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Durability of thermochemical heat storage demonstrated through long-term repetitive CaCl₂/H₂O reversible reactions

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Thermochemical heat storage is a promising technology for improving thermal energy efficiency. In this study, $CaCl_2$ and H_2O were selected as the reactant and working medium, respectively, assuming the utilization of low-grade waste heat. To investigate the durability of the $CaCl_2/H_2O$ reaction, 1000 repetitive operations were conducted at the same $110\,^{\circ}C$ charging and discharging temperatures. During the long-term repetitions, a decrease in the average volumetric power density was observed. The peak value in repetitions 901–1000 was 11% lower than the peak value in the initial 50 repetitions. This trend was mainly caused by a decrease in the heat transfer rate; it was observed after the repetitive experiments that reactant particles had moved out of the heat exchanger. Although a decreasing trend in the power density was observed, a peak value of $Q = 320\,kW/m^3$ and a conversion ratio of approximately 0.7 were observed in repetitions 901–1000. In addition, approximately 90% of the stored heat was released in all 1000 repetitions. Thus, using long-term repetitions (1000), this study confirmed the durability of the $CaCl_2/H_2O$ reaction for thermochemical heat storage. *Published by AIP Publishing.*
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I. INTRODUCTION

Concerns about energy resource shortages and environmental pollution have demanded effective methods for thermal energy utilization. This problem has been addressed, in part, through heat cascading practices. However, these practices result in substantial unrecovered waste heat because of their low temperatures. Thus, it is necessary to recover the waste heat and appropriately reuse it or transform it to a desired temperature. Thermochemical heat storage is a heat management technology that shows potential for reducing waste heat and fuel consumption.[1,2] Thermochemical heat storage systems that use a gas–solid reaction offer a higher thermal storage capacity and a wider temperature application than absorption-based heat management systems.[3] These systems—comprising a reactor and an evaporator/condenser that stores a working medium (e.g., water or ammonia)—utilize waste heat by repetitive heat charging and discharging operations using reversible endothermic and exothermic reactions. Moreover, the reaction temperature of the charging and discharging operations can be controlled by the working medium gas pressure relative to the evaporator and condenser. Thus, various operation modes using various reactions can be selected, such as heat storage,[4–6] heat enhancement,[7] heat upgrading,[8,9] and refrigeration.[10]

Thermal applications using $CaCl_2$ have been extensively demonstrated. This material is commonly used because of its low cost, nontoxicity, and thermochemical stability.[11,12] In our previous study, we investigated the potential use of the $CaCl_2/H_2O$ reversible reaction shown in Eq. (1)[13] to support heat upgrading from 90–120 $^{\circ}C$ to 140–160 $^{\circ}C$.[14]

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$$CaCl_2 \cdot H_2O + H_2O \rightleftharpoons CaCl_2 \cdot 2H_2O + 52.7\,kJ/mol. \qquad (1)$$
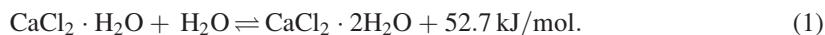
To achieve practical application of such a system, a higher volumetric power density and longer-term durability are required.

The present study focused on the latter requirement. Repetitive durability is one of the main technical challenges preventing practical use of thermochemical heat storage. Stable charging/discharging operations over 1000–10 000 repetitions are generally necessary for practical applications. The assumed basis for this challenge is the progressive and irreversible sintering or swelling/contracting of single reactant particles during the exothermic and endothermic reactions. The former issue results in the deactivation of the reactant, but this has been primarily reported in reaction systems with high charging temperatures (e.g., CaO/H_2O, MgO/H_2O, and CaO/CO_2).[15–18] Sintering of the reactant particles is likely not as much of a concern in the $CaCl_2/H_2O$ reaction system. The latter issue results in the aggregation or movement of the reactant particles and has the potential to affect the particle reaction rate or heat and mass transfer in the packed bed. Therefore, it is necessary to investigate the potential for swelling/contracting of the reactant particles in long-term repetitions.

Few studies have attempted to quantify the long-term durability of the heat input/output performance—a key parameter for assessing practical applications. In 2012, Kito evaluated the performance of a $CaBr_2/H_2O$ reaction system in a packed bed reactor over 2000 repetitions.[19,20] These efforts were, however, limited in scale ($CaBr_2 = 30\,g$). A larger-scale durability evaluation is required to adequately assess the practical use of thermochemical heat storage. In this study, we used a larger-scale reactor using the $CaCl_2/H_2O$ reaction system ($CaCl_2 = 530\,g$) over 1000 repetitions to quantify the long-term durability of the heat input/output performance.

II. MATERIALS AND METHODS

A. Materials

In this study, we used a reagent anhydrous $CaCl_2$ powder (>95% purity) obtained from Wako Chemicals (Japan). The powder was dried in an electric furnace at $180\,°C$ for 24 h. The $CaCl_2$ particles were unified using sieves by diameter ($d_p = 125–250\,\mu m$) and placed in the reactor used in the repetitive experiments.

B. Repetitive experiments

Figure 1 shows the apparatus used for the repetitive experiments, which comprised three decompression chambers, an evaporator, a condenser, and a reactor. Each of these components was connected with vapor flow tubes. The components and vapor flow tubes were covered with glass wool and a combination of glass wool and electric heaters, respectively, to prevent vapor condensation or heat loss. Each component was also connected to a thermostat bath as a heat source. The heat medium fluids supplied from the thermostat bath were circulated through the components.
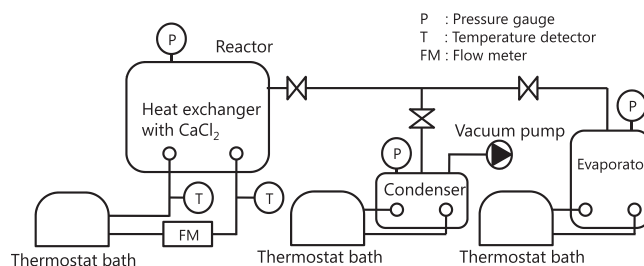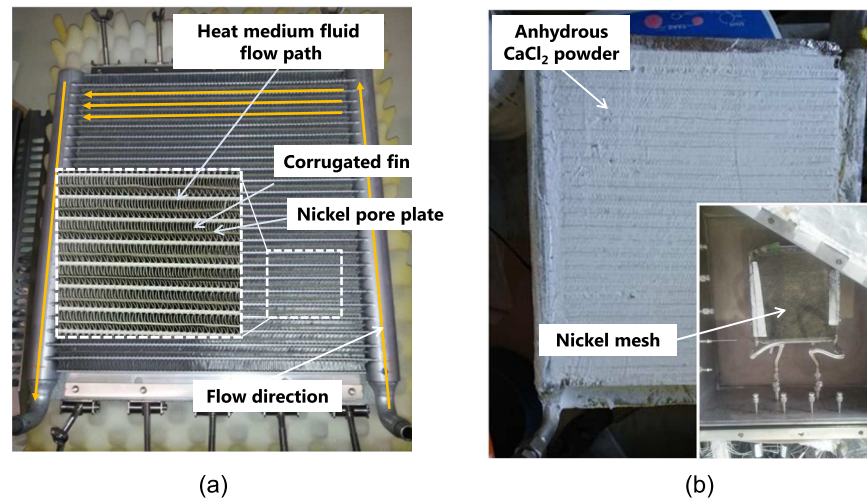

FIG. 1. Experimental apparatus.

FIG. 2. Corrugated aluminum fin-type heat exchanger: (a) with no particles and (b) filled with anhydrous $CaCl_2$ powder, covered with nickel mesh, and placed inside the chamber.

Figure 2 shows the corrugated aluminum fin-type heat exchanger used in the repetitive experiments. The heat exchanger had an entire volume capacity of 1.1 l and measured 250 mm × 200 mm × 20 mm (without the header). The pitch of the fluid flow path was 8 mm, and the pitch of the corrugated fin was 1.5 mm. Nickel pore plates were inserted along the center of the fluid flow paths to support vapor flow. The heat exchanger was filled with 530 g of the anhydrous $CaCl_2$ particles (the filling fraction based on filling space was 0.42), covered on the top and bottom with nickel mesh, and installed in the reactor. As a final step before initiating the repetitive experiments, the three components and vapor flow tubes were deaerated.

Figure 3 depicts the reported reaction lines for the hydration and dehydration of $CaCl_2$[12,21] as well as the experimental conditions (vapor pressure and inlet temperature of the heat medium fluid tempering the reactor) used in this study (denoted by solid black circles). Because hysteresis effects have been reported in previous studies,[12,21,22] the reaction conditions were selected carefully. Although high discharging temperatures of 140–160 °C are optimal, a lower discharging temperature of 110 °C (the same as the charging temperature) was used in this study to decrease the repetition cycle time. The evaluation of durability under high discharging temperature conditions will be considered in a future study.

The single cycle time was 3600 s:1200 s for the discharging operation, 600 s of downtime, 1200 s for the charging operation, and another 600 s of downtime. During the discharging operation, the water vapor was transported from the evaporator to the reactor, where the exothermic reaction subsequently occurs. During the charging operation, the endothermic reaction charged the heat in the reactor, and the released water vapor was transported to the condenser. The downtime was included to allow for any corrections to the initial reactor temperature to be made. Switching between the operations was implemented using the control valves on the vapor flow tubes.

The fluid temperatures at the heat exchanger's inlet and outlet were measured using platinum resistance temperature detectors, and the fluid flow volume was measured using a turbine flow meter from Japan Flow Controls Co. Ltd. (Japan). Thermal H350, obtained from JULABO (Germany), was used as the heat medium fluid in the reactor with a flow rate of 2.2 l/min. Water was used in the evaporator and condenser.

The evaluation parameters including the average volumetric power density, Q, conversion ratio, X, and heat utilization coefficient, η, were calculated using following equations:

$$Q = \frac{\int_0^t C_{p,f} \cdot \rho_f \cdot F \cdot \Delta T}{t \cdot V_{HEX}}, \tag{2}$$
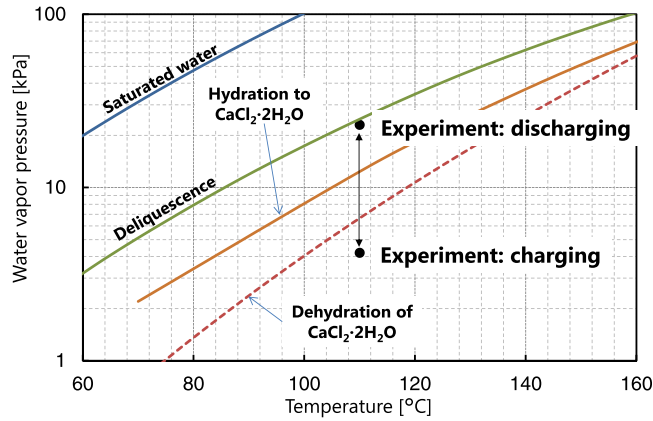
FIG. 3. $CaCl_2$ hydration/dehydration reaction lines[12,21] (solid black circles denote this study's experimental conditions in the reactor).

$$X = \frac{\int_0^t C_{p,f} \cdot \rho_f \cdot F \cdot \Delta T}{\Delta H_{theo}},$$ (3)

$$\eta = \frac{X_{dicharging}}{X_{charging}}.$$ (4)

III. RESULTS AND DISCUSSION

Figure 4 shows the reactor's heat medium fluid inlet/outlet temperature difference, ΔT, over time for repetitions 701–710 during the charging and discharging operations. At $t = 0$ s, the valve between the reactor and the evaporator or condenser was opened to allow vapor transformation. During the discharging operation, ΔT increased simultaneously with the opening of the valve, confirming that the heat generated from the reaction increased the temperature of the heat medium fluid. Conversely, during the charging operation, ΔT decreased simultaneously with the opening of the valve, confirming that the heat medium fluid transferred heat to the reactor. The temperature differences observed for repetitions 701–710 during the charging and discharging operations were highly consistent; observations among the repetitions were all within 4%. These results demonstrate high repeatability during short-term repetitions.

Figure 5 shows the average volumetric power density, Q, over time for all 1000 repetitions during the charging and discharging operations. The results were averaged within various repetition ranges (i.e., repetitions 1–50, repetitions 51–90, repetitions 104–200, etc.) for ease of display and interpretation. During charging operations, a negative ΔT value produced a negative average volumetric power density value. During both charging and discharging operations, a decrease in Q was observed during the long-term repetitions. During discharging operations, a peak value of $Q = 330$ kW/m^3 was measured for repetitions 901–1000. This peak value was 2% lower than the peak value measured for repetitions 401–500 and 11% lower than the peak value measured at the start of the experiment (for repetitions 1–50). During charging operations, a peak value of $Q = -320$ kW/m^3 was measured for repetition 1000. This peak value was 8% higher than the peak value measured for repetitions 401–500 and 18% higher than the peak value measured at the start of the experiment (for repetitions 1–50).

Figure 6 shows the conversion ratio, X, by repetition during 1200 s of discharging operations. Consistent with the observed trends for the average volumetric power density, the conversion ratio decreased during the long-term repetitions. This decreasing trend gradually flattened, and a conversion ratio kept approximately 0.7 during repetitions 500–1000. Similarly, Figure 7 shows the heat utilization coefficient, η, by repetition. Although a modest decrease in the heat utilization coefficient was observed during the long-term repetitions, approximately 90% of the stored heat was released in all 1000 repetitions.
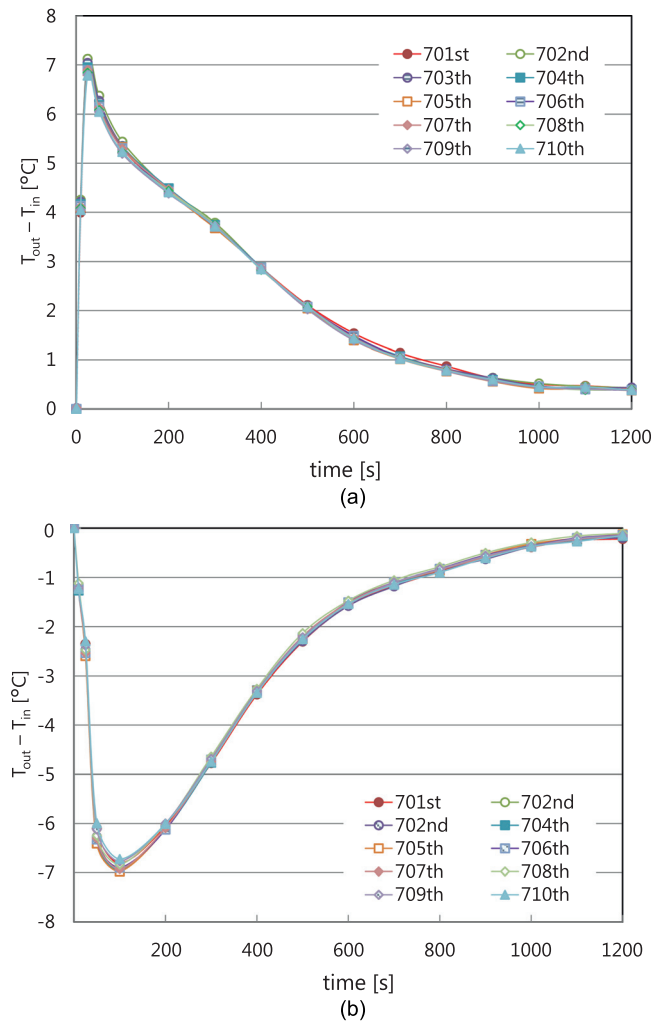
FIG. 4. Reactor's heat medium fluid inlet/outlet temperature difference over time for repetitions 701–710: (a) discharging operations and (b) charging operations.

Based on these results, the durability of the $CaCl_2/H_2O$ reaction for thermochemical heat storage was confirmed during long-term repetitions. For instance, during discharging operations, an average volumetric power density of $Q = 220 \, kW/m^3$ could be obtained at 600 s, even for repetitions 901–1000.

Figure 8 shows top, side, and bottom views of the heat exchanger following the 1000 repetitive reactions. Few reactant particles were lost from the heat exchanger. However, particles that were initially placed between the corrugated fins were transported to the heat exchanger surface/ stainless mesh interface. The packed bed thickness following the repetitions was approximately 7 mm at both the top and bottom surfaces. The transport of the reactant particles from the narrow corrugated fin space to the heat exchanger surface was likely caused by the swelling/contracting of single reactant particles and subsequent repetitive volumetric changes in the packed bed. As shown in Figure 9, the pore volume and Brunauer–Emmett–Teller (BET) specific surface area increased after the repetitive reactions. The Brunauer, Emmett, and Teller (BET) surface area of the particles that were transported to the heat exchanger surface was 2.2 m^2/g, which was 2.3 times larger than the surface area of the original particles. Thus, irreversible sintering did not appear to be the primary cause for the decreased power density. In fact, as depicted in Fig. 6, a higher conversion ratio was observed for repetition 1001 at 6000 s than at the initial repetitions. These collective results suggest that the decreased power density during long-term repetitions
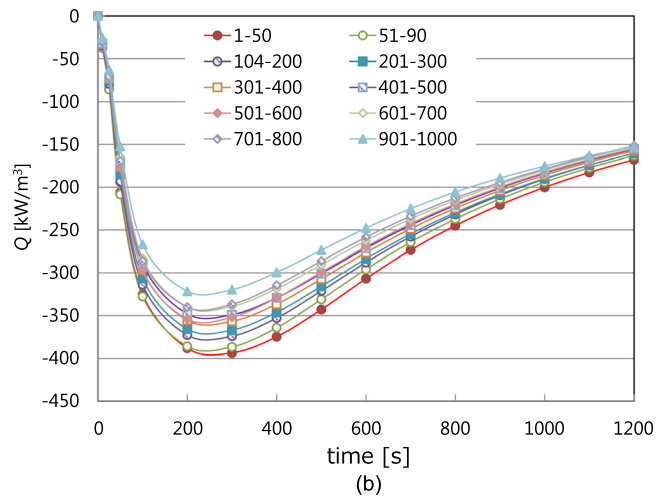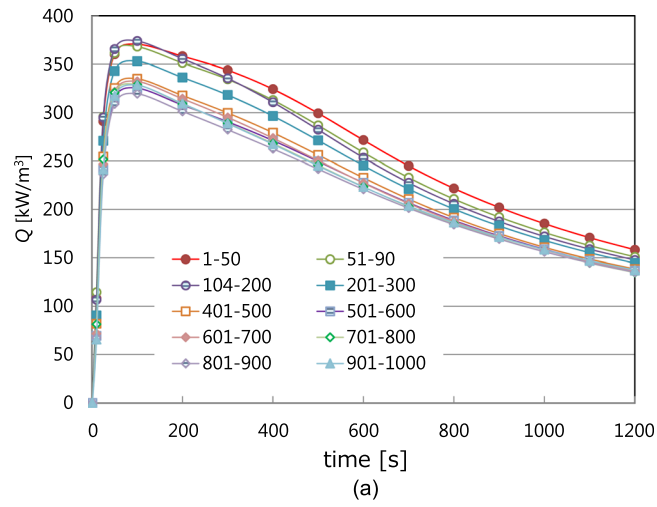
FIG. 5. Average volumetric power density over time for all 1000 repetitions: (a) discharging operations and (b) charging operations.
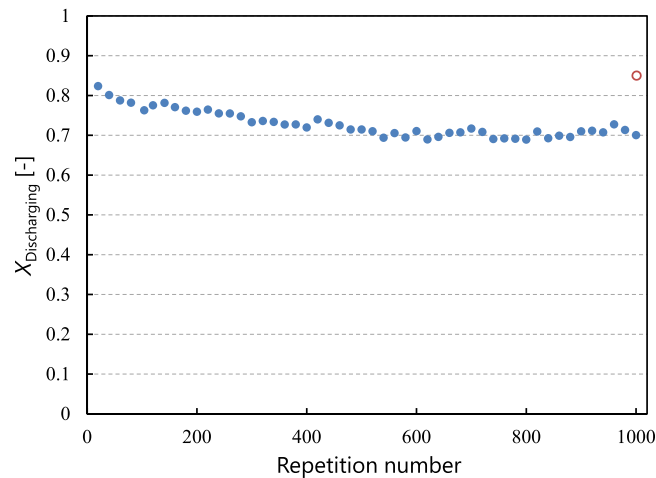

FIG. 6. Conversion ratio by repetition during 1200 s of discharging operations (open red circle denotes repetition 1001 at 6000 s).
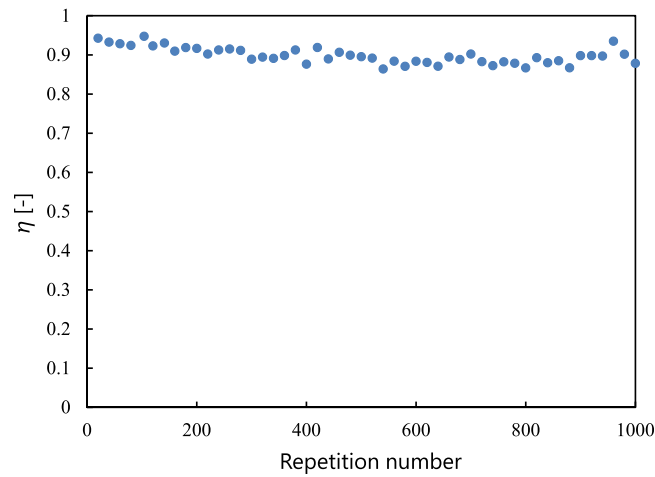
FIG. 7. Heat utilization coefficient by repetition.

was caused by the reduction in the number of particles in the corrugated fin space and longer heat transfer distances, which ultimately decreased the heat transfer rate. As mentioned above, the decreasing trend gradually flattened, and a conversion ratio was kept at approximately 0.7 during repetitions 500–1000. This likely means that the outflow of the particles was almost finished within 500 repetitions.

From these results, durability will become higher with suppressing the outflow of particles. In short-duration repetitions (10 repetitions), this issue has been previously addressed using a jig that mechanically suppresses the outflow of the particles. However, further long-term durability investigation will be reported in the future.
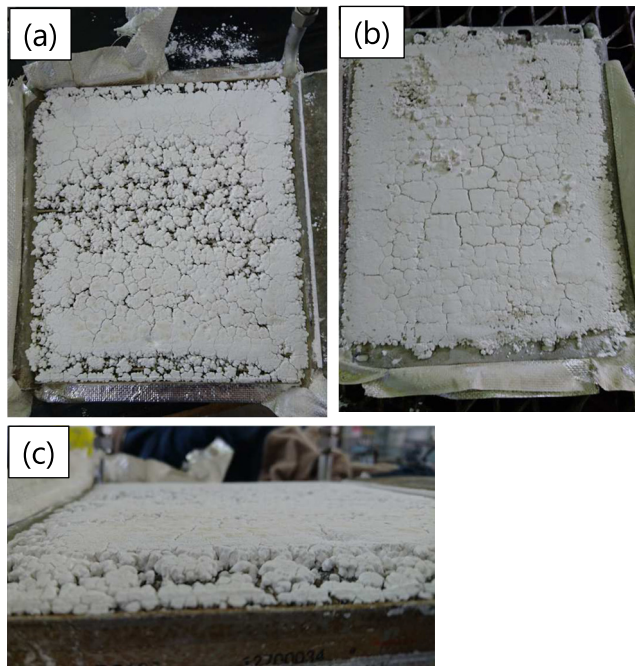

FIG. 8. Heat exchanger packed bed conditions following 1000 repetitive reactions: (a) top view, (b) bottom view, and (c) side view.
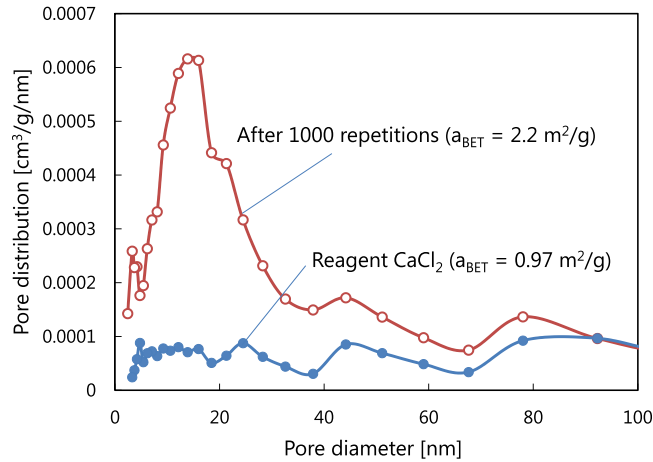
FIG. 9. Results of gas pore analysis.

IV. CONCLUSION

In this paper, experimental results pertaining to the durability of the $CaCl_2/H_2O$ reversible reaction for thermochemical heat storage are presented. Long-term repetitions (1000) were performed, and degradation effects were observed. During discharging operations, a peak average volumetric power density of $330 \, kW/m^3$ was observed for repetitions 901–1000. This peak value was 11% lower than the peak value observed at the start of the experiment (for repetitions 1–50). Comparably, during charging operations, a peak average volumetric power density of $-320 \, kW/m^3$ was observed for repetitions 901–1000. This peak value was 18% higher than the peak value observed for repetitions 1–50. The primary cause of degradation in the average volumetric power density was leaked reactant particles from the corrugated fin space of the heat exchanger. Despite this observed decreasing trend, the conversion ratio during discharging operations was approximately 0.7 for repetitions 901–1000, and approximately 90% of the stored heat was released in all 1000 repetitions. Thus, using long-term repetitions (1000), this study confirmed the durability of the $CaCl_2/H_2O$ reaction for thermochemical heat storage.

NOMENCLATURE

C_p Specific heat capacity ($kJ \, kg^{-1} \, K^{-1}$)
F Flow rate of the heat exchange fluid (l/min)
Q Average volumetric power density (kW/m^3)
t Time (s)
V Volume (m^3)
X Conversion rate (-)
ΔH Heat of reaction (kJ/mol)
ΔT Temperature difference between the inlet and the outlet (°C)
η Heat utilization coefficient (-)
ρ Density (kg/m^3)

Subscripts

charging   Charging operation
discharging   Discharging operation
f   Heat medium fluid
HEX   Heat exchanger
in   Input
out   Output
theo   Theoretical value

[1]C. W. Chan, J. Ling-Chin, and A. P. Roskilly, Appl. Therm. Eng. **50**, 1257 (2013).

[2]S. Spoelstra, W. G. Haijie, and J. W. Dijkstra, Appl. Therm. Eng. **22**, 1619 (2002).

[3]W. Wongsuwan, S. Kumar, P. Neveu, and F. Meunier, Appl. Therm. Eng **21**, 1489 (2001).

[4]M. Zamengo, J. Ryu, and Y. Kato, Energy Procedia **71**, 293 (2015).

[5]M. Schmidt, C. Szczukowski, C. Roßkopf, M. Linder, and A. Wörner, Appl. Therm. Eng. **62**, 553 (2014).

[6]H. Ogura, Energy Procedia **14**, 2048 (2012).

[7]T. Shimizu and H. Ogura, in *Proceedings of Thermal Engineering Conference*, Kumamoto, Japan, 12–13 November (2012), pp. 333–334.

[8]A. Odukoya and G. F. Naterer, Int. J. Hydrogen Energy **40**, 11392 (2015).

[9]T. Li, R. Wang, J. K. Kiplagat, and Y. Kang, Energy **50**, 454 (2013).

[10]R. G. Oliveira and R. Z. Wang, Chem. Eng. J. **138**, 416 (2008).

[11]K. E. N'Tsoukpoe, H. U. Rammelberg, A. F. Lele, K. Korhammer, B. A. Watts, T. Schmidt, and E. K. Ruck, Appl. Therm. Eng. **75**, 513 (2015).

[12]M. Richter, M. Bouche, and M. Linder, Appl. Therm. Eng. **102**, 615 (2016).

[13]Dow Chemical Company, *Calcium Chloride Handbook* (Dow Chemical Company, 2003), p. 6.

[14]M. Yasuda, N. Kobayashi, and T. Esaki, in *Mechanical Engineering Congress*, Hokkaido, Japan, 13–16 September (2015), p. G0600604.

[15]K. Kuwata, N. Kobayashi, T. Esaki, D. Iwase, H. Kita, and S. Yamashita, in Proceedings of the 2015 AIChE Annual Meeting, Salt Lake City, USA, 8–13 November (2015).

[16]Y. Kato, T. Saito, T. Soga, J. Ryu, and Y. Yoshizawa, J. Chem. Eng. Jpn. **40**, 1264 (2007).

[17]M. Aihara, T. Nagai, J. Matsushita, Y. Negishi, and H. Ohya, Appl. Energy **69**, 225 (2001).

[18]M. Kubota, K. Yokoyama, F. Watanabe, N. Kobayashi, and M. Hasatani, Kagaku Kogaku Ronbunshu **27**, 285 (2001).

[19]T. Kito and N. Kobayashi, J. Jpn. Soc. Energy Resour. **33**, 1 (2012).

[20]T. Kito, Ph.D. thesis, Nagoya University, Nagoya (2012).

[21]M. Molenda, J. Stengler, M. Linder, and A. Worner, Thermochem. Acta **560**, 76 (2013).

[22]T. Esaki, T. Kito, H. Huang, and N. Kobayashi, in Proceedings of the 25th International Symposium on Transport Phenomena (ISTP-25), Krabi, Thailand, 5–7 November (2014).