Hot sulfuric acid-resistance of fly-ash-based geopolymer paste product due to the precipitation of natroalunite crystals

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Abstract

In the final exhaust chimney of oil refinery plants, new refractory materials based on geopolymers that have high resistivity to hot sulfuric acid solution, and thus long life-times, are in high demand. In order to investigate the resistance to hot sulfuric acid, a hardened cylindrical fly-ash-based geopolymer paste product (15-mm diameter, 40-mm height) with an average compressive strength of 24 MPa was placed into a Teflon vessel filled with 1.0-M sulfuric acid solution. After heating at 60–220 °C for a fixed duration, the microstructure and compressive strength characteristics were investigated. The geopolymer paste product had no damage after treatment with hot sulfuric acid at various temperatures, although hardened ordinary Portland cement bodies swelled and surface parts broke away after exposure to the same sulfuric acid solution. After the geopolymer paste product was immersed in sulfuric acid at 180 °C for 192 h, the average compressive strength was 25 MPa. With hot sulfuric acid solution treatment, natroalunite ($NaAl_3(SO_4)_2(OH)_6$) formed inside the geopolymer product as a novel crystal phase, which led to an increase in compressive strength by the accompanying densification. The fly-ash-based geopolymer paste product is a candidate material for chimney refractories of oil refinery plants.

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1. Introduction

The use of geopolymers as structural and building materials is expected to increase because of their high mechanical strength and low environmental impact due to their production from industrial wastes such as granite, aluminum hydroxide, red mud, and fly ash [1–5]. However, geopolymers have not yet been used as building materials in Japan due to the rainy weather conditions, whereby alkali ions such as sodium and potassium would be eluted into rainwater, resulting in the corrosion of surrounding metal structures. In locations such as hot springs, infrastructure composed of ordinary Portland cement (OPC) and concrete is subjected to severe chemical corrosion due to the acidic environment, particularly sulfuric acid [6–10]. In such places, using geopolymers as structural and building materials would be advantageous because they have higher resistance to acidic conditions than OPC [11–18].

At some industrial-scale production facilities, large structural materials are required to have high resistance to hot acidic solutions, which are highly reactive. For example, in the final exhaust chimney of oil refinery plants, sulfuric acid condenses at temperatures above 150 °C, which are maintained during plant operation. In such a harsh environment, chimneys constructed from conventional OPC-based refractory materials readily react with the hot sulfuric acid to form $CaSO_4 \cdot 2H_2O$ and/or $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$. As a result, the OPC-based refractory materials expand and eventually decompose [6–10]. In Japan, natural porous fiber-based glass materials consisting of silica with a small amount of alumina (Niijima, Izu Islands, Niijima Production Co., Ltd., Tokyo) are used as chimney refractory materials that are subject to corrosion by hot sulfuric acid solution. However, since hot sulfuric acid penetrates easily into this material due to its porous structure, the life-time of such porous silica refractories is not very long, although it is longer than that of OPC-based refractories. Therefore, new refractory materials based on geopolymers that have high resistivity to hot sulfuric acid solution, and thus long life-times, are in high demand.

In this study, a conventional fly-ash-based geopolymer paste product was fabricated, and its resistance to hot sulfuric acid was investigated. The compressive strength of the geopolymer paste product was examined before and after immersion in hot sulfuric acid for various heating temperatures and times. The crystalline phases of the geopolymer paste product were subsequently analyzed using X-ray diffraction. In addition, the change in microstructure of the geopolymer paste product was observed during hot sulfuric acid solution treatment at a fixed temperature. Finally, the elution of aluminum ions from the geopolymer paste product into the hot sulfuric acid solution was studied to clarify the mechanism of geopolymer paste product resistance to hot sulfuric acid over long periods of time.

2. Experimental procedure

Coal fly ash (Table 1) exhausted from the Chubu Electric Power Co., Inc. Japan was used as a starting material. First, 26 g of the fly ash was mixed with 14 g of 10-M sodium hydroxide solution to form a slurry. The slurry was placed into a plastic cylindrical mold (⌀15 mm), which was then placed into a temperature- and humidity-controlled chamber. After curing at 80 °C and 50% relative humidity for 72 h, the plastic mold was removed from the chamber to obtain the hardened geopolymer paste product. Hardened OPC paste bodies were also prepared as reference samples by first mixing OPC cement powder with pure water in a mass ratio of 5:2 to form a slurry. The hardened OPC paste product was then fabricated using the same method as that for the geopolymer paste product. The porosity of the geopolymer paste product was obtained from the intrinsic density which was calculated by the true density and bulk density. In that case, the true density of the geopolymer paste product was measured by a pycnometer.

Three hardened geopolymer paste products (⌀15 mm, 40-mm height) were immersed in a Teflon vessel containing 80 cm^3 of 1.0-M sulfuric acid to evaluate the resistance to hot sulfuric acid. The Teflon vessel was placed in a closed stainless steel container, which was then heated in an electric furnace at various temperatures between 60 °C and 220 °C for durations of 48–192 h. The sulfuric acid solution was replaced every 48 h to continue the chemical reaction between the sulfuric acid and geopolymer paste product. The electric furnace was heated to a fixed temperature at a rate of 5 °C/min and held at that temperature for a fixed duration. The furnace was then cooled naturally to room temperature, after which the samples were removed from the Teflon vessel and washed thoroughly with water. As a reference, the hardened OPC paste products were subjected to the same treatment in hot sulfuric acid.

The compressive strength of the hardened geopolymer paste product was measured before and after the hot sulfuric acid treatment using a mechanical testing machine (Instron 5582, Instron Japan Co. Ltd.). At least three test pieces were analyzed for each condition. In addition, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX; JEM-6010LA, JEOL, Japan) and X-ray diffraction (XRD; X'pert-MPD, Philips, Netherlands) was carried out before and after the hot sulfuric acid treatment to examine the microstructure/elemental distribution and crystalline phases of the geopolymer paste product, respectively.

Finally, to clarify the mechanism for the resistance of the geopolymer paste product to hot sulfuric acid, the elution of ions into the hot sulfuric acid solution was investigated over time. The concentration of aluminum ions in the hot sulfuric acid solution was analyzed using inductively-coupled plasma atomic emission spectroscopy (ICP; ICP-7000, Shimadzu Co. Ltd., Japan).

3. Results and discussion

3.1 Change in temperature

Fig. 1 shows photographs of hardened OPC paste bodies after immersion in 1-M sulfuric acid at 60–180 °C for 48 h. When OPC reacts with sulfuric acid, the following reactions generally take place:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \qquad (1)$$

$$3Ca(OH)_2 + 3H_2SO_4 + 3CaO \cdot Al_2O_3 + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \qquad (2)$$

which leads to expansion due to the formation of new crystals and disintegration of the hardened body [6–10]. After heating in sulfuric acid at 60 °C, the reaction products shown in Eqs. (1) and (2) started to form, as was evident from the white color of the hardened OPC paste body. In the case of immersion at 80 °C, the OPC paste body started to show signs of decomposition. With increasing temperature, severe damage accompanied by peeling of the outer layer was observed. These results confirm that OPC paste products have poor resistance to hot sulfuric acid.

Fig. 2 shows photographs of the fly-ash-based geopolymer paste products after immersion in 1-M sulfuric acid solution at 60–220 °C for 48 h. At more than 180 °C, the damage accompanied by peeling of the outer layer which were observed in OPC paste products was not confirmed. Therefore, heating temperature increased to 220 °C. Although the same external appearance as that of the original hardened body was maintained for all cases, changes in the microstructure of the geopolymer paste product due to diffusion of sulfuric acid into the hardened geopolymer paste product would affect the mechanical properties. Therefore, the compressive strength of the geopolymers was examined with a mechanical testing machine.

Fig. 3 shows the compressive strengths and the porosity of the geopolymer paste products before and after immersion in sulfuric acid solution at 60–220 °C for 48 h. Although the average compressive strength of the original geopolymer paste product was 24 MPa, after immersion at 60 °C and 80 °C, the average compressive strength decreased to approximately 10 MPa due to an increase in the porosity. Under these conditions, sodium hydroxide remaining in the hardened body is thought to elute into the sulfuric acid solution to form some pores. Starting from immersion at 120 °C, the porosity began to decrease, resulting in an increase in the average compressive strength to approximately 19 MPa. However, although the porosity further decreased after immersion at 180 °C, the average compressive strength also slightly decreased. In general, a decrease in the porosity of a geopolymer paste product leads to an increase in the compressive strength. However, the opposite was observed after immersion at 180 °C, which may be due to changes in the crystalline phases within the geopolymer paste product.

Fig. 4 shows SEM micrographs of the geopolymer paste products before and after immersion in sulfuric acid solution at 80–220 °C for 48 h. At 80 °C, the number of spaces (pores) among spherical particles (cenospheres) [19, 20] increased compared with the original geopolymer paste product. In contrast, at 120 °C, the pores among the cenospheres were filled with newly formed precipitation that formed a dense structure. Furthermore, densification of the geopolymer microstructure progressed at 220 °C. Change of the compressive strength of the geopolymer paste product with temperature, particularly at more than 120 °C, was thought to be caused by this microstructure change and the new precipitated crystal phase. Therefore XRD measurements were conducted to investigate the densification of the geopolymer paste product at higher temperatures due to the formation of new crystals.

Fig. 5 shows XRD patterns of the crystalline phases in the geopolymer paste products before and after immersion in sulfuric acid for 48 h. For heating at both 60 °C and 80 °C, the crystalline phases were the same as those of the original geopolymer paste product. From these results and those presented in **Figs. 3 and 4**, amorphous sodium hydroxide remaining inside the geopolymer paste product under these conditions is considered to elute into the sulfuric acid solution to form some pores. In contrast, a new crystalline phase of natroalunite ($NaAl_3(SO_4)_2(OH)_6$) was detected inside the geopolymer product after immersion in sulfuric acid at 120 °C. The formation of natroalunite crystals can be described as follows:

$$Na^+ + 3Al^{3+} + 2SO_4^{2-} + 6(OH)^- \rightarrow NaAl_3(SO_4)_2(OH)_6 \qquad (3)$$

When the geopolymer paste product is immersed in the sulfuric acid, aluminum ions are eluted from the geopolymer paste product with alkali hydroxide ions [21], and these ions react with sulfate ions to form natroalunite crystals. In addition, natroalunite crystals are more easily formed at temperatures higher than room temperature [22, 23]; therefore, natroalunite crystals were detected after immersion at 120 °C and higher. Furthermore, at 220 °C, analcime, which is a type of zeolite crystal [24-26], was also detected in addition to natroalunite. It has been reported that the precipitation of zeolite decreases the mechanical strength of metakaolin-derived geopolymer bulk bodies [27]. Therefore, the decrease in the compressive strength of the geopolymer paste product after immersion at 220 °C is considered to be caused by the formation of analcime crystals, although the porosity decreased at this temperature, as shown in **Fig. 3**.

After immersion in sulfuric acid at 180 °C for 48 h, the average compressive strength of the geopolymer was 19 MPa, which is sufficient for structural and building materials. However, long-term corrosion tests at 180 °C were also conducted because the precipitated natroalunite can become metastable under acidic conditions [22].

3.2 Immersion for various times at 180 °C

Fig. 6 shows the compressive strength and porosity of the geopolymer paste products before and after immersion in sulfuric acid at 180 °C for various times. After 48 h of immersion, the average compressive strength decreased from 24 MPa of the original geopolymer paste product to 19 MPa. However, the average compressive strength then increased back up to 20 MPa after immersion for 96 h. For 144 h and 192 h of immersion, the average compressive strength reached 25 MPa, which was higher than that of original geopolymer paste product. The compressive strength of a bulk body is generally dependent on the porosity. Here, the porosity of the geopolymer paste product tended to decrease with the duration of immersion at 180 °C; however, the reason for the decrease in compressive strength compared to that of original geopolymer paste product—despite the decrease in porosity after immersion for 48 h—is the change in microstructure and the formation of crystals. Therefore, the crystalline phases of the geopolymer after immersion in sulfuric acid for various times were analyzed using XRD.

Fig. 7 shows XRD patterns of the crystal phases in the geopolymer paste products before and after immersion in sulfuric acid solution at 180 °C for various times. After 48 h of immersion, natroalunite was detected as a new crystal phase in the geopolymer paste product. With longer immersion time, the XRD peak intensities corresponding to natroalunite increased, which indicates an increase in the amount of natroalunite crystals. Therefore, the decrease in the average compressive strength of the geopolymer product after sulfuric acid immersion treatment for 48 h is considered to be caused by the small amount of natroalunite crystal precipitates. The small amount of precipitated natroalunite crystal particles was insufficient to form a connected network, so the distribution of natroalunite particles did not contribute to an increase in the mechanical strength. Natroalunite would have a strong mechanical property. In contrast, the amount of natroalunite crystal particles increased over time at 180 °C and connected with each other, thereby densifying the microstructure and increasing the compressive strength of the geopolymer paste product.

Fig. 8 shows photographs of the geopolymer paste product cross-sections before and after immersion in sulfuric acid solution at 180 °C for 96 h. After 96 h, a whitish ring-like layer was observed several millimeters from the surface of the body. Elemental analysis of this layer indicated no metallic elements except for silicon; therefore, the layer was attributed to the formation of amorphous silica and not the geopolymer. It was thought that sodium and aluminum ions eluted from the geopolymer paste product into the sulfuric acid solution and remaining silica at the surface seemed to form the amorphous silica layer with several millimeters.

Here, the aluminum ion concentration in the sulfuric acid solution was examined. The mass transport of aluminum ions between the solid and the acid solution is considered to be important to understand the microstructural changes in the geopolymer paste product and the resistance to sulfuric acid. It has been reported that aluminum ions can easily leave from the aluminosilicate network structure of a geopolymer in sulfuric acid solution [15]. **Fig. 9** shows the amount of aluminum ions eluted after immersion in sulfuric acid solution as a function of time. The sulfuric acid solution in the Teflon vessel was exchanged every 48 h. In the early stage of the immersion test until 48 h, aluminum ions eluted from the surface of the geopolymer paste product into the sulfuric acid. Therefore, a thin layer from the surface of the hardened body consisted of only an amorphous silica phase derived from the amorphous geopolymer structure. However, after immersion for 96 h and 144 h, the amount of aluminum ions eluted decreased compared with that at 48 h. This decrease in eluted aluminum ions in the sulfuric acid solution is considered to be caused by the formation of natroalunite inside the geopolymer paste product. However, the concentration of eluted aluminum ions increased again after immersion for 192 h. When the concentrations of aluminum, silicon, and sodium ions increased simultaneously, natroalunite could be formed. However, when the amount of the original geopolymer that contributes to the formation of natroalunite crystals decreased over time, the resultant natroalunite began to re-dissolve into the sulfuric acid solution. Therefore, the amount of aluminum ions eluted into the sulfuric acid solution increased again after 192 h.

3.3 Mechanism for resistance to hot sulfuric acid solution

In this section, we discuss the mechanism for the high resistance of the fly-ash-based geopolymer product to hot sulfuric acid. **Fig. 10** shows a schematic diagram of the change in the geopolymer paste product microstructure and elemental elemental maps of the dense regions of the geopolymer body during immersion in sulfuric acid. First, both aluminum and sodium ions are eluted from the surface of the geopolymer paste product into the sulfuric acid immediately after immersion. As shown in **Fig. 8**, an amorphous silica ring layer, which was formerly part of the surface, is formed and reaches several millimeters in depth after 96 h. When sulfate ions diffuse into the amorphous silica layer, natroalunite is precipitated where the concentrations of aluminum, sodium, and sulfate ions increase inside the geopolymer product. The regions where natroalunite is precipitated densify, as shown in **Fig. 4**, and the dense regions could be observed deeper into the geopolymer over time. The border between the natroalunite precipitate region and the original geopolymer product was unclear; therefore, the activation energy for natroalunite precipitation could not be evaluated.

4. Summary

The resistance of a fly-ash-based geopolymer paste products to sulfuric acid solution was examined at temperatures of 60–220 °C for various durations. For immersion in sulfuric acid for longer than 48 h, natroalunite ($NaAl_3(SO_4)_2(OH)_6$) crystals were formed by the reaction among aluminum, sodium, and sulfuric ions, which resulted in an increase in the compressive strength of the geopolymer body due to densification. When the geopolymer paste product was immersed in sulfuric acid at 180 °C for 192 h, the average compressive strength changed from 24 MPa of the original product to 25 MPa. The fly-ash- based geopolymer paste product is a candidate material for chimney refractories of oil refinery plants.

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Figure and Table Captions

Fig. 1 Photographs of OPC paste hardened bodies after immersion in 1-M sulfuric acid at 60–180 °C for 48 h.

Fig. 2 Photographs of fly-ash-based geopolymer paste products after immersion in 1-M sulfuric acid at 60–220 °C for 48 h.

Fig. 3 Compressive strength and porosity of the geopolymer paste products before and after immersion in sulfuric acid at temperatures in the range of 60–220 °C for 48 h.

Fig. 4 SEM micrographs of the geopolymer paste products before and after immersion in sulfuric acid at 80 to 220 °C for 48 h.

Fig. 5 XRD patterns of the geopolymer paste products before and after immersion in sulfuric acid for 48 h.

Fig. 6 Compressive strength and porosity of the geopolymer paste products before and after immersion in sulfuric acid at 180 °C for various times.

Fig. 7 XRD patterns of the geopolymer paste products before and after immersion in sulfuric acid at 180 °C for various times.

Fig. 8 Cross-sectional photographs of the geopolymer paste products before and after immersion in sulfuric acid at 180 °C for 96 h.

Fig. 9 Amount of aluminum ions eluted after immersion in sulfuric acid as a function of time.

Fig. 10 Schematic diagram of the microstructural changes in the geopolymer paste product, and elemental maps of the dense regions during sulfuric acid solution treatment.

Table 1 Chemical composition of the fly ash used in this study.

Fig. 1

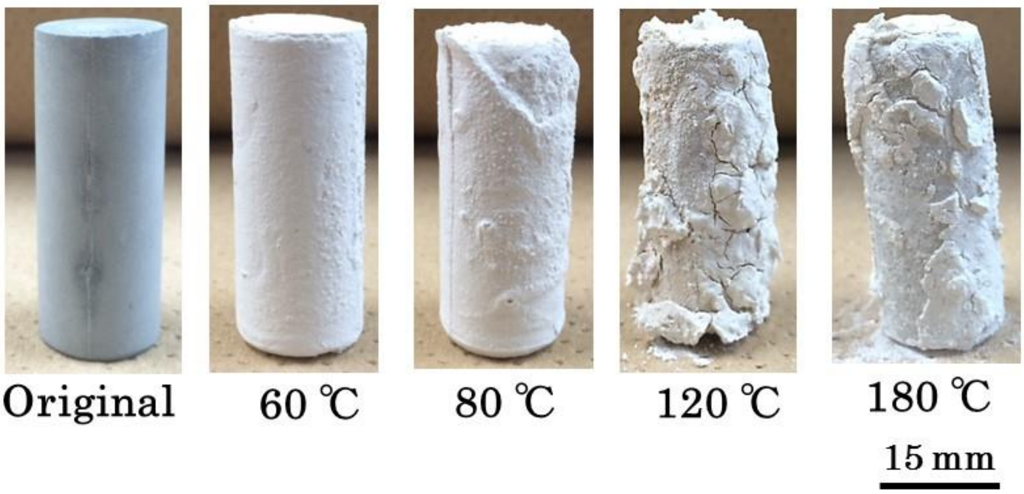
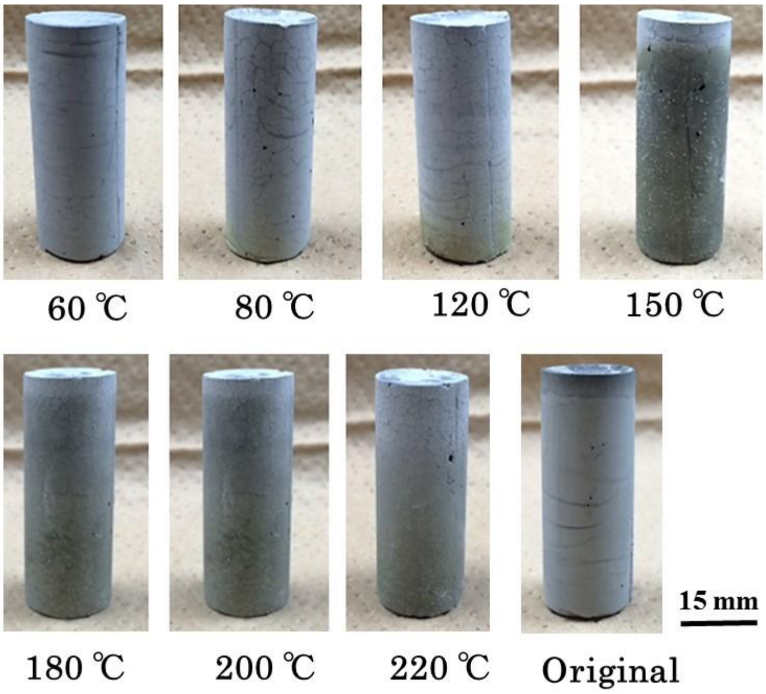


Fig. 2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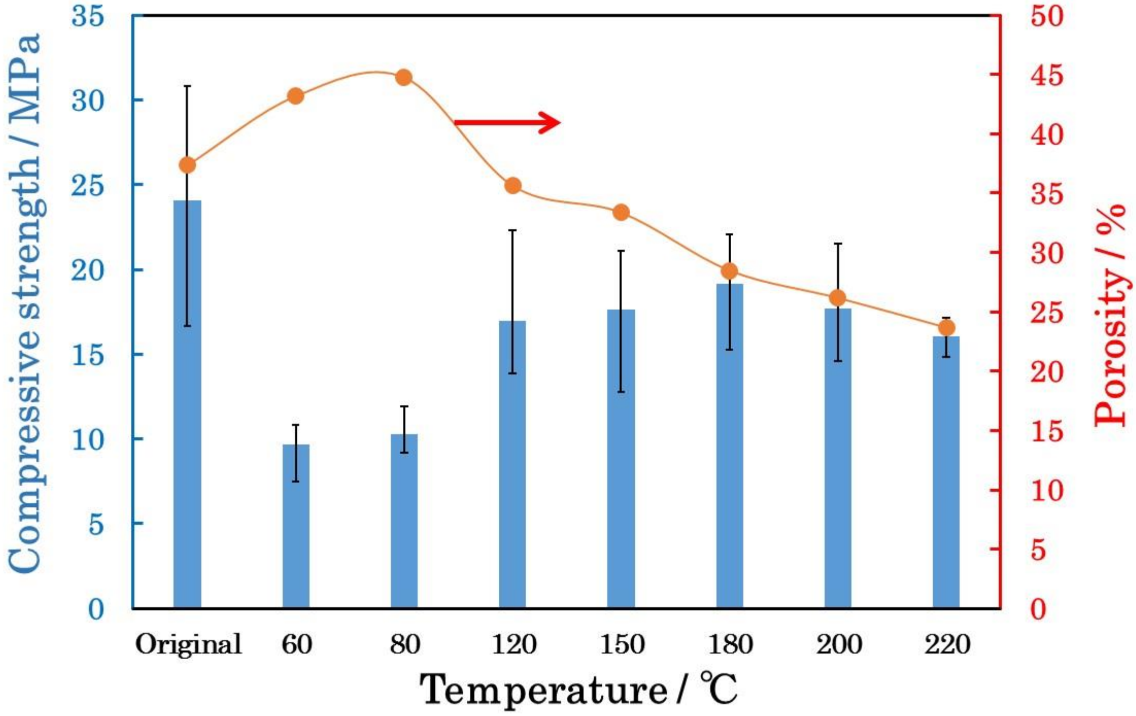
180 ℃ 200 ℃ 220 ℃ Original

Fig. 3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5
10
15
20
25
30
35
Porosity / %
0
5
10
15
20
25
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40
45
50
Original
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80
120
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180
200
220
Temperature / ℃

Fig. 4

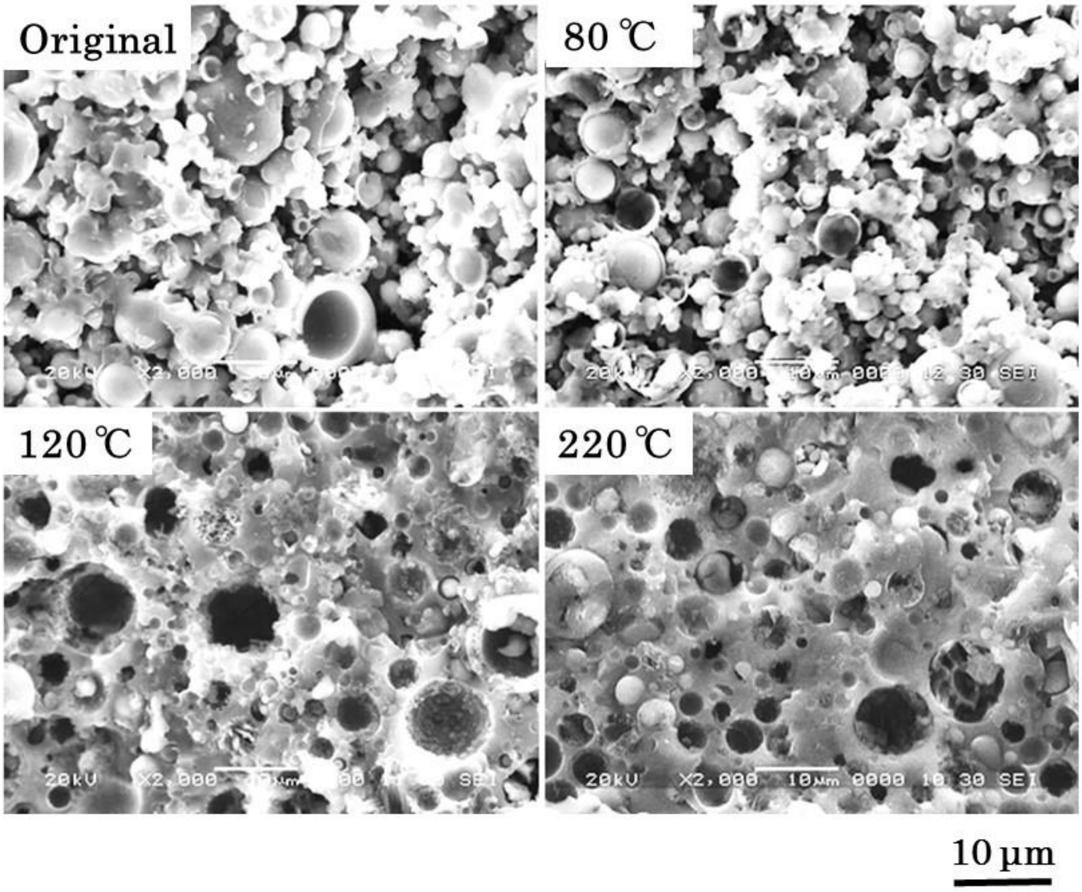


Fig. 5

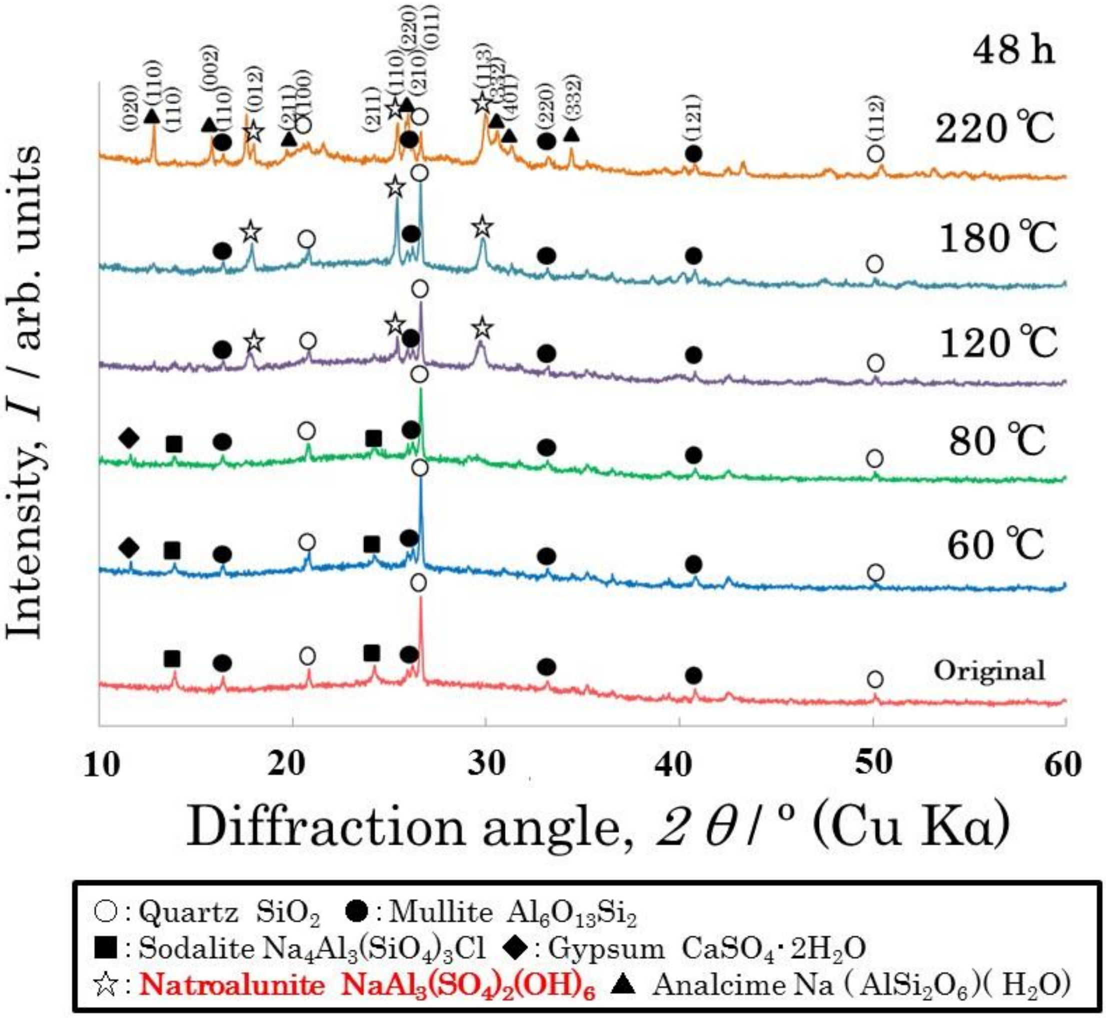
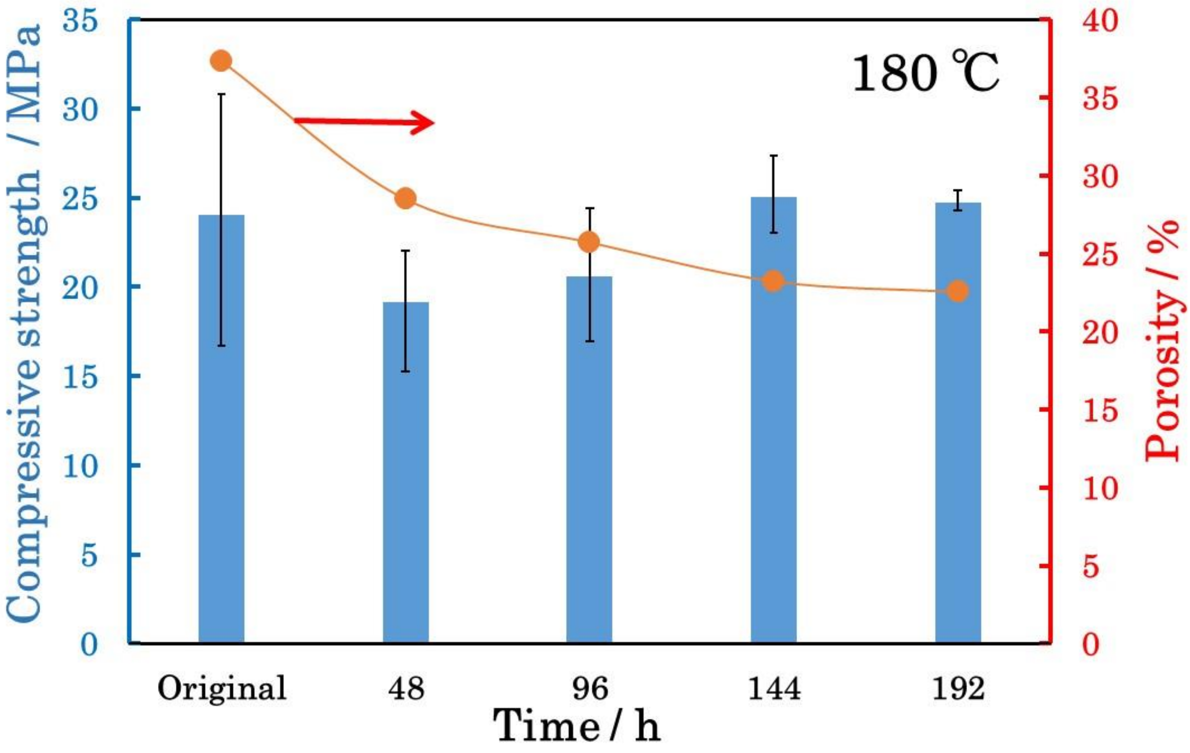

48 h
220 ℃
180 ℃
120 ℃
80 ℃
60 ℃
Original
(020)
(110)
(110)
(002)
(110)
(012)
(211)
(100)
(211)
(110)
(220)
(210)
(011)
(113)
(332)
(401)
(220)
(332)
(121)
(112)
Intensity, I / arb. units
10
20
30
40
50
60
Diffraction angle, 2θ / ° (Cu Kα)
○ : Quartz SiO₂ ● : Mullite Al₆O₁₃Si₂
■ : Sodalite Na₄Al₃(SiO₄)₃Cl ◆ : Gypsum CaSO₄·2H₂O
☆ : Natroalunite NaAl₃(SO₄)₂(OH)₆ ▲ Analcime Na (AlSi₂O₆)(H₂O)

Fig. 6


180 ℃
Compressive strength / MPa
0
5
10
15
20
25
30
35
Porosity / %
0
5
10
15
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40
Original
48
96
144
192
Time / h

Fig. 7

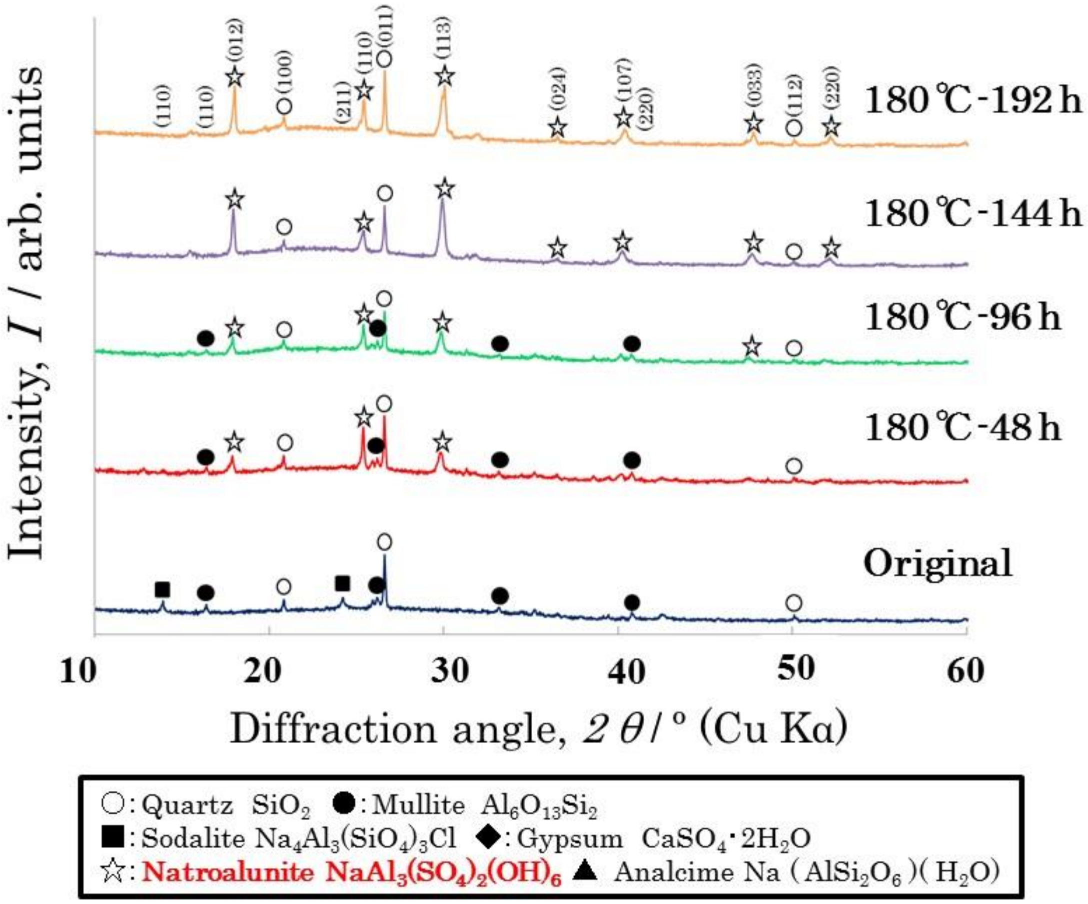
Intensity, I / arb. units
Diffraction angle, 2θ / ° (Cu Kα)
10
20
30
40
50
60
180℃-192 h
180℃-144 h
180℃-96 h
180℃-48 h
Original
(110)
(110)
(012)
(100)
(211)
(110)
(011)
(113)
(024)
(107)
(220)
(033)
(112)
(220)
○: Quartz SiO_2
●: Mullite $Al_6O_{13}Si_2$
■: Sodalite $Na_4Al_3(SiO_4)_3Cl$
◆: Gypsum $CaSO_4 \cdot 2H_2O$
☆: **Natroalunite $NaAl_3(SO_4)_2(OH)_6$**
▲ Analcime Na ($AlSi_2O_6$)(H_2O)

Fig. 8

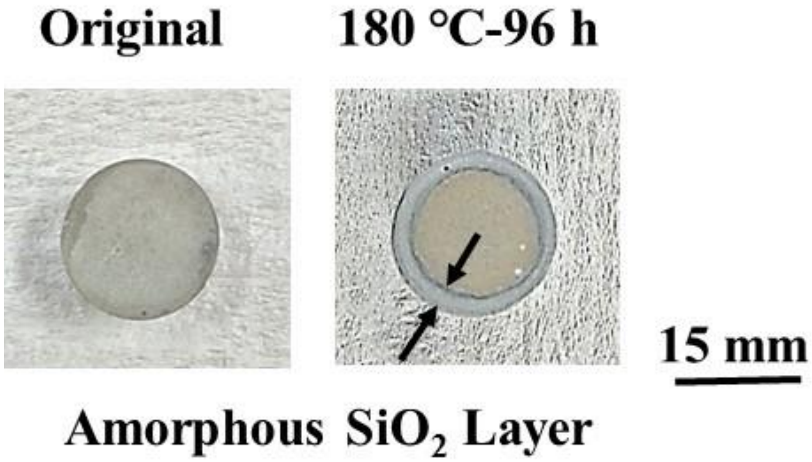

Fig. 9

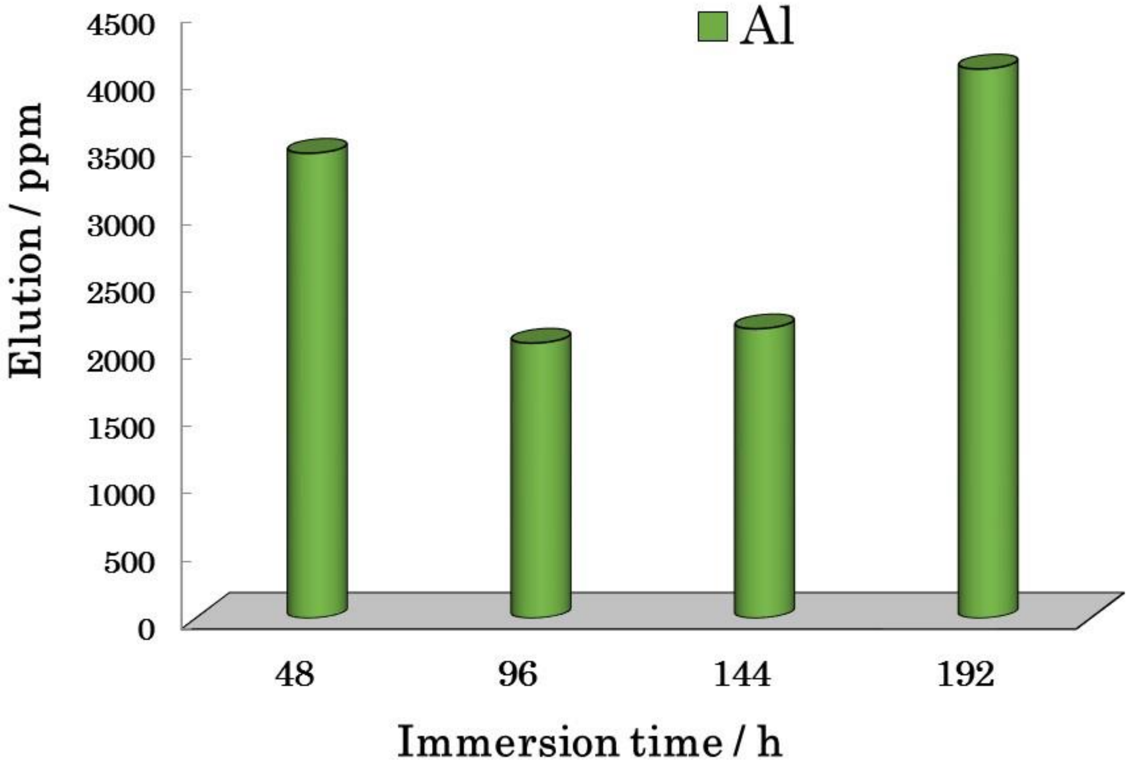
Al
Elution / ppm
4500
4000
3500
3000
2500
2000
1500
1000
500
0
48
96
144
192
Immersion time / h

Fig. 10

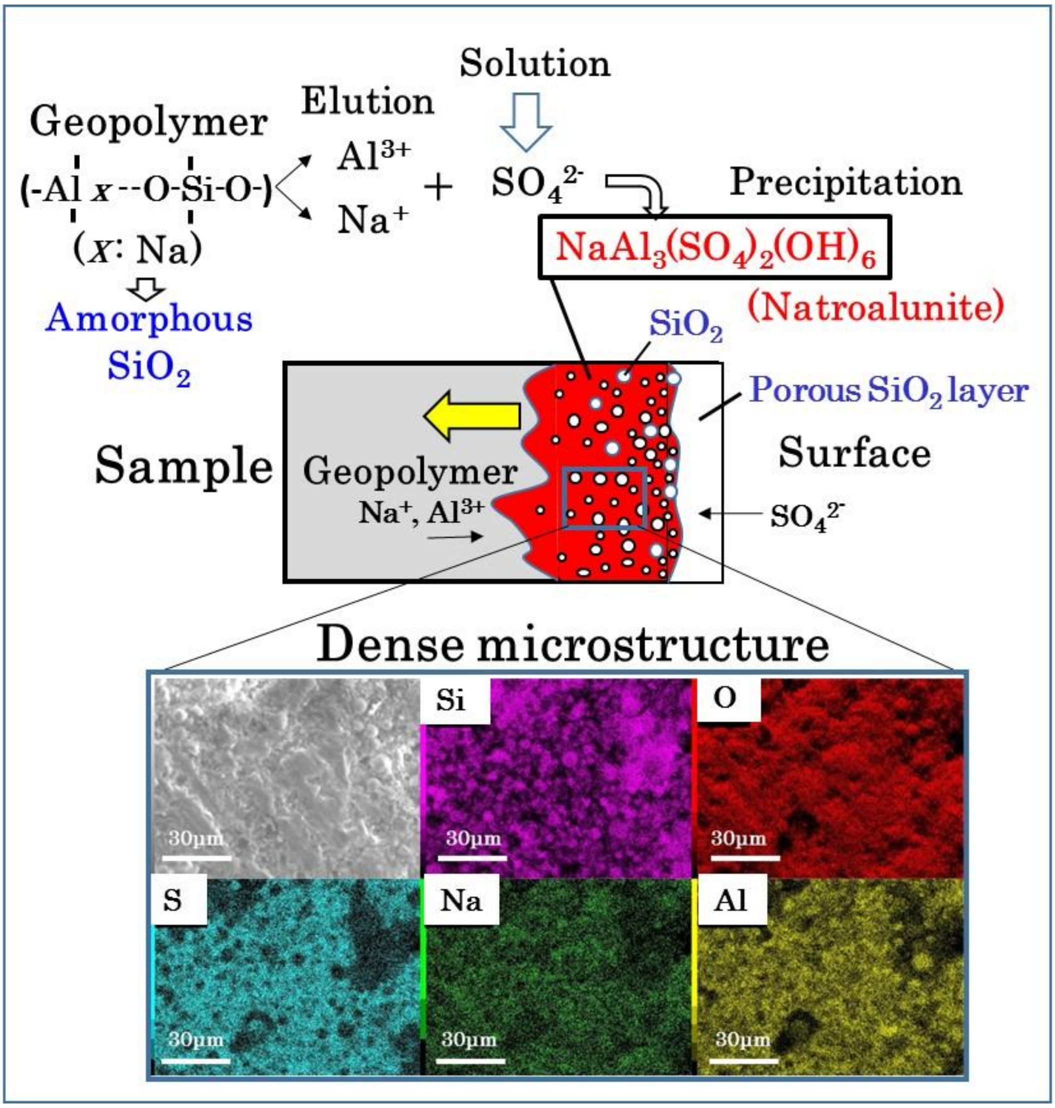
Solution
Geopolymer
Elution
(-Al x--O-Si-O-)
Al3+
Na+
+
SO4 2-
Precipitation
(x: Na)
NaAl3(SO4)2(OH)6
Amorphous SiO2
(Natroalunite)
SiO2
Porous SiO2 layer
Sample
Geopolymer
Surface
Na+, Al3+
SO4 2-
Dense microstructure
Si
O
S
Na
Al
30μm

Table 1

Composition	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**K_2O**	**TiO_2**	**Total**
(mass %)	60.13	25.23	6.47	2.21	1.93	1.19	1.58	1.26	100