

J.-H. HA<sup>\*,#</sup>, Y.-H. PARK<sup>\*</sup>, I.-H. SONG<sup>\*</sup>**ALUMINA COATING TO REALIZE DESIRED PORE CHARACTERISTICS OF SINTERED DIATOMITE MEMBRANE****POWŁOKA TLENKU GLINU DO UZYSKANIA POŻĄDANEJ POROWATOŚCI SPIEKANEJ MEMBRANY DIATOMITOWEJ**

Porous ceramic membranes prepared from natural materials such as diatomite, have lately attracted great interest in industrial applications due to their cost-effectiveness. In this study, we attempted to prepare an alumina coating to be deposited over a sintered diatomite-kaolin composite support layer in order to reduce the largest pore size to below  $0.4\ \mu\text{m}$ ; such a coating could be potentially used in water treatment applications for bacterial removal.

*Keywords:* diatomite membrane, alumina coating, largest pore size

**1. Introduction**

Porous ceramic membranes derived from low-cost natural materials such as diatomite have recently become the focus of great interest as researchers seek to exploit their cost effectiveness [1,2]. Previously, we reported on various approaches for fabricating a sintered diatomite membrane, which allowed for control over membrane characteristics [3-7] such as the largest pore size. The largest pore size is one of the main specifications of a porous ceramic membrane because it indicates the largest size of solute particles that can pass through. However, when fabricating a composite with natural materials, such as a diatomite-kaolin composite support layer or a diatomite-kaolin composite coating, because of the coarse particle size, inherent pores inside particles, and the irregular shape of diatomite, there are practical limitations that hinder reducing the largest pore size of the sintered diatomite membrane to less than  $0.5\ \mu\text{m}$ .

However, most harmful bacteria such as *Escherichia coli*, *Staphylococcus aureus*, *Salmonella*, *Legionella*, and *Pseudomonas aeruginosa* are greater than  $0.4\ \mu\text{m}$  in size [8,9]. Thus, in order to remove bacteria in water treatment applications, the largest pore size of the sintered diatomite membrane must be less than  $0.4\ \mu\text{m}$ . In this study, the focus was on determining how to reduce the largest pore size of a sintered diatomite membrane to less than  $0.4\ \mu\text{m}$ . Alumina particles of different mean particle sizes were applied as a coating on a sintered diatomite-kaolin composite support layer. We investigated whether we could overcome the difference in the degree of shrinkage of the alumina coating and that of the diatomite-kaolin composite support layer. Also, because the diatomite membranes were low-cost, we allowed ourselves to explore using alumina particles from inexpensive coarse ones to expensive fine ones.

**2. Material and methods**

Diatomite (Celite 499,  $7.43\ \mu\text{m}$ , Celite Korea Co. Ltd., Korea) and kaolin (Kaolin,  $1.53\ \mu\text{m}$ , Sigma-Aldrich, USA) were used to prepare the diatomite-kaolin composite membranes. Coarse alumina (aluminum oxide,  $4.67\ \mu\text{m}$ , Sigma-Aldrich, USA), intermediate alumina (ALM-44,  $2.42\ \mu\text{m}$ , Sumitomo Chemical, Japan), and fine alumina (AKP-30,  $0.45\ \mu\text{m}$ , Sumitomo Chemical, Japan) were used to prepare an alumina coating. The above-mentioned mean particle sizes of the starting powders were determined by a particle-size analyzer (LSTM 13 320 MW, Beckman Coulter, USA).

To enhance the sintering of the diatomite particles, the average particle size of the as-received diatomite was reduced to  $7.43\ \mu\text{m}$  by ball-milling [6]. Distilled water was used as a solvent, and the slurry was ball-milled for 24 h with an alumina ball-to-powder volume ratio of 2:1. To incorporate kaolin into the diatomite matrix, diatomite particles were mixed with 10 wt. % kaolin for 3 h by dry ball-milling with a ball-to-powder volume ratio of 2:1. With polyethylene glycol as a binder, the diatomite-kaolin composite support layer specimens were dry-pressed at 18.7 MPa and sintered at  $1200^\circ\text{C}$  for 1 h. A dip-coating process was used to deposit an alumina coating layer onto the diatomite-kaolin composite support layer.

For the coating process, alumina, distilled water, an organic binder (HS BD-25, San Nopco Korea, Korea), and an inorganic binder (AS-40, Sigma-Aldrich, USA) were mixed, dip-coated on a sintered diatomite-kaolin composite support layer, dried at room temperature for 4 h, and then sintered at  $500^\circ\text{C}$  for 1 h. Because micro-cracks could be induced by abrupt water elimination, room temperature should be applied to ensure a low driving force for water evaporation during the drying process.

\* KOREA INSTITUTE OF MATERIALS SCIENCE, CHANGWON, REPUBLIC OF KOREA

# Corresponding author: hjhoon@kims.re.kr

The pore characteristics of the diatomite membranes were examined by scanning electron microscopy (JSM-5800, JEOL, Japan). The air flux was measured by capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., USA). The sintered diatomite-kaolin composite specimen (diameter of 4 cm and thickness of 0.4 cm) was fitted between the O-rings in the bottom of the chamber and the bottom of the chamber insert for capillary flow porosimetry. The flux was then measured automatically by sensors while incrementing the diameter of the motorized valve and the pressure of the regulator.

The largest pore size of the diatomite membrane was measured by the bubble point method. The bubble point method is the most widely used for pore size determination and is capable of determining the largest pore size of a membrane. The method is based on the fact that, for a given fluid and pore size with constant wetting, the pressure required to force an air bubble through the pore is inverse proportional to the size of the pore.

### 3. Results and discussion

Figure 1 (a) shows the largest pore sizes of the as-sintered diatomite-kaolin composite support layers prepared under various processing conditions as a function of the specific flow rate at 175 kPa, following a previously reported method [6].

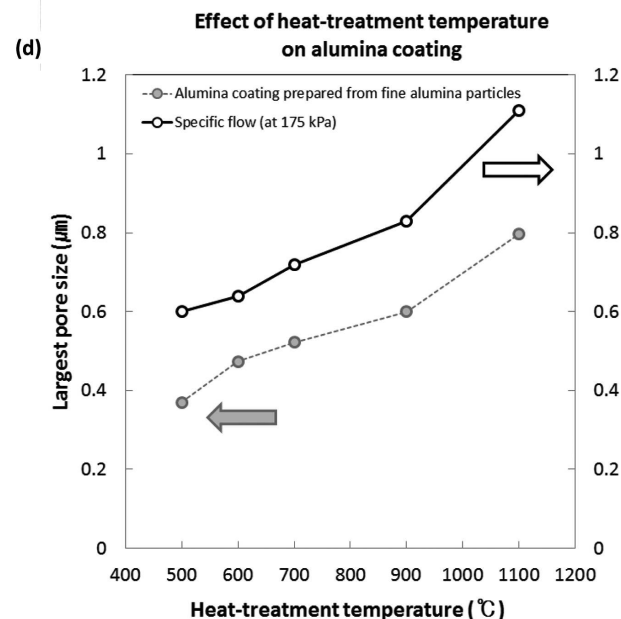
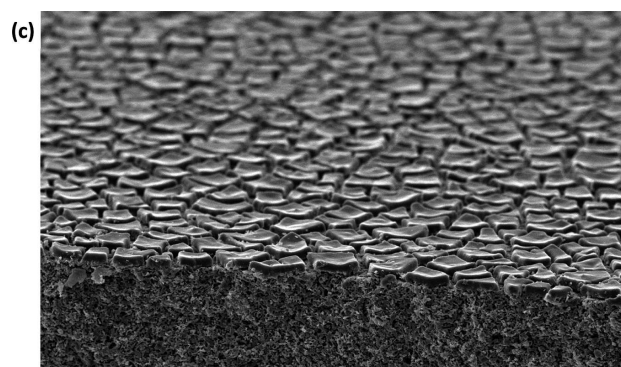
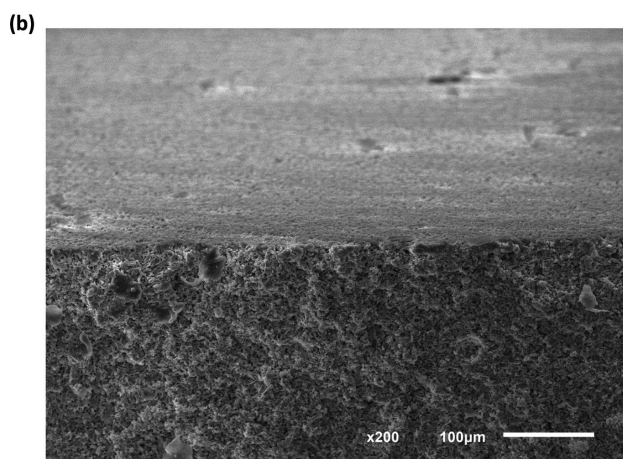
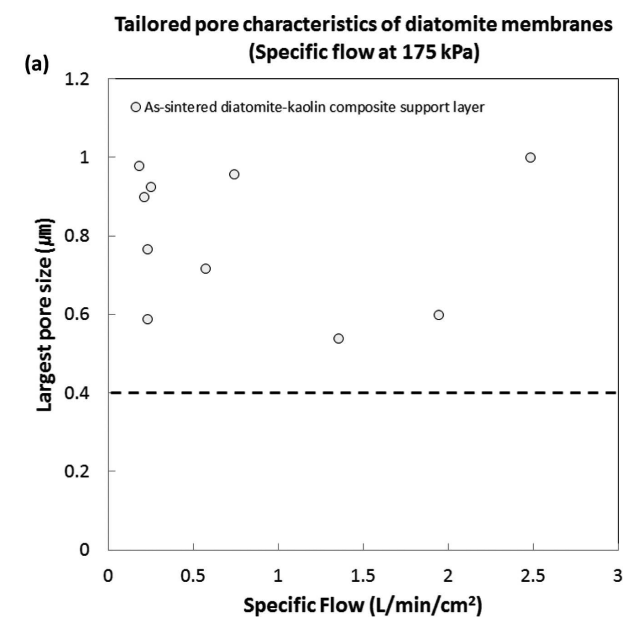


Fig. 1. (a) The largest pore sizes of the diatomite-kaolin support layers created under various processing conditions as a function of the specific flow rate at 175 kPa, (b) cross-sectional SEM image of as-sintered diatomite-kaolin composite support layers, sintered at 1200°C for 1 h with 10 wt. % of kaolin, (c) cross-sectional SEM image of alumina coating, prepared from coarse alumina particles deposited on the diatomite-kaolin composite support layer and then heat-treated at 1200°C for 1 h one time, and (d) the largest pore size and permeability of the alumina coating prepared from fine alumina particles deposited on the diatomite-kaolin composite support layer one time, and heat-treated at 500°C for 1 h

Although the amount of kaolin added and the sintering temperature were controlled within a range of 0 to 100 wt. % and 1000 to 1200°C, respectively, the largest pore size of the diatomite-kaolin composite support layer could not be reduced to below 0.4 μm. Therefore, to reduce the largest pore size of the diatomite membrane by depositing a coating layer, three kinds of alumina particles were introduced as coating layers.

A typical cross-sectional scanning electron microscope (SEM) image of the diatomite-kaolin composite support layer sintered at 1200°C for 1 h with the addition of 10 wt. % kaolin is shown in Figure 1 (b). The addition of 10 wt. % of kaolin to the diatomite support layer can enhance the mechanical strength significantly while retaining an appropriate permeability [6].

Prior to investigating the various processing conditions for preparing a sintered diatomite membrane with an alumina coating, the heat-treatment temperature after the coating

process should be determined. In previous studies, a diatomite coating [5] or a diatomite-kaolin composite coating [4] on a sintered diatomite support layer heat-treated at 1200°C for 1 h could be prepared without micro cracks or defect formation. However, the alumina coating prepared with coarse alumina particles and then heat-treated at 1200°C for 1 h had severe micro cracks, as shown in Figure 1 (c). It is understood that the difference in the linear shrinkage rate between the alumina-based coating and the silica-based support layer abruptly increased at temperatures above 1000°C [10]. Moreover, the diatomite-kaolin composite support layer was sintered before the coating process started, leaving it very little shrinking potential to match the shrinkage of the alumina coating when they were later heat-treated together.

To investigate the effect of heat-treatment temperature on the sintered diatomite membrane, an alumina coating was prepared with fine alumina particles and then heat-treated at 500 to 1100°C for 1 h. Figure 1 (d) shows the largest pore sizes and the specific flow at 175 kPa of the alumina coating deposited on the diatomite-kaolin composite support layer as a function of the heat-treatment temperature. These trends are in good agreement with the pore evolution model of ceramic membranes during constrained sintering [11], which suggests that the pore size and permeability increases in supported membranes as the sintering temperature is increased.

Considering the experimental results shown in Figures 1 (c) and (d) and the results found in literature [12, 13, 14, 15, 16], the heat-treatment temperature after the coating process was confined to 500°C in order to reduce the largest pore size of the sintered diatomite membrane to less than 0.4 μm.

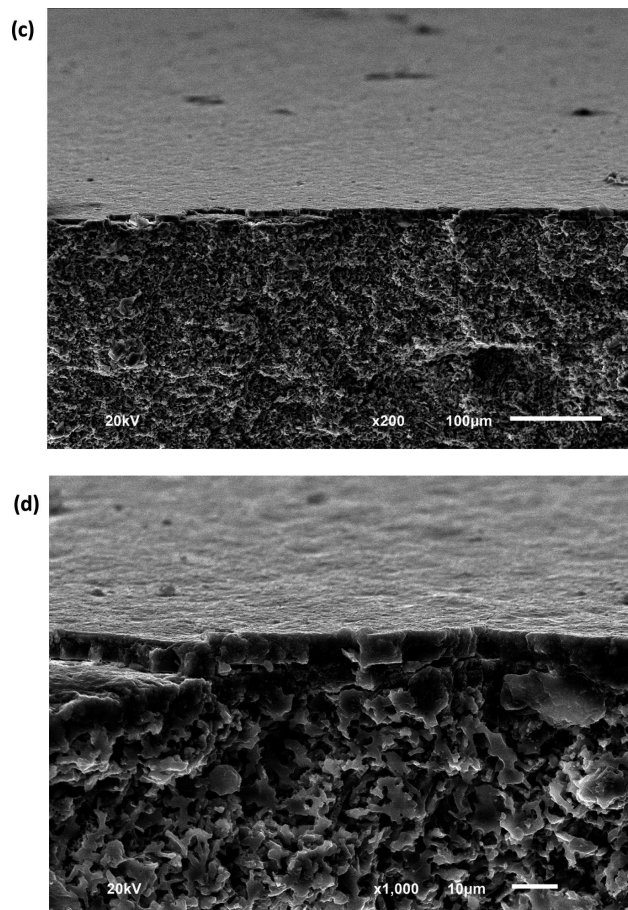
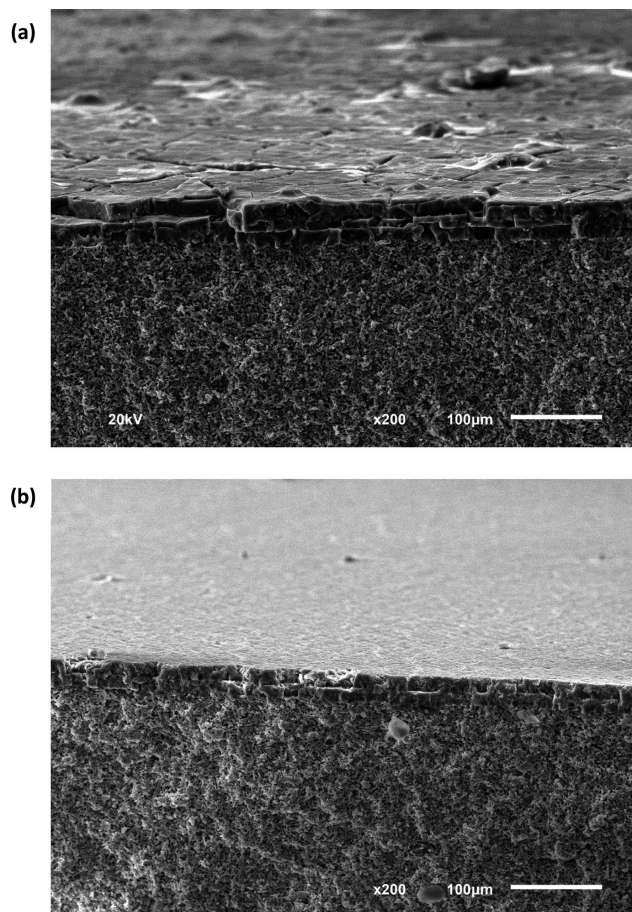


Fig. 2. Cross-sectional SEM images of the alumina coating prepared from (a) coarse alumina particles deposited on the diatomite-kaolin composite support layer four times, and heat-treated at 500°C for 1 h at each time, (b) intermediate alumina particles deposited on the diatomite-kaolin composite support layer two times and heat-treated at 500°C for 1 h at each time, (c) fine alumina particles deposited following the latter method, and (d) high magnification of (c)

The image in Figure 2 (a) is a SEM cross section of the alumina coating prepared from coarse alumina particles on the diatomite-kaolin composite layer, which was coated and then heat-treated at 500°C for 1 h four times in a row. The figure clearly reveals the overlapping of randomly distributed micro-cracks on each alumina coating layer. Therefore, we cannot expect a reduction in the largest pore size by adopting multiple coating layers when the size of the alumina particles is not fine enough to cover the pores of the diatomite-kaolin composite support layer effectively.

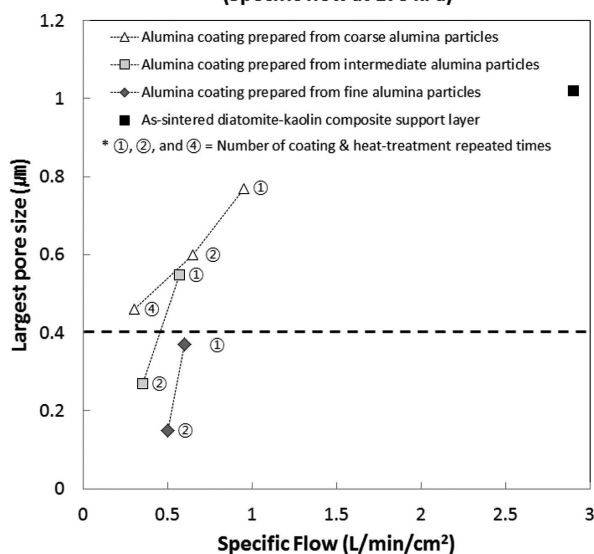
The cross-sectional SEM images in Figure 2 (b) show the alumina coating prepared from intermediate alumina particles on the diatomite-kaolin composite support layers, after heat treatment at 500°C for 1 h two times. Figures 2 (c) and (d) show SEM images of the alumina coating prepared from fine alumina particles following the same method. In contrast to Figure 2 (a), defects or delamination between the alumina coating and the diatomite-kaolin composite support layer were not observed.

Figure 3 (a) shows the overall absence of micro-cracks in the alumina coating prepared from intermediate or fine alumina particles by showing that the largest pore size was significantly reduced. As expected from Figure 2 (a), the largest pore size of the alumina coating prepared from coarse

alumina particles was not reduced to less than  $0.4 \mu\text{m}$ , even after repeating the coating and heat-treatment process four times. These results mean that the overlapping of randomly distributed micro-cracks in each alumina coating layer cannot effectively reduce the largest pore size of the sintered diatomite membrane. In the case of a diatomite-kaolin composite coating [4], the largest pore size of the sintered diatomite membrane could be reduced to approximately  $0.5 \mu\text{m}$  by adopting fine and irregular particles such as kaolin. In this study, by adopting finer and more regular particles such as alumina, the largest pore size of the sintered diatomite membrane could be reduced

to below  $0.4 \mu\text{m}$ . Figure 3 (b) shows that the largest pore size reduced to less than  $0.4 \mu\text{m}$  with decreasing mean particle size of the starting alumina particles. Therefore, it is suggested that the pore characteristics of a sintered diatomite membrane can be precisely tailored to meet the needs of industrial applications by adopting an alumina coating prepared from an appropriate starting particle size. In addition, it is shown that a low-cost sintered diatomite membrane can be successfully capped to be utilized as an alumina platform for further coating with the use of a minimum amount of expensive alumina and without micro cracks or delamination.

(a) Tailored pore characteristics of diatomite membranes (Specific flow at 175 kPa)



(b) Effect of starting particle size on alumina coating

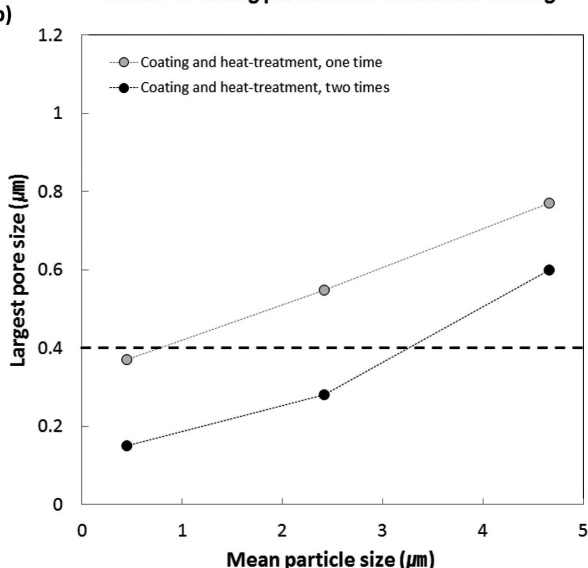


Fig. 3. Largest pore sizes of the alumina coating deposited on the diatomite-kaolin composite support layer (a) as a function of the specific flow rate at 175 kPa and (b) as a function of mean size of starting alumina particles

#### 4. Conclusions

In summary, we prepared a sintered diatomite membrane consisting of an alumina coating and a diatomite-kaolin composite support layer. It should be noted that the largest pore size of the diatomite-kaolin composite support layer could be controlled to less than  $0.4 \mu\text{m}$  by depositing alumina as a coating, which provided an effective means of tailoring the pore characteristics of the sintered diatomite membrane. These findings demonstrate the feasibility of using a modified sintered diatomite membrane as a porous ceramic membrane in water treatment applications.

#### Acknowledgements

This study was supported financially by Fundamental Research Program of the Korean Institute of Materials Science (KIMS).

#### REFERENCES

- [1] N. van Garderen, F.J. Clemens, J. Kaufmann, M. Urbanek, M. Binkowski, T. Graule, C.G. Aneziris, *Microporous Mesoporous Mater.* **151**, 255 (2012).
- [2] B.K. Nandi, R. Uppaluri, M.K. Purkait, *Appl. Clay Sci.* **42**, 102 (2008).
- [3] J.H. Ha, E. Oh, I.H. Song, *J. Ceram. Soc. Jpn.* **121**, 940 (2013).
- [4] J.H. Ha, E. Oh, I.H. Song, *Ceram. Int.* **40**, 2221 (2014).
- [5] J.H. Ha, E. Oh, I.H. Song, *Ceram. Int.* **39**, 7641 (2013).
- [6] J.H. Ha, E. Oh, B. Bae, I.H. Song, *Ceram. Int.* **39**, 8955 (2013).
- [7] J.H. Ha, E. Oh, R. Ahmad, I.H. Song, *Ceram. Int.* **39**, 3881 (2013).
- [8] A. Cooper, R. Oldinski, H. Ma, J.D. Bryers, M. Zhang, *Carbohydr. Polym.* **92**, 254 (2013).
- [9] N. Lebleu, C. Roques, P. Aimar, C. Causserand, *J. Membr. Sci.* **326**, 178 (2009).
- [10] M.C. Tucker, J. Tu, *Int. J. Appl. Ceram. Technol.* **11**, 118 (2014).
- [11] M. Qiu, J. Feng, Y. Fan, N. Xu, *J. Mater. Sci.* **44**, 689 (2009).
- [12] H. Qi, S. Niu, X. Jiang, N. Xu, *Ceram. Int.* **39**, 2463 (2013).
- [13] A.K. Mogalicherla, D. Kunzru, *Int. J. Appl. Ceram. Technol.* **8**, 430 (2011).
- [14] A.L. Ahmad, C.P. Leo, S.R. Abd. Shukor, *J. Am. Ceram. Soc.* **91**, 246 (2008).
- [15] J.H. Ha, E. Oh, I.H. Song, *J. Kor. Powd. Met. Inst.* **19**, 304 (2012).
- [16] B. Bae, J.H. Ha, I.H. Song, Y.D. Han, *J. Kor. Powd. Met. Inst.* **21**, 21 (2014).