confirmation of impression size [10].

For calculation of Young's modulus, the following Sneddon equation is used.

$$\mathrm{E} = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \qquad (2)$$

where,
E : Young's modulus
S : contact stiffness
A : contact area
β : constant depending on the shape of the indenter

Contact stiffness S is obtained by the following equation, in which the slope of the unloading curve corresponds to a simple elastic recovery.

$$\mathrm{S} = \frac{dP}{dh} \qquad (3)$$

The contact area A is obtained by the following equation.

$$\mathrm{A} = 4\frac{\tan\theta}{\cos\theta}{h_c}^2 \qquad (4)$$

$$h_c = h_{max} - h_s = h_{max} - \varepsilon\frac{P}{S} \qquad (5)$$

where,
θ : the angle between the central axis of the quadrangular pyramid and the side surface
h_{max} : the maximum indentation depth
h_s : the displacement of the surface
ε : a constant

Vickers hardness was calculated using the following formula.

$$\mathrm{H} = \frac{P_{max}}{A} \qquad (6)$$

where,
H : Vickers hardness
P_{max} : Maximum load

2.6 Thermomechanical measurement

In order to study the volumetric change under high temperature, thermomechanical measurements were carried out using a thermal mechanical analyzer TMA-60 (manufactured by Shimadzu Corporation).

The sample was heated from room temperature to 500°C at a heating rate of 10°C/min, and expansion and contraction induced by the temperature increase were measured. Samples whose size was adjusted to 3 × 4 × 5mm were used. Borosilicate glass whose linear expansion coefficient is known was used as a standard sample to cancel the deformation due to a temperature change of the testing machine.

3. RESULTS AND DISCUSSIONS

3.1 Powder X-ray diffraction

Fig. 2 shows a diffraction chart of the test specimen whose L / S ratio is 60% and a curing time is 24 hours. The raw FA is also plotted in Fig. 2. Only in NA60, the system containing NaOH, the presence of a peak indicated by a sunspot is confirmed. This is the peak derived from hydroxy sodalite, one of the zeolite phases. Consequently, it is concluded that a zeolite, a crystalline substance, was formed in the case of NA. The peaks other than zeolite were derived from the corundum and FA. Similar trends were reproduced in the cases of different L / S ratio and curing time.

Next, we examine the formation of amorphous materials. A diffraction chart close-up ranging 2θ = 15 to 40° was shown in Fig. 3. Since both LG60 and MIX60 have broad peaks while the positions of the apexes of the peaks are different in FA and NA60, the presence of the amorphous phases can be confirmed. Vertices were found at 22.5° for FA, 25° for NA60, 26° for LG60 and 27° for MIX60, respectively. In the specimens after the reaction, the peak moved to the higher angle side than FA. The movement of this halo peak to the higher angle side is due to the formation of alkaline aluminosilicate gel, which corresponds to the formation of amorphous material [11].

Fig. 4 shows the quantitative values obtained by Rietveld analysis. In NA, as the L / S ratio decreases, the proportion occupied by sodalite tends to decrease.

3.2 NMR measurement

The deconvolution of the ^{29}Si signals is presented in Fig. 5, and the relative composition ratios of the peaks are summarized in Fig. 6. It should be noted here that regarding the Q4 signal, complete quantitative data were not obtained due to the limitation of the measurement setting [9].

The Q4(2Al) peak exists only in LG60 and MIX60. It is inferred that the Q4(2Al) peak is derived from a newly generated substance because this peak is not found in the raw FA. In all the samples, the Q0, Q1, Q2, Q3 peaks in all cases shows a larger proportion than that of FA. The higher proportion of those peaks can be observed in the order of NA60, MIX60, and LG60. Since the proportion of Q0, Q1, Q2, Q3 peaks is a small amount in FA, these results imply that these peaks attribute to the newly formed substances. On the other hand, Q4(0Al) and Q4(1Al) peaks are present in large quantities in FA, and these peaks detected in the other samples are identical. From these observations, it is thought to be originated from unreacted FA.

Only in LG60 and MIX60, Q4(2Al) peak was observed. This Q4(2Al) represents the Si-O-Al-O 3D network with the Si/Al ratio of 1.0. Consequently, it is deduced from the NMR results that only LG60 and MIX60, in which liquid glass was used, can produce a reactant with a 3D network.

3.3 Indentation test

Fig. 7 shows Young's modulus and the Vickers hardness calculated from the load-indentation depth curve (P-h curve) obtained by the indentation test. The gray bar represents Young's modulus, and the white bar represents the Vickers hardness. The values of Young's modulus were 1.76GPa for NA60, 11.35GPa for LG60, and 5.80GPa for MIX60. The values of the Vickers hardness were 4.43HV2 for NA60, 83.98HV2 for LG60, and 38.86HV2 for MIX60. Both Young's modulus and the Vickers hardness increased as the mass of Na_2SiO_3 in the system increased.

3.4 Thermomechanical measurement

The temperature-strain curves obtained by TMA are shown in Fig. 8. NA60 and MIX60 showed contraction as temperature increased. LG60 shrank up to about 200°C like the other specimens, while it expanded sharply thereafter.

3.5 Discussions

Based on the experimental results, we summarize the features of NA, LG and MIX and consider conditions that distinguish GP from AAM.

In the case of NA, the presence of crystalline zeolite was confirmed. Based on ^{29}Si-NMR, Q4(2Al) peak cannot be found, and the proportion of Si for Q3, Q2, Q1, and Q0 network to all the number of Si in the system was large. The obtained Vickers hardness and Young's modulus values of the paste were much

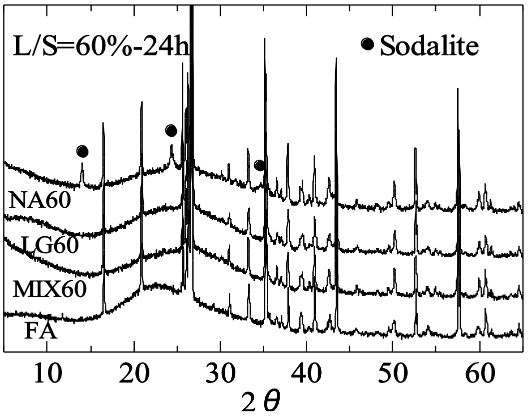

Fig. 2 Presence or absence of zeolite formation

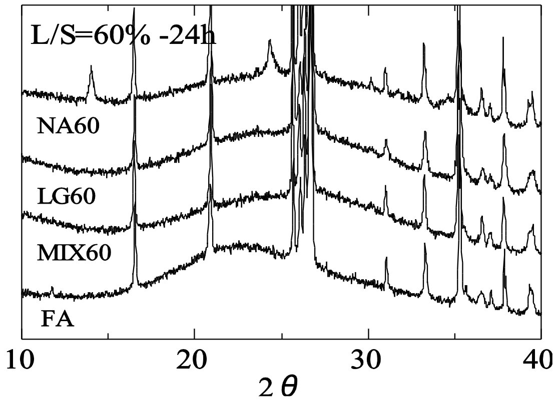

Fig. 3 Variation of the halo peak to the high angle

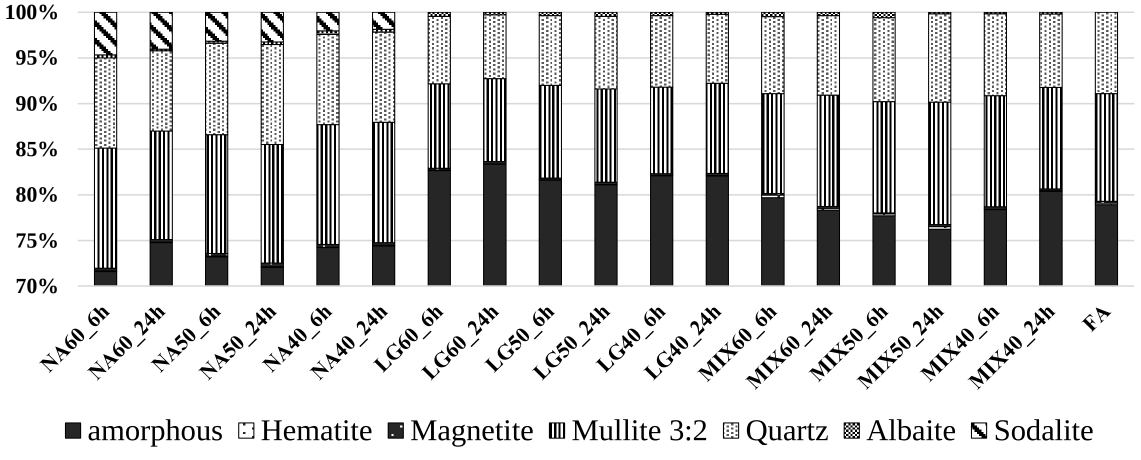

Fig. 4 Quantitative value by Rietveld analysis

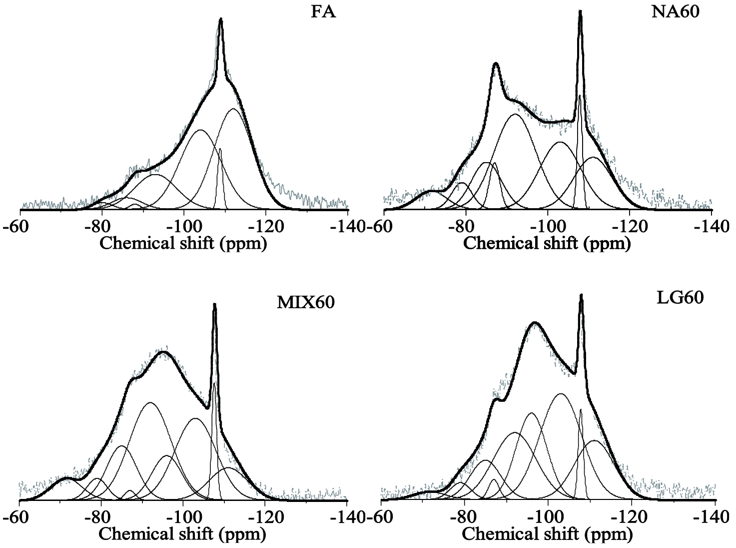

Fig. 5 Deconvolution of NMR signals for FA, NA60, LG60, and MIX60. The samples were cured for 24 hours.

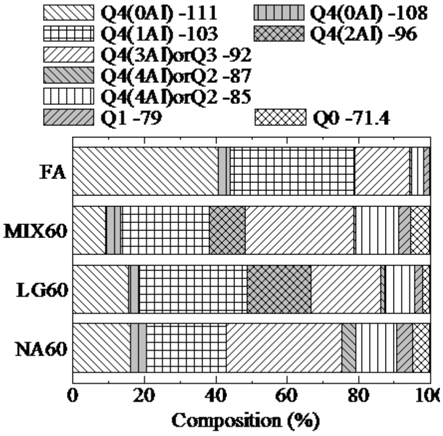

Fig. 6 Relative composition ratios of the ^{29}Si-NMR peak intensity

smaller than those of the other types of the pastes. This paste showed shrinkage under elevated temperature.

In the case of LG, crystalline zeolite was not formed. Based on ^{29}Si-NMR results, Q4(2Al) peak was confirmed. The proportion of Si for Q3, Q2, Q1, and Q0 network to the total number of Si in the system was small. The Vickers hardness and Young's modulus values were large, and this paste expands markedly under elevated temperature.

In the case of MIX, crystalline zeolite was not found by XRD, and based on ^{29}Si-NMR, Q4(2Al) was confirmed and proportion of Si for Q3, Q2, Q1, and Q0 network to the total Si was almost the same as that of NA. The Vickers hardness and Young's modulus values were in between those of LG and NA. This paste shrinks under elevated temperature.

Based on the above characteristics, when reacting with FA, it is considered that the substance generated by the action of the NaOH solution and the one generated by the action of the Na_2SiO_3 solution are different. In LG, only an amorphous phase is generated, and this has a structure of Q4(2Al). In other words, it is a geopolymer, which is an amorphous material with a 3D network. In NA, both crystalline zeolite and amorphous phases were produced. However, since this amorphous phase does not have the structure of Q4(2Al), it is not a geopolymer. It is believed that this amorphous phase is a zeolite precursor. This hypothesis was supported by the fact that the increase in the Q0 to Q3 peak was observed when the NMR signal was compared with that of FA.

Regarding the MIX, crystalline zeolite was not produced. However, the increase in the Q0 to Q3 peak suggested the formation of a zeolite precursor. This hypothesis was consistent with the result that Q4(2Al) peak was confirmed in the ^{29}Si-NMR dataIn the reaction with FA, NaOH solution produces zeolite and its precursor, and Na_2SiO_3 solution produces the geopolymer. Here, the big difference between NaOH and Na_2SiO_3 is the presence or absence of SiO_3^{2-} in the liquid phase. This condition might be an essential condition for the formation of geopolymer.

From the above discussions, it can be concluded that in the FA type hardened pastes under the 80°C curing condition, the one using Na_2SiO_3 is GP, and the one using only the alkali solution not containing SiO_3^{2-} is AAM.

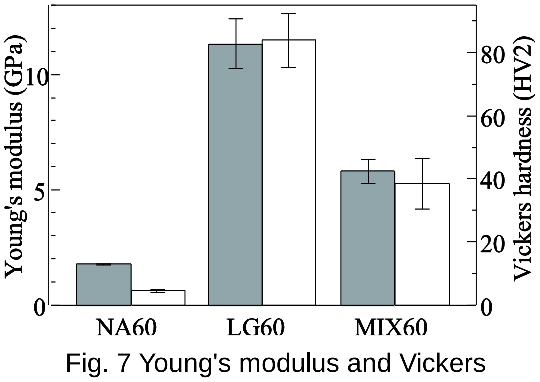

Fig. 7 Young's modulus and Vickers hardness by indentation test

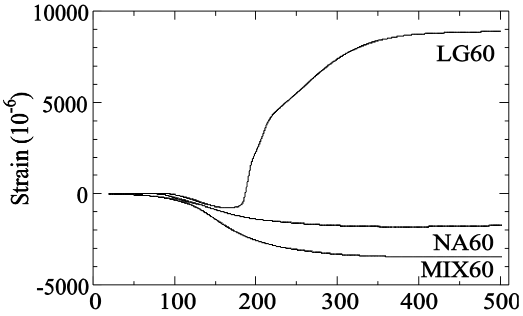

Fig. 8 Expansion / contraction as temperature increase

Next, we discuss the physical properties. LG has a higher Young's modulus because it is composed of geopolymers of a 3D network. NA is composed of crystalline zeolite and amorphous of the low dimensional network, it is thought that strength and Young’s modulus are attributed only to friction between zeolite particles.

It can be said that the existence of zeolite is the key factor of dimensional stability under the elevated temperature condition. It has been reported that hydroxy sodalite produced in NA is thermally stable [12]. The MIX from which the zeolite precursor was prepared had dimensional stability similar to NA. Expansive reaction of LG was not clarified after XRD measurement of the temperature elevated sample. Further investigation is needed on this problem.

In the application of the material to structural members, NA has low Young's modulus and LG has large expansion at high temperature. Both NA and LG are therefore not suitable in structural applicaitons. MIX, which has moderate Young's modulus and is also relatively stable under elevated temperature, has a high potential for structural applications.

4. CONCLUSIONS

1) For the fly ash based alkali-activated material, geopolymer, and their mixture formed under 80°C curing condition, the differences in their properties were investigated, wherein the type of alkaline solution was changed as a key experimental parameter. The use of NaOH solution produces zeolite and its precursor, and the use of Na_2SiO_3 solution produces geopolymer with the 3D network. Consequently, the presence of SiO_3^{2-} in the liquid phase of starting material is the key condition for distingushing the formation of geopolymer from that of alkali-activated material.
2) By using an alkaline solution obtained by mixing NaOH and a Na_2SiO_3 solutions, the fly ash based paste formed under the 80°C curing showed mixed characteristics. The potential of the mixed characteristics is high in structural applications from the viewpoints of dimensional stability in elevated temperature and physical properties like the Vickers hardness and Young’s modulus.

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