Construction and Building Materials 151 (2017) 714–719

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

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

Shinobu Hashimoto *, Tatsuya Machino, Kotaro Ando, Yusuke Daiko, Sawao Honda, Yuji Iwamoto

Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

HIGHLIGHTS

- The fly-ash-based geopolymer has a highly resistivity for hot sulfuric acid solution.
- After immersion in sulfuric acid with 1.0 M at 180 °C for 192 h, the compressive strength was 25 MPa.
- Formation of natroalunite ($NaAl_3(SO_4)_2(OH)_6$) led to an increase in compressive strength.
- The fly-ash-based geopolymer is a candidate refractory material for oil refinery plants.

ARTICLE INFO

Article history:
Received 21 November 2016
Received in revised form 17 May 2017
Accepted 15 June 2017

Keywords:
Geopolymers
Sulfuric acid
Corrosion
Compressive strength
Ion elusion behavior

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.

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

* Corresponding author.
E-mail address: hashimoto.shinobu@nitech.ac.jp (S. Hashimoto).

http://dx.doi.org/10.1016/j.conbuildmat.2017.06.089
0950-0618/

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:

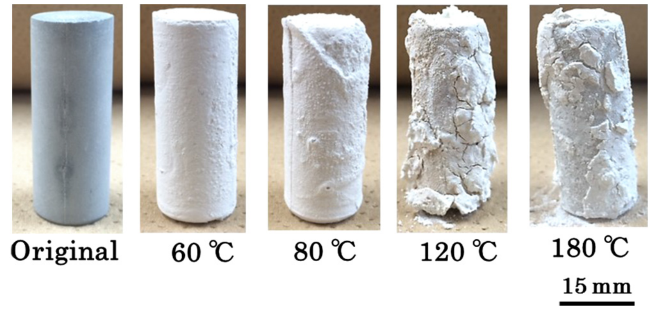

Fig. 1. Photographs of OPC paste hardened bodies after immersion in 1-M sulfuric acid at 60–180 °C for 48 h.

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \tag{1}$$

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

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,

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

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