



CHEMICAL ENGINEERING | RESEARCH ARTICLE

Calcium bromide hydration for heat storage systems

Ai Niwa^{1*} and Noriyuki Kobayashi¹

Received: 09 March 2015
Accepted: 14 June 2015
Published: 07 August 2015

*Corresponding author: Ai Niwa,
Department of Chemical Engineering,
Nagoya University, Nagoya, Aichi, Japan
E-mail: ainy58@energy.gr.jp

Reviewing editor:
Zhibing Zhang, University of
Birmingham, UK

Additional information is available at
the end of the article

Abstract: A chemical reaction is a common and simple way to produce heat for a heat storage system. The reaction produces heat energy without the use of electricity or fuel. The goal of this study was to develop a heat storage system for use in automobiles, which is able to provide heat rapidly via a hydration reaction. A heat storage system without an evaporator stores high-density heat and has a high heat output rate since the solid-liquid product that is formed is transferred as a heat medium to the object that requires heat. The exothermic heat produced from the solid-liquid reaction was measured, and the relationship between the equivalence ratio and the reaction heat was evaluated. The heat output and heat recovered by the heat storage system, which comprised a reaction vessel and a heat exchanger, were measured. We selected solid CaBr_2 because it was the best metal halide for a hydration reaction and had a high heat yield from the dissolution reaction. With this system, we were able to achieve a heat recovery rate of $582 \text{ kJ/L}_{-\text{H}_2\text{O}}$. We found no degradation in the chemical composition of CaBr_2 after it being recycled 100 times.

Subjects: Chemical Engineering; Engineering & Technology; Reaction Engineering

Keywords: heat storage; CaBr_2 ; hydration; dehydration; intermediate temperature range

1. Introduction

There are many studies on heat release and storage systems for recycled waste heat, but an optimal heat storage system for solid-liquid reactions has not yet been achieved. A chemical reaction heat storage system has been the subject of theoretical and experimental studies (Kubota, Kyaw, Watanabe,

ABOUT THE AUTHOR

Ai Niwa is currently a PhD student at the Department of Chemical Engineering, Nagoya University, Japan. Her research interests include heat storage system and condensation and dissolution in heat transfer.

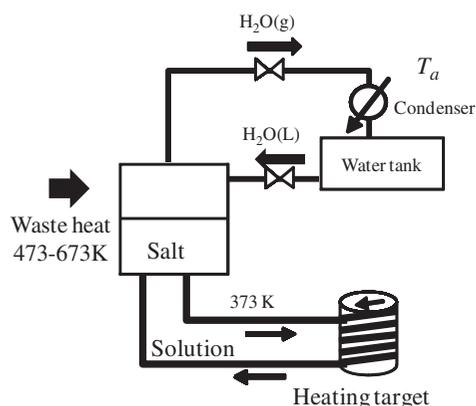


Ai Niwa

PUBLIC INTEREST STATEMENT

A chemical reaction is a common and simple way to produce heat for a heat storage system. The reaction produces heat energy without the use of electricity or fuel. The goal of this study was to develop a heat storage system for use in automobiles and that is able to provide heat rapidly via a hydration reaction. A heat storage system without an evaporator stores high-density heat and has a high heat output rate. The heat output and heat recovered by the heat storage system, which comprised a reaction vessel and a heat exchanger, were measured. We selected solid CaBr_2 because it was the best metal halide for a hydration reaction and had a high heat yield from the dissolution reaction. We were able to achieve a heat recovery rate of $582 \text{ kJ/L}_{-\text{H}_2\text{O}}$. We found no degradation in the chemical composition of CaBr_2 after being recycled 100 times.

Figure 1. Schematic drawing of the heat storage system.



Matsuda, & Hasatani, 2000; Weber, 2008). The performance of chemical reaction heat storage has been affected by management issues, such as mismatches between demand and supply in space, time, and selection of the quality or quantity of heat storage material. For example, turning over a cold car engine requires heat to preheat the engine and the exhaust-cleaning catalyst. If the waste heat can be recycled by heat storage, it would improve fuel consumption rate. We propose a chemical dissolution heat storage system of small size and high output. After conducting experiments on the heat release properties of solid-liquid (S-L) reactions with CaCl_2 and evaluation experiments on the heat of hydration of CaCl_2 , CaBr_2 , and LiBr (Malijejská, 2006; Niwa & Kobayashi, 2015; Niwa, Kobayashi, Hayase, & Fuse, 2014), we selected CaBr_2 to use for these experiments. Recently, a novel research was presented on a gas-solid reaction with MgOH (Kato, Sasaki, & Yoshizawa, 2003). They used a packed-bed reactor at 405 kPa and 373–513 K and obtained output of 10 W. Our goal was to have a system that operates under atmospheric pressure and at 473–673 K and obtain an output of $10 \text{ kW/L}_{-\text{H}_2\text{O}}$. There have been studies on gas-solid reactions, but the use of the ion hydration of a solid-liquid reaction has not been common in industrial research for heat release rate and storage of heat (Dawoud, 2007; Paulik & Paulik, 2005). However, minimization and mobility in the existing heat pump system is difficult because existing system has evaporator. We propose compact system and mobility heat storage system that uses a solid-liquid reaction with high heat output, high heat storage density, and no adverse impact on the environment. The methods used to study the chemical dissolution heat storage system are presented below.

2. Storage mode and solution

Chemical storage has a high heat storage density, especially when a hydrate compound is used. Normally, a large-volume evaporator is used to increase the heat released by the latent heat of evaporation. In some cases, it may be necessary to heat the evaporator quickly to provide water vapor. To avoid this problem, our heat storage system uses the heat of the solution without using evaporation. The solid-liquid reactant is formed and transferred as a heat medium to the heating target. A heat storage system without an evaporator will have a high heat storage density and a high storage rate. Figure 1 presents the solid-liquid reaction for the proposed heat storage system. The system is found to be useful for preheating the automobile engine. We selected CaBr_2 as the solid and H_2O as the liquid according to the results of our experiments and calculations. The goal is to supply the heat by using the chemical reaction with no stirrer and no fresh CaBr_2 within 2 min. Three states of the reaction system existed in the heat storage process: aqueous CaBr_2 state, an anhydrous state with dehydrate for 20 min to store the exhaust heat in 473–673 K, and $\text{CaBr}_2(\text{s}) + \text{H}_2\text{O}(\text{L})$ which is ambient temperature, as shown in Figure 2. $\text{CaBr}_2(\text{aq.})$ is separated into anhydrous $\text{CaBr}_2(\text{s})$ and $\text{H}_2\text{O}(\text{g})$. The $\text{H}_2\text{O}(\text{g})$ is condensed into liquid by the surrounding temperature. The heat of the solution is fed directly to the heat storage target at an intermediate temperature range and the solution is returned to the reactor. Because the solution produced by the reaction does not need an evaporator for heat recovery, the heat storage medium itself can be used as a heat exchange fluid. Besides, Figure 2 shows the cyclic reaction of $\text{CaBr}_2(\text{s}) \cdot 6\text{H}_2\text{O}(\text{L})$.

Figure 2. Proposed hydration reaction cycle of CaBr₂ with 6H₂O.

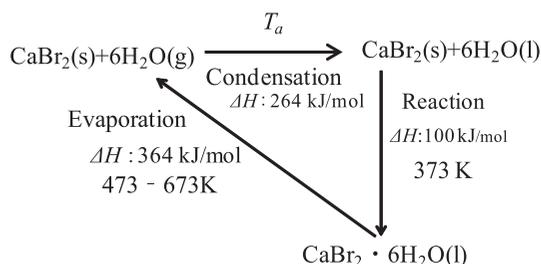
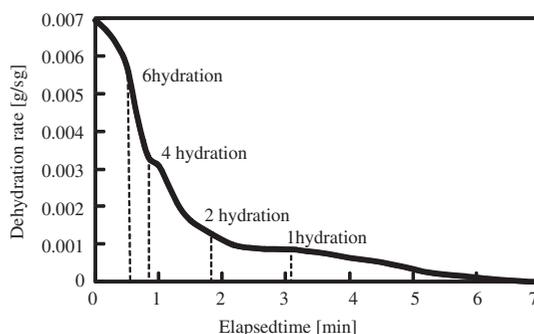


Figure 3. Change in dehydration rate with respect to time.



3. Regeneration by thermogravimetric analysis under preferred conditions

We performed thermogravimetric analysis (TGA) (Shimadzu, Japan, TGA-50) of the reaction rate, heat transfer rate, and the rate of vapor diffusion, all factors that affect the dehydration rate. Influence of the reaction rate was estimated using TGA. Figure 3 shows the change in reclamation velocity over time for dehydration of the generated aqueous solution of CaBr₂ (6.23 mg) and H₂O (13.8 mg) (mixing ratio 3:1). Equation 1 shows that the rate of dehydration [g/s g] is a function of the rate of the decrease of weight with respect to the average weight at a particular point in time.

$$\text{Dehydration rate [g/sg]} = \left(\frac{m_{t_1} - m_{t_2}}{(m_{t_1} + m_{t_2})/2} \right) \left(\frac{1}{t_2 - t_1} \right) \quad (1)$$

where m_{t_1} is the weight at time t_1 , m_{t_2} is the weight at time t_2 , t_1 is the time of the first measurement, and t_2 is the time of the second measurement.

Figure 3 shows that the dehydration of CaBr₂ · 6H₂O (L) has been totally completed within 7 min. Hence it can be implied that the dehydration of CaBr₂ (aq.) can be possibly finished within 20 min and below 473 K in the real system proposed in this research. But the dehydration reaction was finished as in 24 hours when using measuring cylinder as the reactor, which using mainly because of low heat transfer rate and high vapor diffusion resistance. Therefore, it is necessary to improve the rate of vapor diffusion and upgrade the heat transfer rate during the real reactor design.

4. Experimental setup

Anhydrous CaBr₂ was prepared by drying special-grade CaBr₂ · 2H₂O (Kanto Kagaku, Inc., Japan) in a thermostatic oven at 523 K for over 6 hours. The dehydration rate is affected by the heat area and the evaporation area and the volume of solution for quantitative evaluation. The influence of each factor on the dehydration rate using the moisture content of the solute per dehydration time was evaluated using a cylindrical reactor. The volume of solution of each reactor is different, so we evaluated the moisture content by moisture content mass by unit of solute to compare the results. Equation 2 defines the heating area per volume of the solution in a cylindrical reactor:

Table 1. Conditions of preliminary experiment selecting dimension of reactor

	Solution height (cm)	Reactor bore (cm)	Heating area (cm ² /cm ³)	Evaporation area (cm ² /cm ³)
Bench mark (side heating)	6	2.84	1.41	0.17
Half bench mark height (side heating)	3	2.84	1.41	0.33
Quarter bench mark height (side heating)	1.5	2.84	1.41	0.67
Upgrading side on heat area	6	1.66	2.41	0.17
Bench mark plus side and bottom heating	6	2.84	1.58	0.17
Upgrading side heating and bottom heating	6	1.66	2.58	0.17

Figure 4. Comparison of dehydration time for each reactor dimension.

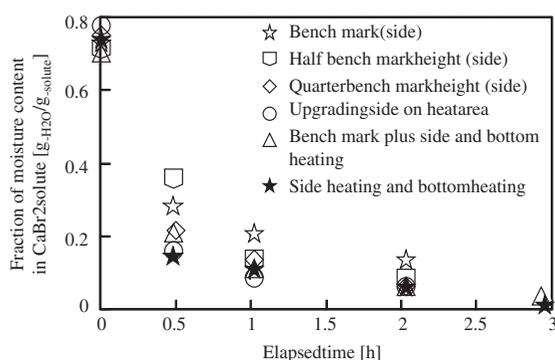
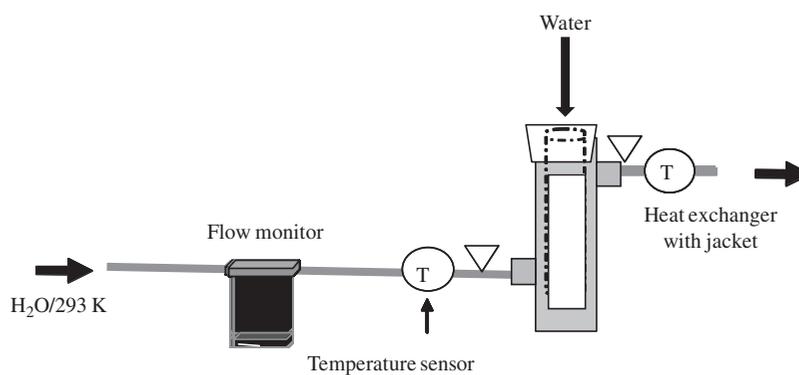


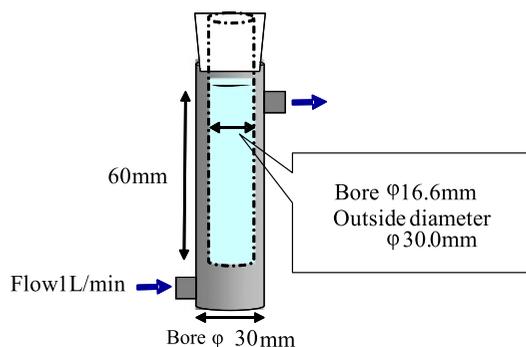
Figure 5. Schematic drawing of experimental set up for quantifying heat recovery.



$$\frac{S}{V} = \frac{\pi DH}{\pi D^2 / 4H} = \frac{4}{D} \tag{2}$$

where V is the volume of the solution (cm³), S is the heating area in square feet (cm²), D is the diameter of the cylinder (cm), and H is the height of the solution (cm). Equation 2 shows that the heating area per volume of the solution does not depend on the height of the solution in the cylinder. Equation 3 gives the evaporation area per volume of the solution:

Figure 6. Details of a reactor with heat exchanger.



$$\frac{S}{V} = \frac{(\pi D^2 / 4)}{(\pi D^2 / 4)H} = \frac{1}{H} \quad (3)$$

Table 1 gives the reactor conditions for the six experiments performed under 298 K. Figure 4 shows the moisture content of the solute with respect to elapsed heating time. In this experiment, the benchmark condition is CaBr_2 (85 g) and H_2O (65 ml) (saturation). The inner diameters of the two reactors used were 2.84 and 1.66 cm. The bottom of the reactors was heated and the effect on the dehydration rate was checked. When the tube's inside diameter was 1.66 cm, there was no dehydration after 1 h, but then the dehydration rate improved so that there was less than $0.01 \text{ g}_{-\text{H}_2\text{O}}/\text{g}_{-\text{solute}}$ after 3 h. When the tube's inside diameter was 2.84 cm, the dehydration rate was inferior to that of the $\phi 1.66$ cm bore tube in the early dehydration period (the first hour), but the $\phi 2.84$ -cm reactor produced the same results as the $\phi 1.66$ cm reactor beginning at 1 h. Therefore, lateral heat of the reactor had a greater impact early in the dehydration process, while the dehydration of the melt at the bottom of the reactor did not contribute much to the process. Figure 4 shows that dehydration starts more than an hour after application of heat and that there was vapor transfer resistance. Another way to cause all the solutes to become anhydrous is to change the reactor's configuration to a more horizontal shape.

Figure 5 shows the heat recovery measurement device, which consists of a thermostatic bath, two thermometers, a flow meter, and a jacketed heat exchanger (HEX). The reactor filled with solid is placed into the jacketed heat exchanger, where it is in direct contact with the heat exchanger's cooling fluid, which cools the heat exchanger to 293 K. After verifying that there is no temperature difference between the inlet and the outlet of the heat exchanger, ultrapure water is added to soak the solid, which becomes a saturated aqueous solution. The solution is stirred for 1 min after the start of dissolution. The heat of reaction is recorded as the temperature rises of the heat exchange fluid between the heat exchanger inlet and outlet once per second, starting when the reaction begins upon solid-liquid mixing. Equation 4 describes the amount of heat recovered, estimated by the difference in temperature measured at the inlet and the outlet.

$$Q = FC_p \rho \Delta T_{\text{out-in}}, \quad (4)$$

where Q is the heat recovered (J), F is flow rate (m^3/s), C_p is specific heat capacity ($\text{J}/\text{kg}/\text{K}$), ρ is the density (kg/m^3), and $\Delta T_{\text{out-in}}$ is the temperature differential (K) for the water between the inside and outside of a reactor.

Figure 6 shows the specifications of the jacket-type heat exchanger. The net heat output of the solid was evaluated in this experiment. The temperature rise of exchanger water indicated a heat exchange efficiency of about 99%. This experiment was carried out to measure the amount of heat recovery for $\text{CaBr}_2 \cdot n\text{H}_2\text{O}$ for dehydration heating times of 0.5, 1, 2, and over 3 h.

Figure 7. Weight fraction of dehydration versus dehydration time.

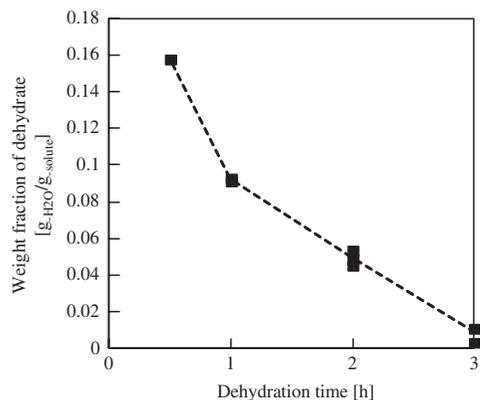


Figure 8. Weight fraction of dehydration versus heat value and fraction of heat value.

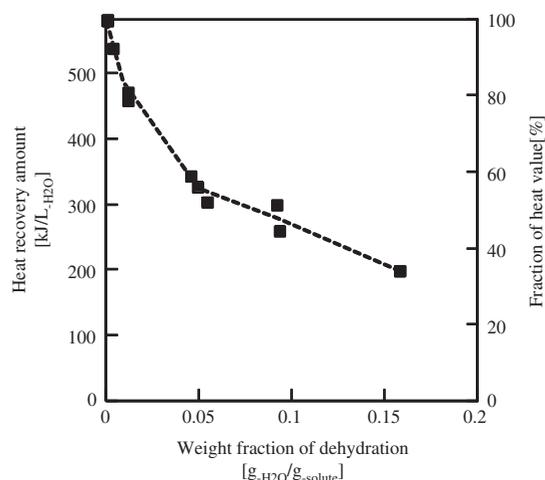
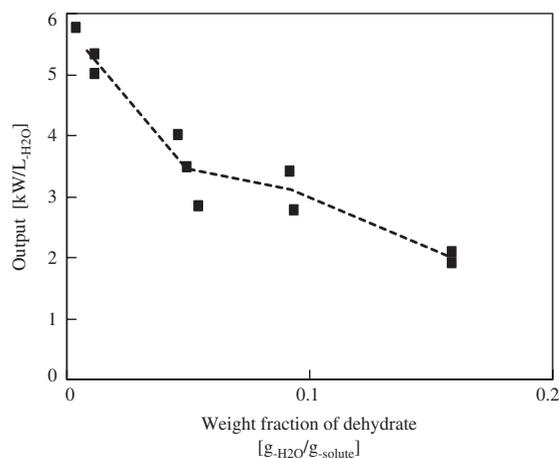


Figure 9. Heat output of CaBr₂·nH₂O.



5. Results and discussion

5.1. Heat release characteristic and dehydration time

The heat value and output of CaBr₂ (11.7 g) and H₂O (9 ml) (saturation) were measured in this experiment. Figure 7 shows the weight fraction of dehydration versus dehydration time from the experimental results. The results show that there was almost complete dehydration of CaBr₂ after heating for 3 h. The dehydration rate of CaBr₂ (0.768 g-water/g-solute) slowed down 30 min after the start of

Figure 10. Heat release output versus elapsed time with aqueous CaBr_2 dehydration over 3 h.

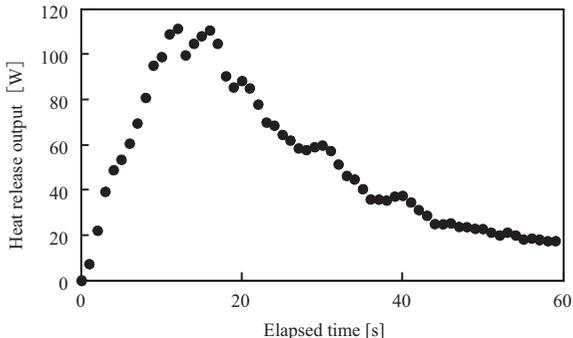


Figure 11. Time course of heat release output at different regeneration.

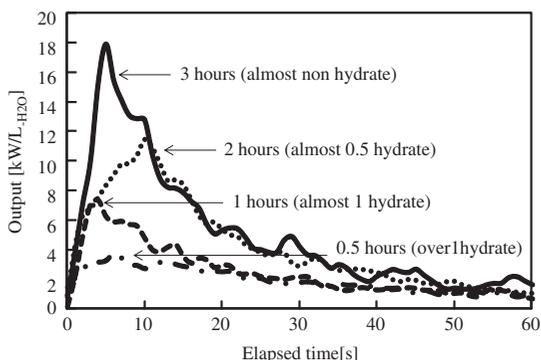
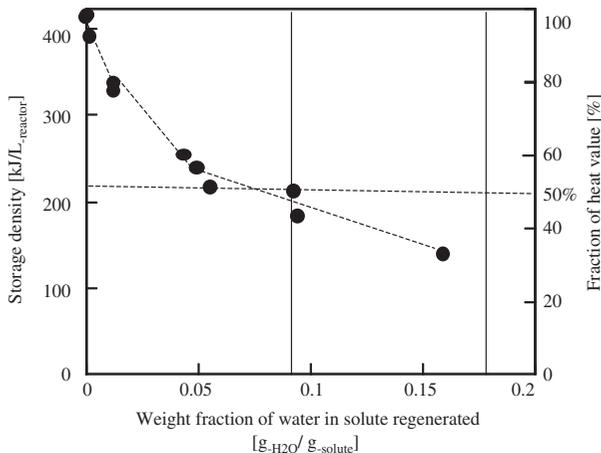


Figure 12. Relationship between weight fraction of water in solute and heat storage density of CaBr_2 or CaBr_2 hydrate.



dehydration. Figure 8 shows the weight fraction of dehydration versus the heat value and fraction of heat value. One plot in Figure 8 has heat values on the left y axis and the fraction of heat values on the right y axis. Another plot shows dehydration at 0.5, 1, 2, and 3 h. Fraction of heat value (%) is the heat value of CaBr_2 measured by this experiment as a fraction of the standard (100%) heat value of fresh CaBr_2 per 1 L- H_2O (622 kJ/L-water).

From the results of this experiment, we found that the dehydration status of 0.05 $\text{g}_{\text{H}_2\text{O}}/\text{g-solute}$ had a large increase in the amount of heat released. The heat value of CaBr_2 hydrate is different from that of CaBr_2 anhydrate. The heat recovery amount of the solid after 3 h of dehydration was 582 kJ/L- H_2O . Figure 9 shows the dehydration state of CaBr_2 versus its heat output. The amount of heat recovered increased substantially when the state of dehydration was 0.1 $\text{g}_{\text{H}_2\text{O}}/\text{g-solute}$. $\text{CaBr}_2 \cdot n\text{H}_2\text{O}$ that underwent dehydration over 3 h without the stirrer yielded as much heat as when the stirrer was used.

Thus, agitation with dissolution is thought to have promoted and improved the heat transfer of boiling dissolution. The upright reactor without a stirrer showed excellent radiation performance.

The average heat 1 min after mixing the dehydrate solid for 3 h was 5.78 kW/L_{-H₂O}, which is slightly less than the heat value of fresh CaBr₂ stirred with a screw agitator (6.03 kW/L_{-H₂O}) (Niwa et al., 2014). We used Equation 5 to evaluate the performance of the heat exchanger in heat recovery (Robert, 1999). The maximum temperature of the CaBr₂ aqueous solution was 369 K under the circumstances of the solution inside the reactor. The CaBr₂ is dehydrated after 3 h. Natural convection heat transfer (heat recovery under bad conditions) was simulated from 369 K using the physical properties for hot water inside the reactor. A reactor was designed using Equation 5. The tube wall was 0.5-mm-thick SUS304-grade stainless steel and the outside reactor contained water at 293 K. The natural convection thermal resistance of the inside container was 0.0839 K/W, the conduction thermal resistance of the inside reactor wall was 0.0036 K/W, and the forced-convection thermal resistance of the outside reactor was 0.0211 K/W. Each value is the main factor in natural convection heat transfer. The maximum thermal power of heat recovery under the above conditions was calculated to be 460 W.

$$\frac{h_0 D}{k} = \frac{0.03 \text{Re}^{0.75} \text{Pr}}{1 + 1.74 \text{Re}^{-0.125} (\text{Pr} - 1)} \quad (5)$$

where h_0 is the outside heat transfer coefficient (W/(m² K)), D is the tube diameter (m), k is thermal conductivity (W/(m K)), Re is the Reynolds number, and Pr is the Prandtl number.

Figure 10 shows the heat release rate over 3 h of dehydration. The maximum heat output was ~120 W (Max 12 kW/L_{-H₂O}, Average 5.79 kW/L_{-H₂O}). Figure 10 also shows that there was no limit to heat recovery. The net output is measured using Figure 10.

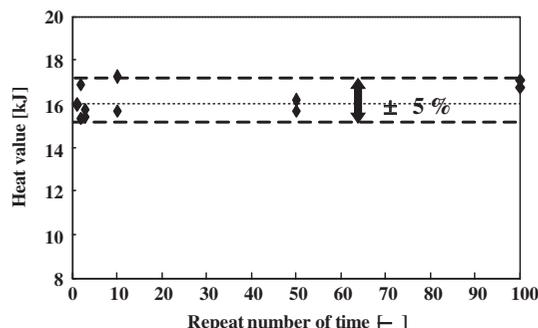
Figure 11 shows solution output of hourly dehydration CaBr₂. When it is supposed that the entire enthalpy of reaction of CaBr₂ at 6.5 mol/L_{-H₂O} can be released as output in 1 min, the average theoretical output is 11 kW/L_{-H₂O}. The experimental value was at most 18 kW/L_{-H₂O} and only 5.1 kW/L_{-H₂O} during the first 1 min of output, on average. Evaporation of water with vertical reactor through a tube in the wall during boiling causes rise of fused material with an air bubble from the bottom. As a result, the solution vaporization area expands. However, the average output is half of the theoretical value. This is because dehydrated (i.e. supersaturated) CaBr₂ cannot dissolve further solid CaBr₂ and the hydration reaction proceeds to boil dry abruptly.

The heat performance of the non-dehydrated state is almost the same as that of the dehydrated state. The heat of dissolution was measured using dissolution and dehydration as a unit. As a result, performance of the solid state was proportional to the weight fraction of the dehydrated state. If the dehydration rate needs to be improved, then the reactor design needs to be changed to improve the heat value and performance. Our results show that heat obtained without a stirrer by boiling the CaBr₂ to dissolve it was about the same as that obtained when a stirrer was used. This confirms the excellent performance of the reactor and the vertical radiation of the heat by not stirring. The theoretical output of 6.5 mol/L_{-H₂O} is 11 kW/L_{-H₂O} for 60 s. The average output during the first 1 min of the dissolution reaction is 6.5 kW/L_{-H₂O}, about 60% of the theoretical average output. Figure 12 presents the experimental results for heat storage density and weight fraction. The monohydrate achieves less than half the fraction of heat value of anhydrous CaBr₂. The reactor should be designed to increase the dehydration rate, and a non-hydrate material should be used to increase the heat of the solution.

5.2. Cyclic reaction

The cyclic procedure of the solution and regeneration was performed 100 times. The solution heat was measured for each reaction that used regenerated CaBr₂ powder 30 g (regenerated at 523 K in constant temperature oven) with H₂O 0.1 L. Figure 13 shows that no heat was lost over 100 cyclic reactions.

Figure 13. Amount of recycled heat recovered using regenerated $\text{CaBr}_2 \cdot \text{aq}$.



6. Conclusion

The heat output and dehydration rate of calcium bromide were measured in a heat recovery experiment and a thermogravimetric analysis was conducted. The goal of this study was to develop a heat storage system for use in automobiles that is able to provide heat rapidly via a hydration reaction. The heat recovered amount by the experimental setup, which comprised a reactor and a jacket-style heat exchanger, were measured. With this system, we were able to achieve a heat recovery of $582 \text{ kJ/L}_{-\text{H}_2\text{O}}$. The value achieved 90% of the theoretical heat value. During the first 1 min of reaction, heat recovery reached 73% of the theoretical value. The theoretical output of $6.5 \text{ mol/L}_{-\text{H}_2\text{O}}$ of CaBr_2 is $11 \text{ kW/L}_{-\text{H}_2\text{O}}$ for 60 s. The average output during the first 1 min of the dissolution reaction is, on average, $5.79 \text{ kW/L}_{-\text{H}_2\text{O}}$, about 52% of the theoretical average output. We found no degradation in the chemical composition of CaBr_2 after it being recycled 100 times.

Funding

The authors received no direct funding for this research.

Author details

Ai Niwa¹

E-mail: ainy58@energy.gr.jp

Noriyuki Kobayashi¹

E-mail: koba@nuce.nagoya-u.ac.jp

¹ Department of Chemical Engineering, Nagoya University, Nagoya, Aichi, Japan.

Citation information

Cite this article as: Calcium bromide hydration for heat storage systems, Ai Niwa & Noriyuki Kobayashi, *Cogent Engineering* (2015), 2: 1064218.

References

- Dawoud, B. (2007). On the effect of grain size on the kinetics of water vapor adsorption and desorption into/from loose pellets of FAM-Z02 under a typical operating condition of adsorption heat pumps. *Journal of Chemical Engineering of Japan*, 40, 1298–1306. <http://dx.doi.org/10.1252/jcej.07WE163>
- Kato, Y., Sasaki, Y., & Yoshizawa, Y. (2003). Thermal performance measurement of a packed bed reactor of a magnesium oxide/water chemical heat pump. *Journal of Chemical Engineering of Japan*, 36, 833–839. <http://dx.doi.org/10.1252/jcej.36.833>
- Kubota, M., Kyaw, K., Watanabe, F., Matsuda, H., & Hasatani, M. (2000). Study of decarbonation of CaCO_3 for high temperature thermal energy storage. *Journal of Chemical Engineering of Japan*, 33, 797–800. <http://dx.doi.org/10.1252/jcej.33.797>
- Malijejská, I. (2006). Solid-liquid equilibrium in the acetic acid-acetophenone and acetic acid-formamide systems. *Journal of Molecular Liquids*, 125, 72–75. <http://dx.doi.org/10.1016/j.molliq.2005.11.019>
- Niwa, A., & Kobayashi, N. (2015). Study on compact and high power storage system by means of a liquid-solid reaction system using CaCl_2 and water for a motive use. *Transactions of the JSRAE*, 32, 1–10.
- Niwa, A., Kobayashi, N., Hayase, T., & Fuse, T. (2014). Basic characteristics of heat discharge in a heat storage system using solid-liquid hydration reaction of CaCl_2 , CaBr_2 or LiBr . *Kagaku Kogaku Ronbunshu*, 40, 486–491. <http://dx.doi.org/10.1252/kakoronbunshu.40.486>
- Paulik, F., & Paulik, J. (2005). Thermogravimetric examination of the dehydration process of calcium bromide hydrate under quasiisothermal and quasi-isobaric conditions. *Journal of Thermal Analysis and Calorimetry*, 27, 409–418.
- Robert, F. D. (1999, January). Heat transfer in agitated jacketed vessels. *Chemical Engineering*, 90–99.
- Weber, R. (2008). Long-term heat storage with NaOH . *Vacuum*, 82, 708–716. <http://dx.doi.org/10.1016/j.vacuum.2007.10.018>



© 2015 The Author(s). This open access article is distributed under a Creative Commons Attribution (CC-BY) 4.0 license.

You are free to:

Share — copy and redistribute the material in any medium or format

Adapt — remix, transform, and build upon the material for any purpose, even commercially.

The licensor cannot revoke these freedoms as long as you follow the license terms.

Under the following terms:

Attribution — You must give appropriate credit, provide a link to the license, and indicate if changes were made.

You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use.

No additional restrictions

You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits.



Cogent Engineering (ISSN: 2331-1916) is published by Cogent OA, part of Taylor & Francis Group.

Publishing with Cogent OA ensures:

- Immediate, universal access to your article on publication
- High visibility and discoverability via the Cogent OA website as well as Taylor & Francis Online
- Download and citation statistics for your article
- Rapid online publication
- Input from, and dialog with, expert editors and editorial boards
- Retention of full copyright of your article
- Guaranteed legacy preservation of your article
- Discounts and waivers for authors in developing regions

Submit your manuscript to a Cogent OA journal at www.CogentOA.com

