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In-situ formation of novel geopolymer–zeolite hybrid bulk materials from coal fly ash powder

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Geopolymer–zeolite hybrid bulk materials were formed in-situ from as-received coal fly ash powder by a simple two-step treatment: (1) immersing the coal fly ash powder packed within a cylindrical acrylic pipe into a 3.5 mol/l Na(OH) solution at 80°C and (2) subsequent curing in a temperature–humidity-controlled chamber at a fixed condition: 50°C and 50% relative humidity. The content of the formed Na-X type (conversion ratio from the starting coal fly ash) in the sample was optimized to be approximately 10% when the duration of the immersion in Na(OH) solution reached 72 hours. The compressive strength at room temperature of the in-situ formed bulk samples exhibited a clear tendency to increase with both alkali immersion time and curing time, which could be due to the increase of the amount of the in-situ formed geopolymer. As a result, after the 96-hour-alkaline immersion followed by the 21 days curing, the average compressive strength at room temperature achieved 5.4 MPa. This value was found to be more than four times higher than that of the samples without curing treatment (1.3 MPa).

Key-words : Geopolymer, Zeolite, Coal fly ash, Compressive strength, Specific surface area

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1. Introduction

In Japan, the amount of coal fly ash discharged from power plants totals more than 10 million ton per year. In 2007, approximately 97 mass% of the total discharge amount of coal fly ash was reused as a reinforcing material for cement or asphalt. However, the amount of the cement and concrete-based construction materials has been decreasing year by year. Various research studies concerning the effective use of coal fly ash have been undertaken. In particular, synthesis of zeolite micro powders using coal fly ash is thought to be an attractive reuse method.[1),2)]

Recently, geopolymer materials have become of interest for their formation demonstrating low energy, high mechanical properties, high chemical stability and low cost product made from an industrial waste such as coal fly ash.[3)–7)] Such geopolymer is amorphous to semi-crystalline and formed through inorganic polycondensation of alminosilicate hydrate gel with dehydration.[8)] Further, geopolymer is similar to zeolite in chemical composition, so it has been reported that some parts of geopolymers have been converted into zeolites.[4),6)] In spite of these studies, generally speaking, geopolymers cannot coexist with zeolite, because the formation conditions of each substance are quite different.

In this study, we attempted to create novel geopolymer–zeolite hybrid bulk materials using as-received coal fly ash as starting powders. This hybrid material should have both a high specific surface area and a high mechanical strength originating from the in-situ formed zeolite and geopolymer, respectively. In our attempt to form this hybrid material, a novel two-step treatment technique was developed. The as-received fly ash powder packed within a mold, was immersed in an Na(OH) solution, and then cured in a temperature–humidity-controlled chamber without the mold. The formation conditions, such as alkali immersing time and curing time, were carefully examined. The in-situ formed bulk samples were studied using X-ray diffraction and other spectroscopic analysis. Finally, the compressive strength of the bulk samples are evaluated and discussed to show the importance of the in-situ formation of geopolymer to yield the final rigid bulk materials.

2. Experimental procedure

Coal fly ash (JIS type-II) discharged from a Japanese power plant was used as-received. The chemical composition is shown in **Table 1**. Sodium hydroxide (NaOH 99%; Kishida Chemical Industries, Ltd) of reagent grade was used. Firstly, in order to form the bulk shape of the coal fly ash, 4.8 g of coal fly ash was put into a cylindrical acrylic pipe mold with an internal diameter of 15 mm and a length of 30 mm. Both the bottom and top of the pipe were sealed with porous lids. Subsequently, the acrylic pipes filled with the coal fly ash were immersed in a 3.5 mol% NaOH solution (solution/ash is 8.55 in mass ratio) in flask. This flask was set on the hot plate and kept at 85°C for various multiples of 24 h (the samples were defined as 24 h:A-24), 48 h:(A-48), 72 h:(A-72), 96 h:(A-96). After alkali immersion treatment, the samples were washed with distilled water. In order to form the condensed geopolymer through a dehydration reaction inside the sample, the samples after the alkali immersion treatment without the cylindrical acrylic pipe mold were cured at

Table 1. Chemical composition of as-received coal fly ash (mass%)

SiO_2	56.04
Al_2O_3	30.15
Fe_2O_3	4.97
CaO	2.79
MgO	1.31

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50°C and 50% in relative humidity for 7 or 21 days, using a temperature–humidity-controlled chamber. The crystalline phases of the samples were examined by powder X-ray diffraction analysis (XRD: XD-D1; Shimazu Co., Ltd). A quantitative analysis was performed on the in-situ formed Na-X zeolite using XRD. Na_2SO_4 (99.9% Kishida Chemical Industries, Co., Ltd) was used as an internal standard. The master curve indicating the content of Na-X zeolite was established from the XRD intensities: Na-X zeolite (111) of the samples with various ratios of the commercial Na-X zeolite (Zeoramu F9: TOSO Co., Ltd) and coal fly ash. The specific surface area of the samples were measured by N_2 adsorption method using Flowsorb III (Micrometrics. Co., Ltd). The pore volume and pore size distribution of the in-situ geopolymer–zeolite hybrid bulk samples were evaluated using N_2 sorption isotherm analysis (Model: Autosorb-1, Quantachrome Instruments). The micropores ($r_{pore} < 2.0$ nm) and mesopores ($2.0\,\text{nm} \leqq r_{pore} < 50\,\text{nm}$) of the in-situ geopolymer–zeolite hybrid bulk samples were characterized by the SF[9),10)] and BJH[11)] method, respectively. The microstructures of the samples were observed using a scanning electron microscope (SEM: JSM-6360LVS; JEOL Co., Ltd). In order to analyze the formation of geopolymers, Fourier Transform infra red (FT–IR) spectra were recorded on KBr pellets containing the cured samples using a Spectrum 100 (PerkinElmer Co., Ltd). The compressive strength of the samples was measured using an INSTRON5582 (INSTRON Co., Ltd.). The number of the test pieces at each condition was three.

3. Results and discussion

3.1 Formation of the zeolite and specific surface area

The X-ray diffraction patterns of the samples were almost the same before and after the curing treatment.

Figure 1 shows the XRD patterns of A-24, A-48, A-72, and A-96 before curing and the starting coal fly ash used as-received. In addition to the distinct diffraction peaks assigned to α-quarts and Mullite, the starting powder exhibited a halo peak that seemed to be the amorphous phase. After the alkaline immersion for 24 hours, a new diffraction peak began to appear at around $2\theta = 6$ degrees which agreed with Na-X zeolite. The Na-X zeolite-derived diffraction peak intensity increased consistently with the alkaline immersion time, and achieved the maximum at A-72. Finally, at A-96, Na-P zeolite and hydroxysodalite were both detected in the sample. According to quantitative analysis, the amount of the formed Na-X zeolite in A-72 was estimated to be approximately 10%. Thus, alkali treating time had an influence on the formation of different types of zeolite, as reported in a previous paper.[12)]

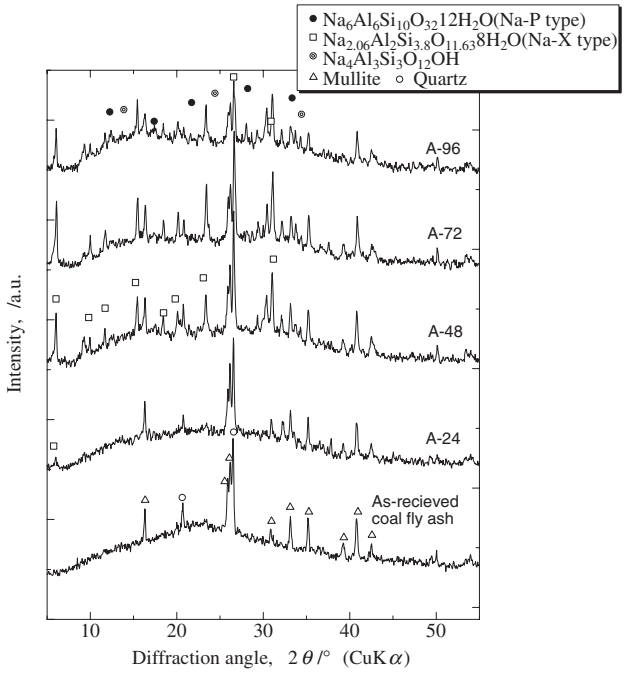

Fig. 1. XRD patterns of the samples after alkali treatment and coal fly ash used as-received.

Table 2. Specific surface areas of coal fly ash, commercial Na-X zeolite and the samples after curing for 21 days

Sample	Specific surface area (m^2/g)
As-received coal fly ash	1.68
Commercial Na-X zeolite	359.0
A-24	16.9
A-48	85.4
A-72	119.1
A-96	111.3

It should be noted that the typical amorphous diffraction halo peak remained even after the alkaline immersion treatment for 96 hours (A-96), and the precursor for the geopolymer, an amorphous alminosilicate hydrate gel, was expected to remain within the sample.

Table 2 shows the specific surface areas of the crushed and powdered samples of A-24, A-48, A-72, and A-96 after curing for 21 days. As references, the specific surface areas of the as-received coal fly ash and commercial Na-X zeolite (Zeoramu F9: TOSO Co., Ltd) were also measured and determined to be $8\,m^2/g$ and $359\,m^2/g$, respectively (listed in Table 2).

The specific surface area of the samples increased consistently with the alkali treatment time up to 72 hours, and those of A-24, A-48, and A-72 were 16.9, 85.4, and $119.1\,m^2/g$, respectively. However, the specific surface area of A-96 ($111.3\,m^2/g$) was slightly smaller than that of A-72, which could be explained by the formation of Na-P zeolite and hydroxysodalite with a lower a specific surface area as detected by the XRD (Fig. 1). The maximum surface area was obtained from A-72, and the value corresponded to approximately 33% of commercial Na-X zeolite. On the other hand, according to X-ray quantitative analysis, the amount of the Na-X zeolite in A-72 (which seemed to include maximum amount of Na-X zeolite in all samples) was estimated to be approximately 10%. That is, the specific surface area of the sample was thought to be higher compared to that of the estimated amount of Na-X zeolite. As a result, the formed sample may show a micro structure with higher porosity, as well as the presence of zeolite crystals.

Furthermore, we examined the pore size distribution for the sample (A-72). **Figure 2** shows the micropore size distribution for A-72. As a result, micropores of 0.8 nm contained in the Na-X zeolite were detected. This result revealed that the zeolite was not completely embedded in the amorphous to semi-crystalline alminosilicate matrix: geopolymer. Further, **Fig. 3** shows the mesopore size distribution of A-72. In Fig. 3, mesopores of 3.8 nm were also detected in the sample, which could contribute to the increase in the specific surface area. According to a previous report,[13)] there is the possibility that the geopolymer has mesopores at approximately 3.5 nm in diameter, but this has not yet been clarified. From this point of view, further investigation is needed.

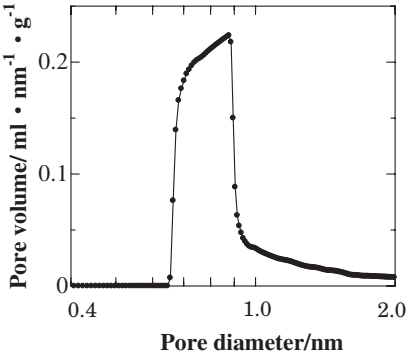

Fig. 2. Micropore size distribution of A-72 after alkali treatment and curing for 21 days.

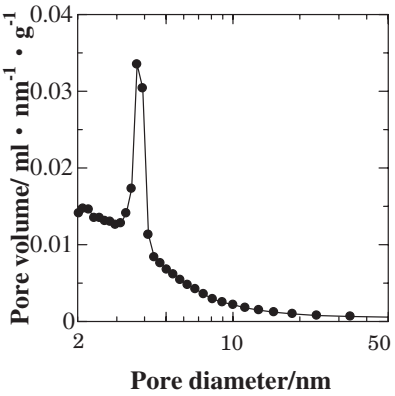

Fig. 3. Mesopore size distribution of A-72 after alkali treatment and curing for 21 days.

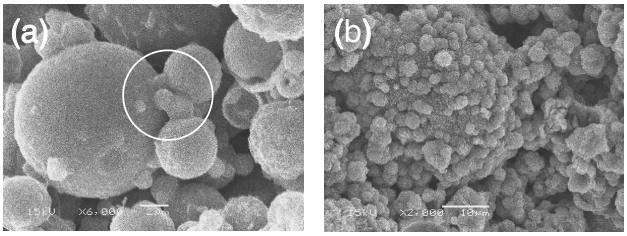

Fig. 4. SEM photographs of the fracture surfaces of the (a) A-24 and (b) A-96 after alkali treatment. The white circle in (a) indicates a typical structural feature composed of spherical coal fly ash particles connected with the in-situ formed precursor.

3.2 Microstructure observations

Figure 4 shows typical SEM images of the fracture surfaces of A-24 and A-96 before curing. The alkali immersion treatment promoted in-situ formations of precipitates that seemed to be of the amorphous phase, and the precipitates connected the original spherical particles (marked by a white circle in Fig. 4(a)). The amorphous-like precipitates could be the precursors for zeolite and geopolymer, i.e. the amorphous alminosilicate hydrate gel.

After the alkali immersion treatment for 96 hours (Fig. 4(b)), the original microstructural feature composed of isolated spherical fly ash particle changed to a rather continuous and refined state, the spherical fly ash particles was covered with the precursor, then a significant number of small particles of several micro meters in size, which appeared to be zeolite were thought to have formed on the in-situ formed surface precursor layer.

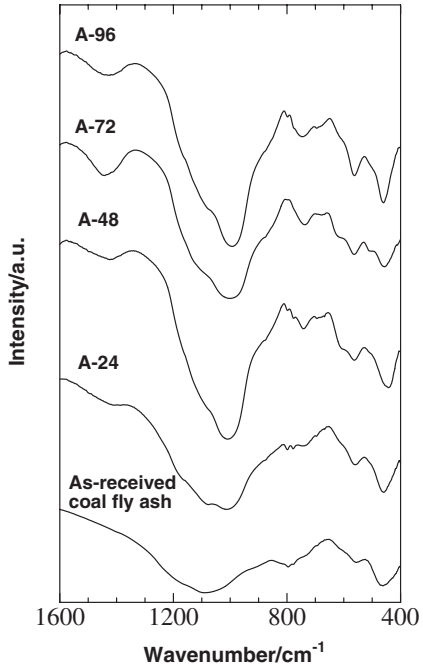

Fig. 5. FT–IR spectra of the samples after alkali treatment and curing for 21 days.

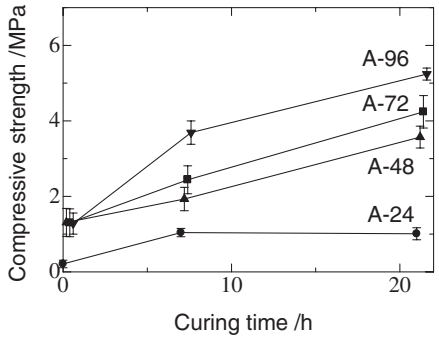

Fig. 6. Compressive strength of the samples after alkali treatment and curing for 7 and 21 days.

3.3 Formation of geopolymer

Figure 5 shows FT–IR spectra of the samples of A-24, A-48, A-72, A-96 after curing for 21 days, and coal fly ash used as-received. The fly ash displayed a typical absorption band around 1085 cm^{-1}, assigned to the asymmetric stretch vibration of T–O (T = Al, Si). After the alkali immersion treatment, the T–O asymmetric stretch band became shaper and shifted towards a lower frequency at around 1000 cm^{-1}, indicating the formation of amorphous to semi-crystalline aluminosilicate.[4),7)] In other words, this absorption band shift behavior was considered to be caused by the formation of the geopolymer.

3.4 Compressive strength

Figure 6 shows the compressive strength of the samples after curing for 7 and 21 days. The average compressive strength increased with curing time. In addition, with curing for 21 days, the minimum average strength of 1.3 MPa was obtained at A-24 and the maximum average strength of 5.4 MPa was obtained at A-96. That is, it was concluded that alkali immersing time also had a sufficient effect on the increase of compressive strength.

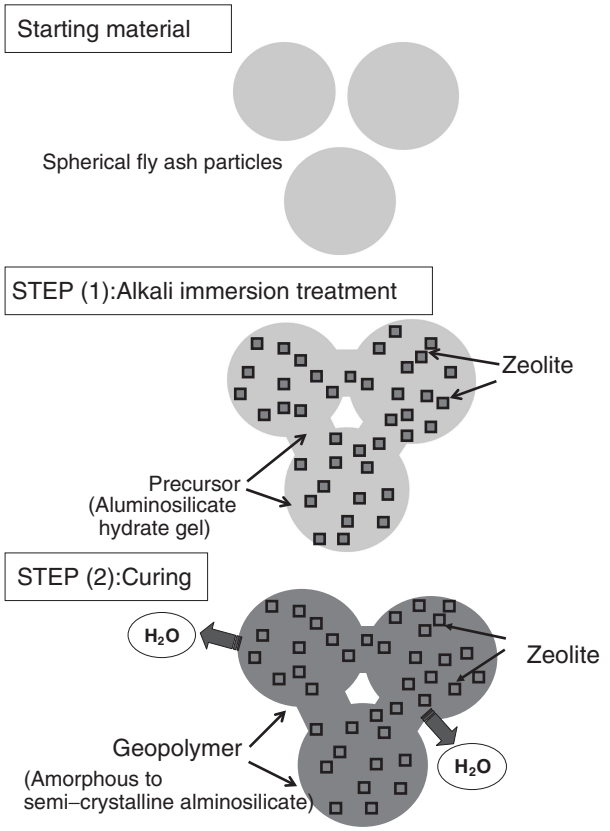

Fig. 7. Schematic illustration of the formation mechanism of geopolymer–zeolite hybrid bulk material from coal fly ash powders.

Consequently, the amount of the formed geopolymer was thought to have increased with the alkali treatment time and subsequent curing time due to the increase of the compressive strength.

3.5 Formation process of geopolymer–zeolite hybrid material

Figure 7 shows a schematic illustration of the in-situ formation of the geopolymer–zeolite hybrid bulk material investigated in this study. After the first treatment step of the alkali immersion, the bridged structure of the spherical fly ash particles connected with amorphous-like precipitates was frequently observed, as shown in Fig. 4(a) and Fig. 7(STEP-1). Subsequently, the microstructure uniformity composed of well-connected fly ash particles could proceed. When the fly ash packed within the cylindrical acrylic pipe was immersed in the Na(OH) solution, the distance between the fly ash particles became very close and most of the particles easily connected to each other and with the amorphous aluminosilicate hydrate gel, which lead to the above mentioned microstructure development. With an increase in the alkali immersion time, zeolite crystals were formed on the surface precursor layer, as shown in Fig. 4(b) and Fig. 7(STEP-1).

Finally, during the second treatment step of the curing, the formation of the geopolymer, namely amorphous to semi-crystalline alminosilicate, can be explained as follows: the precursor formed in-situ by the alkali immersion treatment was converted into geopolymer through the inorganic-polycondensation process governed by the dehydration reaction.[8)] The amount of the formed precursor increased with an increase in the alkali immersion time. In addition, the longer the curing time, the further the polycondensation reaction of the precursor proceeded, yielding higher amount of the geopolymer. Therefore, for both alkali immersing time and curing time, the compressive strength was thought to be increase due to the increase in the amount of the in-situ formed geopolymer, as shown in Fig. 7. Thus the in-situ formation of the novel geopolymer–zeolite hybrid bulk materials from as-received coal fly ash powder could be successfully achieved by the two-step treatment developed in this study.

4. Conclusions

Geopolymer–zeolite hybrid bulk materials were fabricated by immersing coal fly ash powder packed within an acrylic pipe in a NaOH solution at 80°C for various times and subsequent curing at 50°C and 50% relative humidity. The maximum compressive strength of the resultant bulk samples after the alkali immersion of 96 h followed by 21 days curing reached 5.4 MPa due to the effective amount of the in-situ formed geopolymer. The maximum specific surface area of the sample after alkali immersion for 72 h was 119.1 m^2/g, while the content of the in-situ formed Na-X type zeolite in the bulk sample was estimated at approximately 10 mass %.

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