- Technical Paper -

MICROSTRUCTURE AND ELEMENT COMPOSITION OF AMORPHOUS IN FA-BASED ALKALI ACTIVATED MATERIAL AND GEOPOLYMER

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ABSTRACT

Fly ash based alkali activated material and geopolymer were synthesized at 80°C and the reaction products in each hardened paste were investigated. ²⁹Si-NMR, ²⁷Al-NMR and FT-IR measurements were conducted to discuss the network structure of the amorphous phase. SEM-EDX was measured to understand the element composition. It was suggested that the hardened paste with a large proportion of Na element inhibited the network formation of Si-O-Si or Si-O-Al, and thus the amorphous phase having a low dimensional network structure increased.

Keywords: geopolymer, alkali activated material, fly ash, microstructure, element composition

1. INTRODUCTION

1.1 Background

With the various environmental problems in recent years, efforts are required to build a sustainable society in all fields. 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. CO₂ is also generated by thermal decomposition of limestone contained in cement clinker. Energy efficiency in cement production in Japan is at the highest level in the world, and in order to further reduce CO₂ emission, it is necessary to reduce CO₂ derived from raw materials. In addition, it is necessary from the viewpoint of environmental conservation, to effectively utilize fly ash (FA), which is mainly discharged by combustion of coal at a coalfired power plant.

Research on the alternative binders using FA that can substitute for cement is underway as one of the methods to promote both the reductions of CO₂ emissions by cement production and the effective utilization of FA. Alkali Activated Material (AAM) is one of them. It is a hardened paste formed by amorphous material originated from dissolved FA which is enhanced by high alkali condition [1]. Also, Geopolymer (GP) is another paste matrix composed of an amorphous phase having a three-dimensional (3D) network by the liquid glass [2]. However, the reaction mechanism of AAM and GP has not been fully clarified. Regarding the differences in reaction products due to alkali solutions, the following have been confirmed by electron micrographs. When an alkali solution containing silicon tetroxide anion is used, it forms a geopolymer, but it is rare to form it when using an alkaline solution containing no silicon

tetroxide anion [3].

In this paper, in order to elucidate the reaction mechanism of FA-based AAM and GP, parametric studies were conducted.

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 (Na₂SiO₃ 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 hardening process. By mixing FA, which is an aluminosilicate material, with alkaline liquid glass, ions such as Al³⁺ and Si⁴⁺ are eluted from FA and act as a crosslinking 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 matrices are produced using any alkaline solution and that the zeolite species depends on the kind of alkaline solution, and the condition of temperature rise during hydrothermal synthesis.





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1.4 Effect of alkaline solution on reaction products

For the fly ash based AAM, GP, and their mixture formed under 80°C heat curing condition, Matsuda et al. [6] have been reported. In order to investigate the differences in their properties, the type of alkaline solution was changed as a key experimental parameter. The use of NaOH solution produces zeolite and low dimensional amorphous, and the use of Na₂SiO₃ solution produces amorphous with the threedimensional silicate network. It was inferred that the difference in these reaction products depends on presence of SiO_3^{2-} in the solution. This is presumed to be due to how Si, which is essential for the production of zeolite and geopolymer, is supplied. When Na₂SiO₃ solution is used, it is supplied from disorderly distributed SiO₃²⁻ derived from solution, whereas when NaOH solution is used it is supplied only by dissolution of FA. It is considered that the difference in the supply route of Si due to the difference in the aqueous solution used affects the reaction product.

1.5 Research objective

In the hardened paste using FA and alkali solution, it was shown that reaction products differ depending on the type of alkali solution [6]. However, the amorphous phases have many unclear points, so further investigation is necessary to elucidate the effect of the solution on the reaction product.

In this paper, by investigating the network structure and element composition of the amorphous phase, we aim to understand the influence on reaction products due to the difference in alkali solution and to clarify the reaction mechanism of paste using FA and alkaline solution.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and formulations

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 (NA60 in Table 1) [5], while amorphous phase is formed when a Na_2SiO_3 solution (liquid glass) is used (LG60 in Table 1) [4]. Consequently, in the case where both NaOH and Na_2SiO_3 are used (MIX60 in Table 1), it is expected

Specimen	L/S ratio	Mass ratio (%)			
name	(%)	FA	Na ₂ SiO ₃	NaOH	
NA60	60	62.5	0	37.5	
LG60	60	62.5	37.5	0	
MIX60	60	62.5	20.84	16.66	

Table 1 Formulation

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 formed. In each of these 3 systems, solid mass to liquid ratio of 60%was prepared, while both NaOH solution and Na₂SiO₃ solution are considered as the liquid phases. The parameters of the experiments are summarized in Table 1.

For the mixture proportion, the NaOH solution diluted to 7 mol / L was used. For the Na₂SiO₃ 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 (Table 2).

2.2 Preparation of specimen

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

The samples were placed into a $3 \times 13 \times 135$ mm steel mold. After the placing, curing in air at 80°C was carried out 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) with sealed condition.

2.3 ²⁹Si – NMR analysis

²⁹Si Dipolar Decoupling (DD) Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were acquired using a Bruker Avance 300MHz spectrometer equipped with a 9.4T wide bore magnet. Samples were packed into 7mm ZrO₂ 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 Q_0 , Q_1 , Q_2 or Q_4 (4Al), Q_4 (3Al) or Q_3 , Q_4 (2Al), Q_4 (1Al), and Q_4 (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].

Table 2 Properties of fly ash	

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Density	ig.loss	Surface Area
Mass ratio (%)			(g/cm^3)	(%)	(cm ² /g)	
64.5	23.9	4.8	5.3	2.3	2.1	3880



Fig. 2 Deconvolution of ²⁹Si-NMR signals [6]

 Q_2 or $Q_4(4Al)$, $Q_4(3Al)$ or Q_3 , each have the same chemical shift, so it is difficult to distinguish them. However, in this paper it is assumed that the peak at -85 to -87ppm is Q_2 , and the peak at -92ppm is Q_3 . Because the point where Si/Al < 1 is not confirmed from the result of Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) described later, it is considered that the presence of substances having structures of Q4(4Al) and Q4(3Al) is a trace amount.

2.4 ²⁷AI- NMR analysis

²⁷Al MAS NMR spectra were collected on ECA700 spectrometer (JEOL; magnetic field of 16.4 T) using a CPMAS probe with o.d. of 3.2mm and ZrO₂ rotors at a spinning frequency of 18kHz. A recycle delay of 0.5s was used and the total accumulation time was 6400s. ²⁷Al chemical shifts were referenced using AlK $(SO_4)_2$ ·12H₂O as the external reference (0ppm).

Based on the report of Pardal et al.[10], the chemical shift value of tetracoordinate Al was set at 60 to 70ppm for Al [IV]-a and 72ppm for Al [IV]-b. Al [IV]-a is the bridging site, Al [IV]-b is the pairing site in C-S-H. Because of the scarcity of proven data on geopolymer, the data of C-S-H are used.

2.5 FT-IR analysis

The infrared absorption spectrum was measured by FT-IR ALPHA (manufactured by Bruker) and total reflection measurement (ATR method) using diamond.

2.6 FE-SEM and EDX analysis

Observation of fractured surface of each samples was performed by secondary electron image of field emission scanning electron microscope (FE-SEM (JSM-7500FA, JEOL)).

Element composition analysis of the fracture surface of the specimen was performed with an energy dispersive X-ray analyzer (EDX (JED - 2300 F)) attached to FE - SEM. The analysis targets were Na, Al, Si, Ca and Fe.

3. RESULTS AND DISCUSSIONS

3.1 29Si - NMR

The deconvolution of the ²⁹Si signals is presented in Fig. 2, and the relative composition ratios of the peaks are summarized in Fig. 3. The data shown here are quoted from reference [6]. It should be noted here that quantification of Q₄ is difficult, because relaxation time is long. It is impossible to compare the absolute amount of Q₄ in each sample. However, since the measurement conditions are the same, relative comparison between different samples is meaningful [9].

Comparing the shape of the signal of each sample, it is found that the peak is dominant at the lower magnetic field side in NA60. On the other hand, the peak ratio is larger on the higher magnetic field side in LG60. It can be said that the signal shape of MIX60 has an intermediate characteristic of peak distribution in the other two samples. The peak on the high magnetic field side indicates the existence of Q4 having a three-dimensional structure, and the peak on the low magnetic field side is derived from the existence of Q_0 . Q_1 , Q_2 , Q_3 having a two or less dimensional structure. Therefore, it is assumed that NA60 has a large proportion of substances having a two or less dimensional structure, and LG60 has a large proportion of 3D structural substance.

In all the samples, the Q_0 , Q_1 , Q_2 , Q_3 peaks 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 Q_0 , Q_1 , Q_2 , Q_3 peaks is small in FA, these results imply that these peaks attribute to the newly formed substances. On the other hand, $Q_4(0Al)$ and $Q_4(1Al)$ 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.

3.2 ²⁷AI- NMR

The results of ²⁷Al-NMR are shown in Fig. 4. The peak of Al[VI] detected at 9ppm does not differ significantly between FA and any sample. The peak position of FA is 60ppm, and the peak positions of LG60, MIX60 and NA60 are shifted to lower field side to 63, 64, 67ppm, respectively. The peak is sharper as the peak position shifts to the lower magnetic field side.

In C-S-H, Al[IV]-a corresponding to the bridging site is detected as a relatively broad peak at 60 to 70ppm and Al[IV]-b corresponding to the pairing site is detected as a sharp peak at 72ppm [10]. That is, the broad peak of 60 to 70ppm indicates the presence of Al forming a 3D network, and a sharp peak of 72ppm indicates the presence of Al forming a two – dimensional (2D) network.

It is considered from this fact that, in the LG60 and MIX60, where the peak position is detected on the higher magnetic field side and the peak shape is relatively broad, the proportion of Al-O bond contributing to the formation of the 3D network is high, and that, in the NA60 where, the peak position is detected on the low magnetic field side and the peak shape is sharp, the proportion of Al-O bonds contributing to the formation of a 2D network is higher.

3.3 FT-IR

Fig. 5 shows the infrared absorption spectrum of 500 to 1300cm⁻¹ of each specimen and FA. There are peaks at 970 to 980cm⁻¹ in NA60, 1000cm⁻¹ in LG60, 990cm⁻¹ in MIX60, and 1050cm⁻¹ in FA. In tobermorite, the following has been reported [11]. The stretching mode of O-SiCa_x at the pairing site has a peak at about 940cm⁻¹ and the stretching mode of Si-O connecting different SiO₄ at the crosslinking site (Q₃ and Q₄ in ²⁹Si-NMR) has a peak at about 1050cm⁻¹. Therefore, it is inferred that, as the peak is closer to 1050cm⁻¹, the proportion of a 3D network becomes higher while as the closer to 940cm⁻¹, the proportion of the lower dimensional structure becomes higher. The results of FT-IR suggests the same conclusion as ²⁹Si-NMR. That is, the ratio of Si-O bonds forming a 3D network in LG60 is high, the proportion of Si-O bond forming a 2D network in NA60 is high, and MIX60 shows the characteristic between LG60 and NA60.

3.4 FE-SEM and EDX

From the results of XRD, zeolite is found as a new crystalline phase only in the case of NA, and amorphous phase is confirmed in all cases [6]. After that we will discuss based on this result.

The SEM images of the fractured surface of NA60 is shown in Fig.6. Spherical materials considered to be FA is scattered. The surface of FA is covered with ragged particulate matter. This is considered to be zeolite, which is a crystalline material [6] [12]. It is considered that FA was dissolved by the alkaline solution and re-solidified on the surface to produce the zeolite. In addition, this hardened paste is constituted by zeolites precipitated on the surface of the FA with each other, and many voids portions are present.



Fig. 5 The infrared absorption spectrum

The SEM images of LG60 is shown in Fig.7. Spherical FA is present, but unlike NA60, formation of zeolite is not confirmed. However, a layer is formed around the FA, and a high density substance fill the space among FAs. This is considered to be an amorphous phase with a 3D network.

The SEM images of MIX60 is shown in Fig.8. Zeolite is not formed on the surface of FA. Acicular material is formed on the surface of the indentation formed by FA dropping out. It is inferred that the stratified substance confirmed around the FA in LG60 is the one in which this acicular substance grew. Also, similarly to LG60, a high density substance is



generated among FAs, but since the fine particles are formed on the surface thereof, the surface texture is rough compared to LG60.

The element composition obtained by EDX at points indicated by white dots in the SEM images is summarized in Table 3 to 5. We focus on the ratio of Na, Si, and Al, which is thought to be related to the skeleton of the network structure of the reaction product. The points with small (Si + Al) / Na ratio are shown by gray shade in Table 3 to 5. The (Si + Al) / (Si + Al)Na ratio was small at most points in NA60. The (Si + Al) / Na ratio is relatively large only at the point of NA2 which is located at the layer around the trace where FA was dropped out, and the (Si + Al) / Na ratio is small in all points in zeolite. In MIX60, the (Si + Al) / Na ratio was small at Points 3, 4 and 5. In particular, Points 3 and 4 are similar in shape and composition to the points which is regarded as zeolite in NA60. In LG60, the (Si + Al) / Na ratio was small at Points 1 and 4. These points are distant from FA, and the (Si + Al) / (Si + Al)Na ratio was large at Point 2 located in the layer near FA. Also at Point 5, which is located away from FA as at Points 1 and 4, the (Si + Al) / Na ratio is large, so the dispersion of (Si + Al) / Na ratio is seen at these points.

3.5 Discussions

The basic unit of zeolite structure is a tetrahedral structure of SiO_4 or AlO_4 , and these are connected three-dimensionally to form crystals. Geopolymer is considered to be a 3D amorphous substance having a skeleton structure similar to zeolite [4]. Therefore, it is important to grasp the state of Si and Al in order to judge whether or not the formed amorphous phase is a geopolymer. From the results of ²⁹Si-NMR and FT-IR, it was LG60 that the ratio of Si-

O bonds contributing to the formation of a 3D structure was the largest, followed by MIX60. On the other hand, it was suggested that the proportion of Si-O bonds forming the two dimensional or less structure was the largest in NA60 and then in MIX60. From the results of ²⁷Al-NMR, it was expected that the ratio of Al-O bonds forming a 3D structure was high in LG60 and MIX60, and the proportion of Al-O bonds forming a 2D structure was high in NA60.

Based on the discussion so far, NA60 using only NaOH solution as an alkaline solution has a low percentage of 3D structure and features with a large proportion of structures with two or less dimensions. However, since hydroxy sodalite which was confirmed to be produced only by NA60 by XRD is a crystalline substance having a 3D structure, the characteristic of NA60 that the proportion of low dimensional network is large is considered to be due to the amorphous phase [6].

The relationship between the network structure and element composition of amorphous phase in LG60, MIX60 and NA60 will be discussed. It was shown that LG60 has a high proportion of 3D structure, NA60 has many 2D structures, and in MIX60 the proportion of both 3D structure and 2D is between LG60 and NA60. The characteristics of this network structure and the (Si + Al) / Na ratio obtained by EDX are considered to have a correlation. From the result of the obtained element composition, it is inferred that there are many points where the proportion of Na element is high in the order of NA60, MIX60, LG60. That is, the more points with high the ratio of Na, the less the 3D structure and the more the 2D structure. In a zeolitelike amorphous phase formed by a tetrahedral structure of SiO₄ and AlO₄, a 3D network is formed by forming Si-O-Si or Si-O-Al from Si-O⁻. However, Na atom, having a valence of 1, is considered to inhibit the formation of Si-O-Si or Si-O-Al by forming Si-O⁻.Na⁺ in equilibrium with the negative charge of Si-O⁻[13].

When only NaOH solution is used as an alkaline solution in the FA based hardened paste, it is considered effective to accelerate the reaction by raising the concentration of the NaOH solution to create a high pH environment. This is because it is considered to promote dissolution of FA and increase supply of Si. However, attention should be paid to excessive supply of Na, since Na atoms may interfere with 3D network formation of the amorphous phase. Especially, in the system using Na₂SiO₃ solution to which Si is supplied even if the dissolution of FA is gradual, it is necessary to consider the balance between the effect of FA dissolution promotion and inhibition of network formation by increasing the Na concentration.

4. CONCLUSIONS

- On the fly ash-based alkali activated material, geopolymer and mixtures thereof formed under curing conditions of 80°C, the network structure and the elemental composition of the amorphous phase in each hardened pastes were investigated. In the hardened paste using only the NaOH solution, the proportion of the 2D structure was high and the proportion of Na was also high. In the system using only Na₂SiO₃ solution, the proportion of 3D structure was high and the proportion of Na was low.
- 2) A correlation was found between the ratio of Na and the network structure of the amorphous phase. In the case of a hardened paste containing a large proportion of Na, there was a tendency to increase the structure of low dimension was observed. This is considered to be due to the fact that Na⁺ bonds with Si-O⁻ to inhibit the formation of 3D network of Si-O-Si or Si-O-Al. Therefore, consideration must be given to the supply amount of Na in the preparation of the hardened paste.

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