Received: 08 February 2021 | Revised: 17 Jun 2021 | Accepted: 24 June 2021

DOI: 10.1002/ces2.10100

International Journal of Ceramic Engineering & Science

RESEARCH ARTICLE

Pore-forming process in dehydration of metakaolin-based geopolymer

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Abstract

The geopolymer catalyst supports utilized in the nuclear waste containers for the Fukushima Daiichi Nuclear Power Station will be required to have high porosity and durability. This work presents the synthesis of a potassium and metakaolin-based geopolymer and its performance upon dehydration. During water content measurements of the samples, it was seen that in the demolded samples, the water content quickly decreased to less than 30% within 7 days, while the samples that had the cap removed from the container retained more than 50% of the water after 28 days. The pore size distribution of the samples that were post-cured at different temperatures up to 28 days did not vary greatly with respect to the average pore size. We can infer that structurally stable pores were formed in the first 4 days and were not affected by the post-curing rate, which may be related to rheological properties and the drainage path of water or hydrogen gas during post-curing.

KEYWORDS

catalyst supports, dehydration, geopolymers, pores, radioactive waste

1 | INTRODUCTION

On March 11th, 2011, a huge earthquake and the following tsunami caused the cooling of the reactors the spent fuel pools of the Fukushima Daiichi Nuclear Power Station to fail. A large amount of the spent fuel melted into the cooling water, which caused radioactive contamination in the reactor and the turbine buildings.

Radiolysis of the water due to the radioactive contamination can produce hydrogen and oxygen, and a large amount of hydrogen gas may cause a hydrogen explosion.[1] Fine radioactive waste particles combine with the water to form a slurry, making it difficult to remove the water. Thus, the radioactive slurry should be stored in containers with catalysts that promote hydrogen–oxygen recombination.[2] In a similar accident at Three Mile Island Nuclear Power Station, a Pt-Pd-Al_2O_3 catalyst was used.[3] Due to the large amount of nuclear waste in Fukushima, this solution is not feasible due to the high cost and large volume. From the perspective of sustainability in the storage of radioactive wastes, it is very important to choose catalysts and their supports that are inexpensive and have long-term chemical stability.

One possibility, geopolymer, is an inorganic polymer composed of AlO_4 and SiO_4 tetrahedral structural units and a three-dimensional network structure.[4] Clays (kaolinite), metakaolin, and certain industrial wastes (such as fly ash and furnace slag) and other inexpensive inorganic materials can be utilized as the raw materials to synthesize the geopolymer.

It can be solidified at room temperature and has stable chemical properties. Due to these reasons, the development of geopolymer as a candidate material for nuclear waste containment application was carried out.[5]

Metakaolin is formed after kaolin is thermally activated. When metakaolin is used as the source of the aluminosilicate, the synthesized geopolymer is purer and easier to characterize than geopolymers produced from other industrial wastes. The most commonly used alkaline metal activators are Na and K.[6] Due to the fact that initial Na-based activating solutions are much more viscous than K-based solutions and polymerize much faster, K-based geopolymers appear to have more homogeneous structure than Na-based geopolymers with the same Si/Al ratio.[7] In this research, K-based activating solutions and metakaolin were chosen to prepare the geopolymer catalyst supports.

Geopolymer is typically produced by a condensation reaction of aluminosilicate minerals containing amorphous alumina and silica with alkali, water glass, or phosphoric acid. Under strong alkali or acidic conditions, an amorphous three-dimensional network gel is forming.[8,9] With respect to the addition of a solution in the raw materials for the geopolymer synthesis, there must be a certain water content in the geopolymer. Previous studies[10] have shown metal species such as Pd, Pt, or Pd-Pt to be very sensitive to the effects of humidity poisoning resulting from the water molecules formed in the H_2/O_2 recombination reaction which can affect the activity of both the alumina-supported and the silica-supported catalyst. The inhibitory effect of water on the catalyst and thus the control of the water content in the catalyst supporting matrix is important. From previous research, the weight loss is due to the dehydration of adsorbed water and begins above ambient temperature and it is proportional to the initial water content.[11] Of major consideration is the fact that the pore size in geopolymer catalyst supports should be controlled.

In consideration of the synthesis of a geopolymer as a catalyst support,[12] the volume of the geopolymer needs to be maintained at a stable level. However, during curing, shrinkage takes place which is primarily caused by the loss of water in the drying process.[13] It is desirable to maintain the pore size during curing.

Geopolymers contain pores and penetration of external species occurs through the pore network, which may degrade the mechanical properties. The reduction of pore size increases the compressive strength of the material.[14] Porosity and pore size distribution in the potassium and metakaolin-based geopolymer were tailored by simple change in synthesis conditions.[1] Therefore, the timing of pore formation in geopolymer synthesis is fundamental in understanding its influence on the durability of geopolymers. A previous study showed that increasing the water content in the geopolymer binders led to a significant decrease in viscosity, compressive strength and to the growth of pore volume and pore size.[15] water only acts as a solvent in the formation of the hardened geopolymer and provides workability.[16]

In this study, geopolymer is synthesized with various temperatures and then dehydration performed to observe the pore size change. The pore size with the same initial curing temperature and different post-solidification temperatures was measured, so as to analyze the effect of dehydration on the pore size distribution.

2 | EXPERIMENTAL

Geopolymer samples were made of silica fume (Tomoe Engineering Co., Ltd, EFACO silica meets the requirements of EN 13263-1 and EN 13263-2), mixed with metakaolin (SOBUE CLAY & CO., LTD, kaolin Lot 501) powders, potassium hydroxide(VETEC, moisture content 85%), and potassium silicate solutions(FUJIFILM Wako Pure Chemical Corporation, concentration, 50%), with molar ratios of Al: Si: K: H2O = 1:2.1:0.8:8.[17]. The composition of samples is shown in Table 1.

The potassium silicate, potassium hydroxide powders, and the distilled water were mixed (respectively 28.12, 5.11, and 25.38 wt.% of the total geopolymer weight). The solution was stirred until complete dissolution of the powder. Then, the solution was cooled to room temperature with an ice bath. EFACO silica powder (25.38wt.%) was added to the solution, stirred at a speed of 60 rpm for 1 min, and then metakaolin (30.43wt.%) was added in 2 times, stirring at a speed of 60 rpm for 2 min each time. Finally, the slurry was stirred at a speed of approximately 80 rpm for 5 min to synthesize a geopolymer sample. The synthesis process of the geopolymer samples is shown in Figure 1. After mixing of the raw materials, the mixture was poured in molds with caps to ensure good air tightness (the weight change of the sample with cap in 4 days, the result showed that the weight changed within 0.025%). The curing treatment processes are shown in Table 2. Then, samples were cured at 60°C for 4 days (Curing 1). The six samples were then divided into three groups (1, 2, and 3), with each group consisting of two samples. For each group, one sample was completely demolded, and the other was kept in the mold, but the cap was removed. Finally, the three groups of samples were further cured at RT, 60 and

TABLE 1 Sample composition

Materials	K_2SiO_3	H_2O	KOH	SiO_2	Al_2O_3 2~3SiO_2	Total
Composition wt%	28.12	25.38	5.11	10.95	30.43	100

80°C for 28 days (Curing 2). The curing treatment processes are shown in Table 2.

The volume of each sample was calculated from the height and diameter as determined by a caliper to enable the shrinkage coefficient of the sample for 28 days in Curing 2 to be calculated.

The change in recorded mass after sample curing on days 4–28 enabled the water content in the sample to be estimated. Since our sample will be used for hydrogen recombination catalyst carrier, we only consider the distribution of large pores here, because mesopores and micropores contribution to air flow is limited. According to previous studies, SEM can observe pores larger than 50 μm[18]; therefore, SEM was used to measure pores in this research. According to the method of calculating the area of the circle and the number of pores in the circle, the pore distribution of the equivalent circle can be obtained.[19] We cut 3 mm from the bottom of the sample and assume that the cross section is circular. Approximately 500 pores were observed on the cross section to analyze the pore distribution.

In order to better dehydrate the geopolymer, the reactions at high temperature were investigated by thermogravimetric-differential thermal analysis (TG-DTA). 23 mg of Sample A (RT, demold) was taken and heated from RT to 1000°C in an air atmosphere at either a heating rate of 10 K/min or 5 K/min to understand variations in kinetics.

To analyze phases in the geopolymer, X-ray diffraction (XRD) with Cu-Kα radiation (0.15418 nm) was used with a scanning angle range of 10–60 degree (a voltage of 40 kV, a current of 40 mA, a scan speed of 10 °/min, and a step of 0.02°).

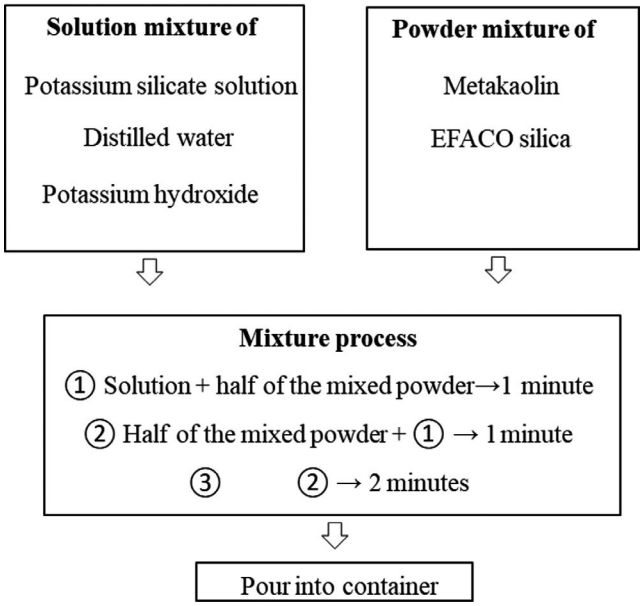

FIGURE 1 The synthesis process of the geopolymer samples

3 | RESULTS

Samples A-F after 28 days are shown in Figure 2. Calculation of the shrinkage of Samples A, C, and E was 2.13%, 5.64%, and 21.65%, respectively. The shrinkage increased with an increase in temperature in Curing 2. Less cracks on the surface of the sample body were observed when samples were cured at low temperatures.

The water content of samples on days 4–28 (Curing 2) is shown in Figure 3. Is there was no mass loss it is possible to remove this assumption, here the water content of the fourth day was assumed as 100%. At room temperature in the demolded sample, the water content quickly decreased to less than 30% within 7 days, while, in the open cap samples, more than 40% of water remained after 28 days. With an increase in temperature in Curing 2, the decrease in water accelerated as expected.

The pore size distributions are shown in Figure 4. The average pore size was almost the same among all the samples.

TG-DTA results of Sample A are shown in Figure 5. Weight loss shifted to higher temperature as the heating rate increased. Previous work has indicated that the dehydration temperature could be increased when a faster heating rate was applied.[20] A similar peak shift was observed in Figure 5 so it is possible that the peak between 200 and 300°C is due to dehydration of free water.

TABLE 2 Curing treatment process

Group number	Sample number	Curing 1		Curing 2		
1	A	Temperature	Time	Treatment	Temperature	Time
		60°C	4 days	Demold	RT	28 days
	B			Open cap		
2	C			Demold	60°C	
	D			Open cap		
3	E			Demold	80°C	
	F			Open cap		

Curing condition	Sample A RT without case	Sample B RT with case	Sample C 60°C without case	Sample D 60°C with case	Sample E 80°C without case	Sample F 80°C with case
Samples body after 28 days						

FIGURE 2 Samples (A-F) after 28 days

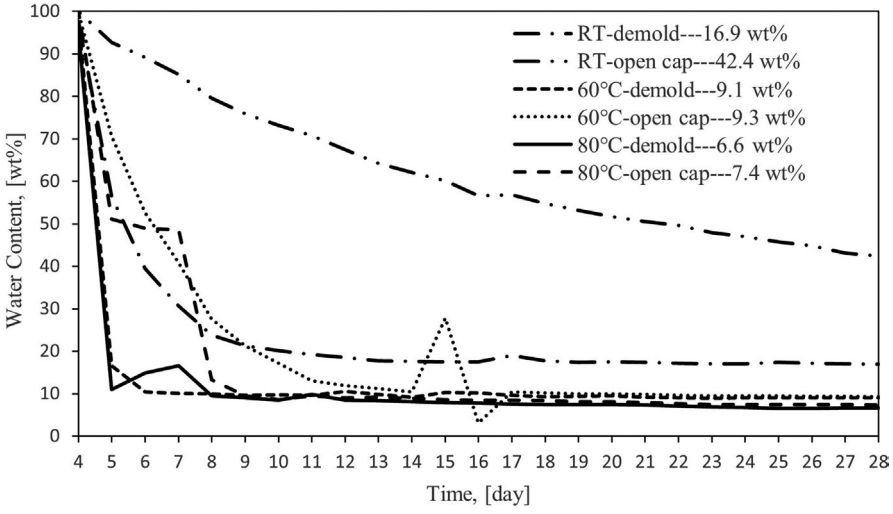

FIGURE 3 The water content of samples on days 4–28 (Curing 2)

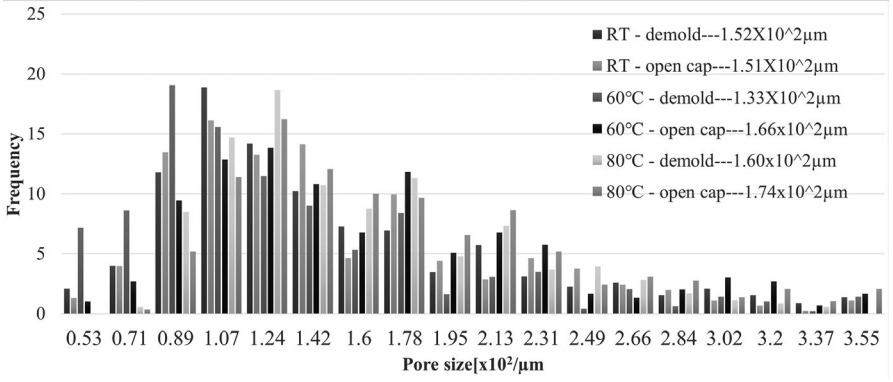

FIGURE 4 The pore size distributions

XRD patterns of the geopolymer samples after heating to different temperatures are shown in Figure 6. At 200°C, peaks for TiO_2 were seen, which have originated from the impurities in the metakaolin. Some small peaks for illite, andradite, and SiO_2 were also visible. Except for these sharp peaks, a broad peak at 27°C was seen, which is different from those of metakaolin and silica. This indicates the presence of an amorphous geopolymer phase up to 1000°C. This is due to the difficulties of zeolite formation in a potassium-based geopolymer.

4 | DISCUSSION

As shown in Table 2, Curing 1 was conducted at the same temperature for 4 days and then samples were changed to

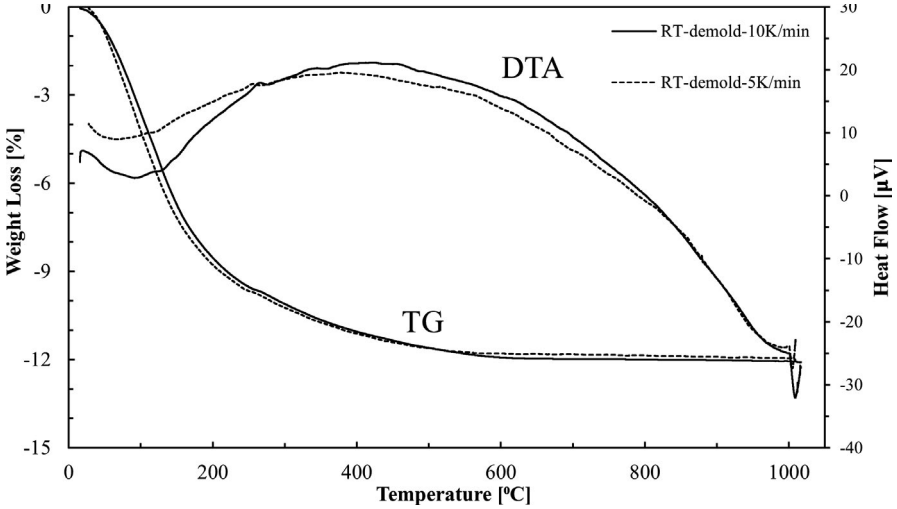

FIGURE 5 TG-DTA results of Sample (A)

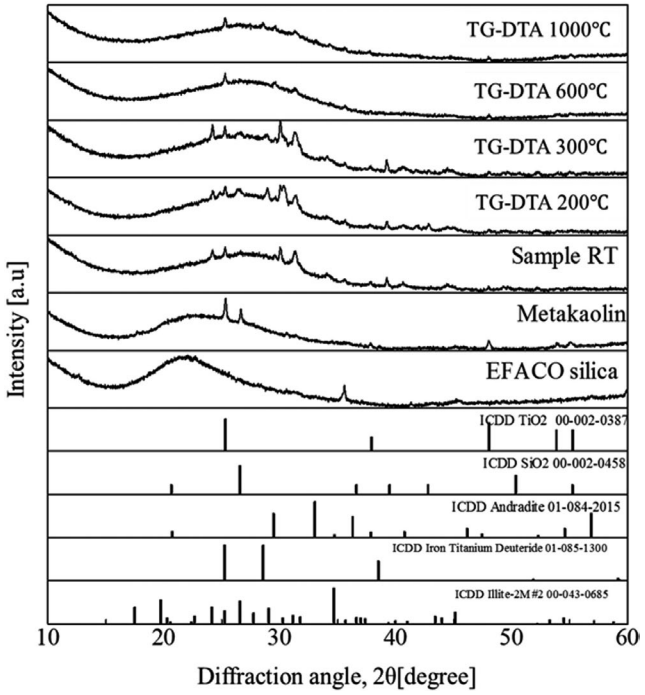

FIGURE 6 XRD patterns of the geopolymer samples after heating to different temperatures

a different temperature for Curing 2. The water content decreased, and the sample cracked at relatively high temperatures (60 and 80°C).

As well known, a large number of pores in the length range of 5–20 nm[21] have been identified by a TEM and a gas adsorption porosity method. These pores are filled with a large amount of free water discharged from the condensation polymerization reaction.[22,23] The polycondensation reaction causes the geopolymer to form a network structure, which is the solidification process of the geopolymer.[4] From a macro point of view, the phenomenon that the rheological property changes during solidification process is from a paste to a solid. Previous research[16] has shown that the evaporation of pore water in the geopolymer and the loss of bound water leading to the reorganization of the aluminosilicate at high temperatures may cause the shrinkage around the pores, which leads to micro-cracks and then open channels. The open channels then accelerate the release of water. However, the average pores size in this study was varied between 150 and 170 μm and the pore distribution still shows almost the same after the same initial curing and different post-curing. The different release speed of water and hydrogen gas does not significantly affect the pores that we measured. This indicates that the pores size may have stabilized within four days because the rheological properties changes are almost negligible after 4 days. To our knowledge, the behavior of pore size during dehydration has not been mentioned before.

The XRD pattern indicated that when the sample was heated to 1000°C, some new crystalline phases (andradite and iron titanium deuteride) were generated, which may improve the thermal stability of the sample; however, it is unlikely that the geopolymer will encounter these temperatures in service.

5 | CONCLUSIONS

The application of geopolymers in nuclear waste treatment has been proposed in many studies. For example, geopolymers are used as hydrogen recombination catalysts, which have been proven to effectively reduce the concentration of hydrogen to prevent hydrogen explosions.[24] However, the application of geopolymers in catalyst supports is rarely mentioned. In this study, the synthesis and dehydration of a potassium metakaolin-based geopolymer were performed for hydrogen recombination catalyst support.

Pore size was almost the same in samples cured at the same curing temperature for 4 days and was not affected by

the curing conditions applied thereafter. Water continued to evaporate until approximately 300°C, where most of the free water was released. Most of the weight loss occurs below 400°C. The bound water began to be partially released, but some of the bound water still formed a strong chemical bond and was not released up to 1000°C. The geopolymer phase did not go through a significant phase transformation over this temperature range. With regards to the implementation of the geopolymer, this is encouraging in that if heat is emitted from the radioactive sludge, it will not have an impact on the poor size and thus reduce its efficiency.

ACKNOWLEDGEMENTS

This work was supported by ADVAN ENG. Co., ltd.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Yang Y, Le T-C, Kudo I, Do T-M, Niihara K, Suematsu H, et al. Pore-forming process in dehydration of metakaolin-based geopolymer. *Int J Ceramic Eng Sci*. 2021;3:211–216. https://doi.org/10.1002/ces2.10100