Preparation of potassium and metakaolin based geopolymer foam with millimeter sized open pores for hydrogen recombining catalyst supports

Taro UTSUMI¹, Toshiharu TERASAWA², Isamu KUDO³, Tsuneo SUZUKI¹, Tadachika NAKAYAMA¹, Hisayuki SUEMATSU¹,³ and Toru OGAWA⁴

¹Extreme Energy-Density Research Institute, Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka, Niigata 940-2188, Japan
²Department of Nuclear System Safety Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka, Niigata 940-2188, Japan
³ADVAN ENG. co., ltd., 3399-34, Shimami-cho, Kita-ku, Niigata 950-3102, Japan
⁴Japan Atomic Energy Agency, Collaborative Laboratories for Advanced Decommissioning Science, 790-1 Motooka Ohtsuka, Tomioka Town, Futaba County, Fukushima 979-1151, Japan

A method to control the millimeter-sized open porosity in geopolymer foam was attempted to produce hydrogen recombining supports for radioactive waste canisters. The raw materials were mixed with silicon powder as a foaming agent. Geopolymer foams with open porosities as high as 81% were obtained by a water bath treatment before pouring the slurry into the mold. The increase in the open porosity of geopolymer foam was observed by an increase in the water bath treatment time. It was thought that the viscosity of slurry increase induced the pores trapped inside the geopolymer foam and connected to form millimeter-sized and open pores. It was concluded that a simple method with a foaming agent and a water bath treatment to prepare geopolymer foams with high open porosity was developed.

©2020 The Ceramic Society of Japan. All rights reserved.

Key-words : Geopolymer, Open porosity, Hydrogen recombiner, Catalyst support

[Received September 4, 2019; Accepted November 22, 2019]

1. Introduction

The Fukushima Daiichi Nuclear Power Station was damaged by an earthquake and a tsunami on March 11, 2011. The nuclear reactors that lost their cooling function due to the earthquake and the tsunami caused nuclear fuel meltdown. Fuel debris composed of nuclear fuel, control rod and structure materials was deposited at the bottom of the nuclear reactor.¹ In some of the radioactive wastes, water is mixed with particles to form slurry and is difficult to evaporate. In storing these radioactive wastes, hydrogen explosion by the gas generated by radiolysis of water is a concern. For this reason, hydrogen management is cited as a problem in waste storage.²

Similar radioactive wastes with water have been treated and stored in decommissioning of Three Mile Island Unit 2 (TMI-2). Core debris with water was stored in canisters with Pd–Pt–Al₂O₃ catalysts to promote hydrogen–oxygen recombination.³ On the other hand, Fukushima Daiichi Nuclear Power Station has to operate multiple radio-

nuclides removal and other systems for water treatment, which yield larger volume of radioactive wastes with water than that from TMI-2. Until 2017, 600 m³ of radioactive wastes has already been stored⁴ and the volume is estimated to increase to 6500 m³.⁵ Thus, it is important to develop an inexpensive catalyst and the support which consists of metal or inorganic materials and has high open-porosity.

Geopolymer is an amorphous inorganic polymer material based on aluminosilicate proposed by Davidovits.⁶ The solidification reaction of the geopolymer proceeds as follows. A mixture mainly composed of aluminosilicate with metal and hydroxyl ions in an alkaline solution is used as a raw material. In the solution, hydroxyl ions react with aluminum and silicon (Si) to separate aluminate and silicate. After that, the two substances undergo a dehydration condensation reaction, whereby a monomer constituting the geopolymer is produced. Gelation occurs by bonding of these monomers, and polycondensation reaction is repeated to form geopolymer by curing.⁷

In previous studies, dense and porous geopolymers for structural⁸ and insulating⁹–¹¹ applications have been made, respectively. As a feature of the geopolymer, it
has similar strength and superior acid and alkali heat resistance to those of cement. Furthermore, as a porous material, studies have been made for use in heat insulators and filters. For the former application, closed pores are favorable to decrease the heat diffusivity, while the latter applications prefer micrometer sized open pores.

For the catalyst support application, millimeter sized open pores are needed to allow gases going through the geopolymer foams. In potassium and metakaolin based geopolymers, open pores were introduced by adding oil droplets. Since the oil droplets with size less than 1 mm were suspended in the alkaline solution, the pore size was as large as 1 mm. Comparing to the oil droplets, gases can be generated by adding foaming agents and expand the volume easily in the alkaline solution.

As a method of generating a gas and adding pores in a geopolymer, a chemical reaction using Si powder is known, 

\[
4\text{H}_2\text{O} + \text{Si} \rightarrow 2\text{H}_2 + \text{Si(OH)}_4. \]

However, no attempts have been reported to apply the potassium and metakaolin based geopolymer foams for catalyst supports with high open porosity with \(>1\) mm.

Geopolymer is a candidate material for a matrix to manage highly activated nuclear wastes because of its stability under radiation. This property is good for the application to hydrogen recombining catalyst supports in radioactive waste canisters, however, development of geopolymer foams to this application had not been reported. The porous geopolymer catalysts for nuclear waste canisters stay on a very stable floor. Comparing to automobile catalyst supports subjected to harsh vibration from the engines, not so high external stress are expected to fracture the geopolymer catalyst supports. If they are fractured, it is not expected to change the catalytic properties. This is another reason why the geopolymer foams with high open porosities can be used for the catalyst supports for nuclear wastes.

In this research, the above chemical reaction is used to add porosity to the geopolymer foam. In order to use geopolymer as a catalyst supports, the synthesis conditions were optimized to increase the viscosity of the solution. This process can maximize the open porosity and optimize the pore diameter which are greatly related to the performance of the catalyst.

2. Experimental

As raw materials, potassium hydroxide (VETEC, moisture content 85%), microsilica (Elkem, Japan, 971-U) and metakaolin (Imerys-specialities, Japan, PoleStar450) powders and potassium silicate solution (Wako concentration, 50%) were used. For a foaming agent, Si powder (Nilaco, 100 mesh, purity 99.9%) was added.

Regarding the preparation of the geopolymer foam, a method reported by Henon et al. was chosen as shown in Fig. 1. The potassium silicate and the potassium hydroxide powders with contents of 24.48 and 11.00 wt.%, respectively, were mixed with distilled water of 26.52 wt.% and stirred for 20 min. To the solution, metakaolin and microscilla powders with contents of 20.00 and 18.00 wt.%, respectively, were added and stirred for 3 min to prepare a slurry. Thereafter, in a water bath, the slurry was heated at 70°C and further stirred for 0–20 min. After the stirring, Si powder with a content of 0–20 wt.% was added to the slurry and poured into a mold with size of \(\varphi 38 \times 61.5\) mm. The slurry was cured at 70°C for 48 h in air to make a foam. Then, the foam was taken out from the mold.

To confirm geopolymerization, powder X-ray diffraction (XRD) patterns of the foam were recorded and compared with those of the geopolymer foams in previous studies. For the measurements, RINT-2500PC (Rigaku with Cu-Kα radiation of 0.15418 nm) was used. The patterns were obtained using the following conditions: a voltage of 40 kV, a current of 40 mA, a scan speed of 10 °/min, and a step of 0.02°.

Open porosity and apparent bulk density of the prepared foams were measured. First, the apparent volume was determined by measuring the diameter and height of the foam using a caliper assuming a cylindrical shape. The weight of foam was measured using an electronic balance. The apparent bulk density was determined by dividing the weight of foam by the apparent volume. Then, the true volume was measured by the Archimedes method using water. Finally, the open porosity was calculated from the true and the apparent volumes.

The fabricated foams were cut and their cross sections were observed. The images were taken using a digital camera. Pore size distribution was obtained from multiple images from each sample.

3. Results

3.1 XRD

XRD patterns for the prepared foams are shown in Fig. 2. In the XRD patterns for both geopolymer foams, some sharp peaks, in particular 25, 27 and 36° are seen.
Since their positions are matched to those in raw materials of metakaolin and microsilica, they are unsolved impurity crystalline phases in raw materials. From the result for a foam synthesized with 0 wt.% of Si, a broad peak centered at 27° was seen and the peak position was close to that of XRD patterns of other geopolymer foams. The XRD pattern for a foam synthesized with 2 wt.% of Si was similar to that with 0 wt.%. On the other hand, raw materials of metakaolin and microsilica showed broad peaks around 21° (Fig. 2). From these facts, it was confirmed that the foams produced were geopolymerized.

3.2 Open porosity and bulk density
Open porosity and bulk density changes of geopolymer foams with water bath treatment time are shown in Fig. 3. The amount of Si was 1.0 wt.%. The open porosity increased as the water bath treatment time increased. When the water bath treatment time was more than 20 min, the viscosity of the slurry sharply increased, and a homogeneous foam could not be obtained.

Open porosity and bulk density of the geopolymer foams synthesized with various amounts of Si and a water bath treatment time of 20 min. are shown in Fig. 4. The geopolymer foam with Si had open porosity of about 72 to 81%. Above 0.5 wt.% of Si, the amount of the foaming agent did not greatly affect the open porosity. Above 1.0 wt.% of Si, the bulk density slightly decreased. From these results, it was found that the correlation between the open porosity of the foam and the amount of Si was small. It is
though that the viscosity of the slurry mostly influences the open porosity.

3.3 Cross section observations

Cross sections of the geopolymer foams synthesized with water bath treatment time of 0–20 min are shown in Figs. 5(a)–5(d). The pore diameter existing in the interior increased with the increase in water bath treatment time. In Fig. 5(d), the pore size was as large as 9 mm, which is appropriate for the catalyst support applications allowing gas to go through the geopolymer foam.

4. Discussion

As mentioned before, geopolymer foams had been prepared by addition of Si powder as a foaming agent. However, the former researches had aimed float and insulator applications.13) These products need closed pores. Open porosity measurements of geopolymer foams were limited. In the former research,15) oil droplets had been used as a template for the open pore formation by a foaming agent of hydro peroxide. The maximum pore size was 0.7 mm. On the other hand, in the present samples, the pore size was as large as 9 mm in the sample prepared with a water bath treatment of 20 min and a Si amount of 1.0 wt. % [Fig. 5(d)]. In the present synthesis method, only the foaming agent addition and the viscosity control by a water bath treatment enabled us to optimize geopolymer foams with open porosity of up to 81%.

Furthermore, from Fig. 5, it was observed that the number of open pores connecting with other pores shown by arrows increased with the increase of the water bath treatment time. This corresponds to the result obtained in Section 3.2, and it is expected that the pores become difficult to move due to an increase in the viscosity of slurry and they are connected to other pores to form millimeter-sized open pores.

5. Conclusions

Geopolymer foams with high open porosity was obtained by a foaming aid addition and a water bath treatment before pouring the slurry into the mold. An increase in the open porosity of the foam was observed by an increase in the water bath treatment time. This result seems to be attributed to the viscosity of the slurry increase. The pores are trapped in the foams and connected each other for form millimeter-sized open pores. The open porosity reached 81%.

Acknowledgements This work was supported by ADVAN ENG. co., ltd.

References

1) Investigation Committee on the Accident at the Fukushima Nuclear Power Stations of Tokyo Electric Power Company “II. The Damage and Accident Responses at the Fukushima Dai-ichi NPS and the Fukushima Dai-ni NPS” (2012) http://www.cas.go.jp/jp/seisaku/icanps/eng/03IIfinal.pdf.

2) Nuclear Damage Compensation and Decommissioning Facilitation Corporation “Technical Strategic Plan 2017 for Decommissioning of the Fukushima Daiichi Nuclear Power Station of Tokyo Electric Power Company Holdings, Inc.” (2017) http://www.dd.ndf.go.jp/en/strategic-plan/book/20171005_SP2017eFT.pdf.

3) J. O. Henrie and J. N. Appel, “Evaluation of Special Safety Issues Associated with Handling the Three Mile Island Unit 2 Core Debris” GEND 051 (1985) https://www.osti.gov/servlets/purl/5745202.

4) Nuclear Damage Compensation and Decommissioning Facilitation Corporation, “Technical Strategic Plan 2017 for Decommissioning of the Fukushima Daiichi Nuclear Power Station of Tokyo Electric Power Company Holdings, Inc.” http://www.dd.ndf.go.jp/en/strategic-plan/book/20171005_SP2017eFT.pdf.
5) Tokyo Power Electric Holdings, http://www.tepco.co.jp/nu/fukushima-np/handouts/2017/images2/handouts_170725.02-j.pdf.
6) J. Davidovits, “Geopolymer, chemistry and applications”, 3rd. ed., Institut Geopolymere (2011).
7) P. Duxson, A. Fernandez-Jimenez, J. L. Provis, G. C. Lukey, A. Palomo and J. S. J. van Deventer, J. Mater. Sci., 42, 2917–2933 (2007).
8) M. Uehara, “New Concrete with Low Environmental Load Using the Geopolymer Method” in Quarterly Report of Railway Technical Research Institute. Railway Technical Research Institute (2010).
9) J. Henon, A. Alzina, J. Absi, D. S. Smith and S. Rossignol, Ceram. Int., 38, 77–84 (2012).
10) J. Henon, A. Alzina, J. Absi, D. S. Smith and S. Rossignol, J. Porous Mat., 20, 37–46 (2013).
11) E. Prud’homme, P. Michaud, E. Joussein, C. Peyratout, A. Smith and S. Rossignol, Appl. Clay Sci., 51, 15–22 (2011).
12) P. Duxson, J. L. Provis, G. C. Lukey and J. S. J. van Deventer, Cement Concrete Res., 37, 1590–1597 (2007).
13) M. S. Cilla, P. Colombo and M. R. Morelli, Ceram. Int., 40, 5723–5730 (2014).
14) Y. Liu, C. Yan, Z. Zhang, Y. Gong, H. Wang and X. Qiu, Mater. Lett., 185, 370–373 (2016).
15) C. Bai, G. Franchin, H. Elsayed, A. Conte and P. Colombo, J. Eur. Ceram. Soc., 36, 4243–4249 (2017).
16) E. Prud’homme, P. Michaud, E. Joussein, C. Peyratout, A. Smith, S. Arrii-Clacens, J. M. Clacens and S. Rossignol, J. Eur. Ceram. Soc., 30, 1641–1648 (2010).
17) V. Camtarel, T. Motooka, and I. Yamagishi, “Geopolymers and Their Potential Applications in the Nuclear Waste Management Field -A bibliographical Study-” JAEA, 2017-014 (2017).
18) E. Prud’homme, P. Michaud, E. Joussein, J.-M. Clacens and S. Rossignol, J. Non-Cryst. Solids, 357, 1270–1278 (2011).