Calcium bromide hydration for heat storage systems

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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 CaBr2 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 kJ/LH2O. We found no degradation in the chemical composition of CaBr2 after being recycled 100 times.

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, ...
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 CaCl₂ and evaluation experiments on the heat of hydration of CaCl₂, CaBr₂, and LiBr (Malijevská, 2006; Niwa & Kobayashi, 2015; Niwa, Kobayashi, Hayase, & Fuse, 2014), we selected CaBr₂ 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 kW/L -H₂O. 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 CaBr₂ as the solid and H₂O 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 CaBr₂ within 2 min. Three states of the reaction system existed in the heat storage process: aqueous CaBr₂ state, an anhydrous state with dehydrate for 20 min to store the exhaust heat in 473–673 K, and CaBr₂(s) + H₂O(L) which is ambient temperature, as shown in Figure 2. CaBr₂(aq.) is separated into anhydrous CaBr₂(s) and H₂O(g). The H₂O(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 CaBr₂(s). 6H₂O (L).
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.

\[
\text{Dehydration rate [g/s g]} = \left( \frac{m_{t2} - m_{t1}}{(m_{t1} + m_{t2})/2} \right) \left( \frac{1}{t_2 - t_1} \right)
\]

where \(m_{t1}\) is the weight at time \(t_1\), \(m_{t2}\) 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:
where \( V \) is the volume of the solution (cm\(^3\)), \( S \) is the heating area in square feet (cm\(^2\)), \( D \) 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:

\[
\frac{S}{V} = \frac{\pi DH}{\pi D^2/4} = \frac{4D}{D} \tag{2}
\]

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.
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 CaBr₂ (85 g) and H₂O (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 g -H₂O/g-solute after 3 h. When the tube’s inside diameter was 2.84 cm, the dehydration rate was inferior to that of the φ1.66 cm bore tube in the early dehydration period (the first hour), but the φ2.84-cm reactor produced the same results as the φ1.66 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.

\[ Q = FC_p \rho \Delta T_{\text{out-in}}, \]

where \( Q \) is the heat recovered (J), \( F \) is flow rate (m³/s), \( C_p \) is specific heat capacity (J/kg/K), \( \rho \) is the density (kg/m³), 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 CaBr₂.h2O for dehydration heating times of 0.5, 1, 2, and over 3 h.
5. Results and discussion

5.1. Heat release characteristic and dehydration time

The heat value and output of CaBr$_2$ (11.7 g) and H$_2$O (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 CaBr$_2$ after heating for 3 h. The dehydration rate of CaBr$_2$ (0.768 g-water/g-solute) slowed down 30 min after the start of
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 CaBr₂ measured by this experiment as a fraction of the standard (100%) heat value of fresh CaBr₂ per 1 L-H₂O (622 kJ/L-water).

From the results of this experiment, we found that the dehydration status of 0.05 g-H₂O/g-solute had a large increase in the amount of heat released. The heat value of CaBr₂ hydrate is different from that of CaBr₂ anhydrate. The heat recovery amount of the solid after 3 h of dehydration was 582 kJ/L-H₂O. Figure 9 shows the dehydration state of CaBr₂ versus its heat output. The amount of heat recovered increased substantially when the state of dehydration was 0.1 g-H₂O/g-solute. CaBr₂·nH₂O 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.

\[
h_0D = \frac{0.03Re^{0.75}Pr}{k(1 + 1.74Re^{-0.125}(Pr - 1))}
\]

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.
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 was able to achieve a heat recovery of 582 kJ/L H₂O. 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 mol/L H₂O of CaBr₂ is 11 kW/L H₂O for 60 s. The average output during the first 1 min of the dissolution reaction is, on average, 5.79 kW/L H₂O, about 52% of the theoretical average output. We found no degradation in the chemical composition of CaBr₂ after it being recycled 100 times.
