Operability of a Thermally Driven Magnesium Oxide/Water Chemical Heat Pump

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The operability of a thermally driven chemical heat pump using the magnesium oxide/water reaction system was demonstrated experimentally. The heat pump system, consisting of a packed bed reactor and a water reservoir, was operated thermally with no mechanical work. The thermal output performance of the reactor bed was measured under pressures between 50 and 202 kPa. The heat pump was expected to be applicable as a heat storage system for high efficiency energy utilization in cogeneration.

On démontre de manière expérimentale l'opérabilité d'une pompe thermique chimique activée thermiquement à l'aide d'un système de réaction oxyde de magnésium/eau. Le système de pompe thermique, composé d'un réacteur à lit garni et d'un réservoir d'eau, fonctionne thermiquement sans intervention mécanique. La performance du rendement thermique du lit du réacteur a été mesurée pour des pressions comprises entre 50 et 202 kPa. La pompe thermique devrait pouvoir s'appliquer à un système de stockage de la chaleur pour une utilisation de l'énergie à haut rendement dans la cogénération.

Keywords: chemical heat pump, heat storage, magnesium oxide, water, bed reactor.

The present study attempts to show the feasibility of using a magnesium oxide/water chemical heat pump for effective heat utilization. A chemical heat pump, which manages heat transformation via a chemical reaction, is one type of heat storage and utilization system. A decentralized cogeneration system using a chemical heat pump could be a practical application. A conventional scheme for cogeneration involves using the shaft work and exhaust heat of a diesel, gas engine or micro gas turbine for electrical and heat output, respectively. However, since the demand for the electrical output is generally inconsistent with that for the heat output, a large amount of surplus heat output is occasionally discharged into the atmosphere. The present study examines the applicability of a magnesium oxide/water chemical heat pump as a means of utilising the surplus heat and enhancing the actual energy efficiency of the cogeneration. The heat pump is operated batch-wise and can store heat and transform it to another temperature. A magnesium oxide/water chemical heat pump has been described previously, in terms of reaction kinetics using a thermobalance (Kato et al., 1993, 1996), and also in terms of thermal performance of the packed bed reactor using a laboratory scale heat pump (Kato et al., 1995, 1998b). The thermobalance experiment showed that the heat pump was capable of storing waste heat at around 300°C and amplifying the stored heat at a heat delivery temperature between 100°C and 150°C. A new reactant made from an ultra fine powder of MgO and purified water was found to demonstrate durability to repetitive reaction (Kato et al., 1999, 1998a). The laboratory scale heat pump experiment demonstrated that the heat storage density of the heat pump is large enough compared to a conventional sensible heat storage system.

A particulate reactant packed in a bed reactor is used for the heat pump. Detailed bed reactor experiments are necessary in order to evaluate the practical performance of the heat pump, because in the practical reactor, complex phenomena are induced by chemical reactions, vapour diffusion and thermal conduction in the particle bed. The heat pump system in the previous study required mechanical work because of a design restriction on the condensation process in heat storage. To avoid uneconomical energy consumption, the mechanical work must be dispersed with. After experiments the design of a thermally driven heat pump was needed. A heat output operation study under higher pressure was also required to expand the applicability of the heat pump, because a higher pressure reaction was advantageous for the enhancement of the heat pump output performance. However, reaction pressures less than 80 kPa had been employed in previous studies because of experimental restrictions. Therefore, in the present work a new heat pump system that was thermally driven and capable of being operated above atmospheric pressure was examined.

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Chemical Heat Pump

Chemical heat pumps that use reversible inorganic metal oxide/water reaction system have been discussed because of well reversibility of the reactions and relatively higher heat density of reactants. A calcium oxide/water chemical heat pump has been discussed kinetically by Kanamori et al. (1996) as a heat storage system for utilization of surplus electricity energy, and examined experimentally by Ogura et al. (1999) as a drying system. A chemical heat pump that uses a reversible magnesium oxide/water reaction system to promote thermal energy utilization has been examined by Bhatti and Dollimore (1984), Ervin (1977) and Kato et al. (1993). A three-phase reactor in which a magnesium oxide particle is suspended in tri-ethylene glycol has been discussed by Matsumura et al. (1995) for the enhancement of heat conductivity of the solid/gas reaction system. This heat pump is based on the following equilibria:

$$MgO\,(s) + H_2O\,(g) = Mg\,(OH)_2\,(s), \quad \Delta H^\circ_1 = -81.0\,\text{kJ/mol} \qquad (1)$$

$$H_2O\,(g) = H_2O\,(l), \quad \Delta H^\circ_2 = -40.0\,\text{kJ/mol} \qquad (2)$$

This heat pump enables thermal energy to be stored via the dehydration of magnesium hydroxide (Equation 1) and releases the stored energy on demand via the hydration of magnesium oxide. The principle of this heat pump is shown in Figure 1. The heat pump consists of a magnesium oxide reactor and a water reservoir. The heat pump has two operation modes: heat storage mode and heat output mode. In heat storage mode (Figure 1a), magnesium hydroxide $Mg(OH)_2$ is dehydrated by surplus heat at T_d. Generated vapour is condensed at the reservoir at T_{cd}. In heat output mode (Figure 1b), water in the reservoir is reheated by heat at a low temperature, T_{ev}. The hydration of magnesium oxide proceeded in the reactor by introducing the vapour, and hydration heat output at T_h is generated.

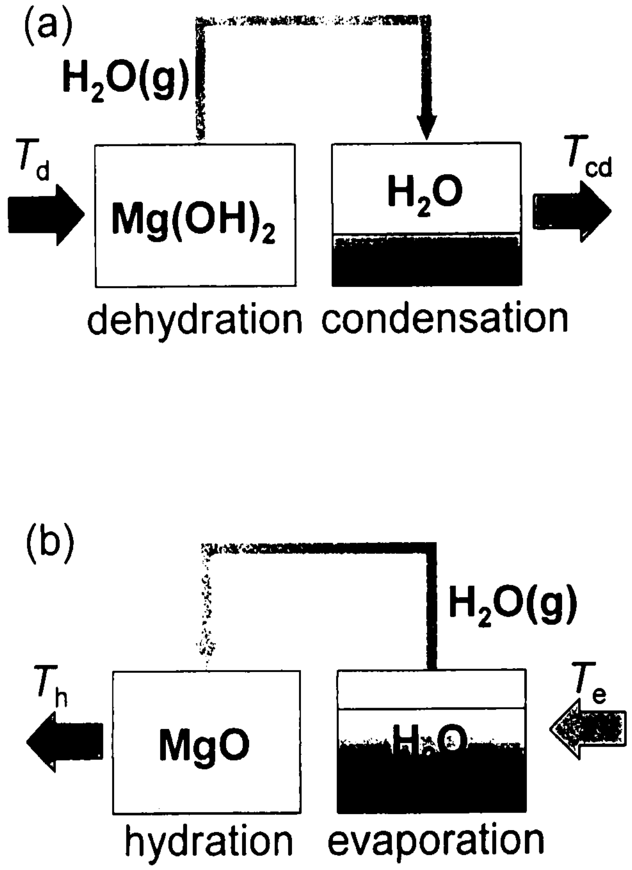

Figure 1. Principle of the chemical heat pump; (a) heat storage mode, (b) heat output mode.

The operation temperature range of the MgO/H_2O chemical heat pump is unique. The heat pump would be unique system that can store a heat at around 300°C and amplify the heat into a heat at around 100°C. The advantages of the heat pump are as follows: 1) exhaust or surplus heat generated from a cogeneration process can be utilized in the heat pump; 2) the reactant materials are safe, economical and environmentally friendly; and 3) longer-term heat storage is possible compared to conventional heat storage systems.

Experimental

A schematic diagram of the experimental apparatus of the thermally driven chemical heat pump is shown in Figure 2. The heat pump consists of a reaction chamber (1) and water reservoir (10). Both chambers are connected by a flexible tube (6) and stop valve (8), and the chambers' temperatures are controlled by joule heaters (4) and (12), and a heating tube (11). Reactant vapour was moved between the chambers through the stop valve by pressure difference alone. Figure 3 shows detail of the cylindrical packed bed reactor (2), which appears in Figure 2, in the reaction chamber. The reactor is made of stainless steel, having an inside diameter of 50 mm and height of 53 mm. 50 g of particle reactant of $Mg(OH)_2$ (avg. diameter of 1.5 mm) is charged in the reactor. The reactor temperature was maintained independently by a joule heater surrounding the outer surface of the reactor (depicted as 3 in Figure 3) aside from inner atmosphere temperature of the reaction chamber. Some thermocouples were installed at some points in the reactor bed in order to measure the bed temperature change.

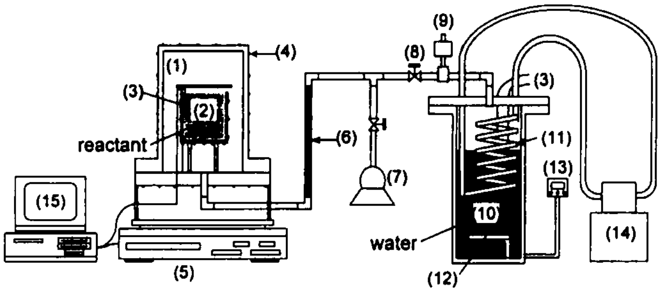

Figure 2. Schematic diagram of thermally driven magnesium oxide/ water chemical heat pump system: 1) reaction chamber; 2) packed bed reactor; 3) thermocouples; 4) joule heater; 5) balance; 6) flexible tube; 7) vacuum pump; 8) stop valve; 9) safety valve; 10) water reservoir; 11) heating tube; 12) joule heater; 13) pressure gauge; 14) circulator of cooling water; 15) computer.

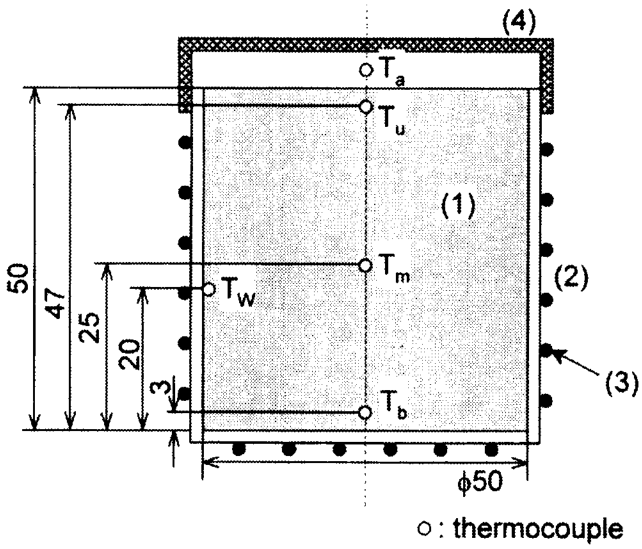

Figure 3. Detailed schematic diagram of the packed bed reactor (dimensions in mm): 1) reactant; 2) reactor; 3) joule heater; 4) insulation cap.

The positions and notations of the thermocouples are depicted in Figure 3. A cap (4) was installed for thermal insulation of the reactor lid. The reaction pressure was generated by the introduction of the vapour from the water reservoir, and the pressure of the vapour was maintained by the reservoir water temperature control using a heating tube and joule heater, (11) and (12) in Figure 2. The pressure was monitored by a pressure gauge. The weight change of the reactor during reactions was measured directly by a balance, (5) in Figure 2. The magnesium hydroxide of the initial reactant was produced from an ultra fine magnesium oxide powder (avg. particle diameter: 10 nm, UBE Materials Co. Ltd.) and water. The ultra-fine oxide powder was hydrated with purified water in a ball mill. After hydration, the pasty product was dried and the resulting flakes were sieved.

Experimental Procedure

The following repetitive cycle operation was carried out during each experiment using the same reactant:

$$Mg(OH)_2 \xrightarrow[\text{Dehydration}]{\text{Heat storage}} MgO \xrightarrow[\text{Hydration}]{\text{Heat output}} Mg(OH)_2 \xrightarrow{\text{Repetition}} \ldots \quad (3)$$

The stable reactivity to the repetitive cycle of the reactant has been demonstrated (Kato et al., 1997). The reactivity was maintained during 24 repeat cycles, after an initial reactivity reduction during the initial 5 cycles. Thereafter, the reactivities under some reaction conditions measured during the 6th to 20th cycles were compared.

After initial removal of residual gas from the apparatus using a vacuum pump, the system was driven thermally with no mechanical pump work. In heat storage mode, dehydration of $Mg(OH)_2$ in the bed was carried out. The stop valve, (8) in Figure 2, was closed initially. A water coolant was circulated in a heating tube in the water reservoir. The dehydration pressure was controlled by the vapour pressure of water in the reservoir. The vapour pressure was kept constant by the reservoir water temperature control using the heating tube. The reactor temperature was raised to a dehydration temperature by the reactor joule heater. Then, MgO and water was generated by dehydration. When the stop valve was opened, the generated vapour condensed in the water reservoir. The reaction progress was measured by the balance and by the thermocouples. The stop valve was closed at the end of the reaction.

In heat output (hydration) mode, the water reservoir was heated to generate a specified reaction vapour pressure. The reactor and reaction chamber temperatures were maintained at a predetermined hydration temperature, which is 25°C higher than the vapour temperature in order to avoid vapour condensation. After the reactor and the reservoir attained the steady state, steam generated by the reservoir was introduced into the hydration chamber via the valve. The magnesium oxide reacted with the steam and heat output was generated.

The reactor's weight change due to the reaction, Δm, was caused by the movement of vapour. Thus, the mole reacted fraction, x (-), is defined as follows:

$$x = 1 + \frac{(\Delta m / M_{H_2O})}{(m_{MgO} / M_{MgO})} \qquad (4)$$

where m_{MgO} is the weight of magnesium oxide in the reactor bed. The hydration experiments started from the dehydrated state. The dehydration of each sample did not proceed to $x = 0$ due to the existence of structural water in the reactant, and the sample saturated at around $x = 0.2$. Hydration saturated at around $x = 0.8$. In order to obtain an objective comparison of the reaction reactivity, the mole reacted fraction change, Δx (-), is defined as:

$$\Delta x = x - x_{ini} \qquad (5)$$

where x_{ini} is the initial reacted fraction of the reaction cycle.

Results and Discussion

Dehydration Operation

The inner wall temperature (T_w) was controlled as the dehydration bed temperature (T_d) by the heater at dehydration operation. Figure 4 gives sample dehydration results: temperature and reacted fraction changes of the bed at a dehydration temperature of 400°C, a water reservoir temperature for vapour condensation (T_{cd}) of 30°C and a reaction chamber inner temperature (T_{rc}) of 100°C are shown. Each notation of temperature in Figure 4 corresponds to the same one in Figure 3. The reaction pressure (P_d) was kept below 5 kPa by the vapour pressure in the reservoir. The inner wall temperature rose to T_d of 400°C relatively rapidly. Because of the low thermal conductivity of the reactant, a temperature difference arose between the wall (T_w) and inner bed (T_m and T_b). The dehydration started at around 280°C. The reaction proceeded rapidly after inner bed temperatures (T_m and T_b) had attained around 280°C. The inner bed temperature

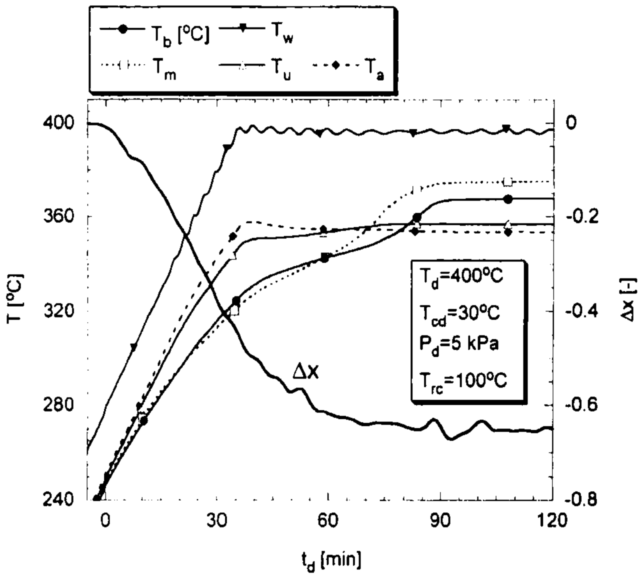

Figure 4. Experimental results of magnesium hydroxide dehydration (heat storage) operation at a bed temperature of 400°C and a condensation temperature of 30°C and a vapour pressure of 5 kPa.

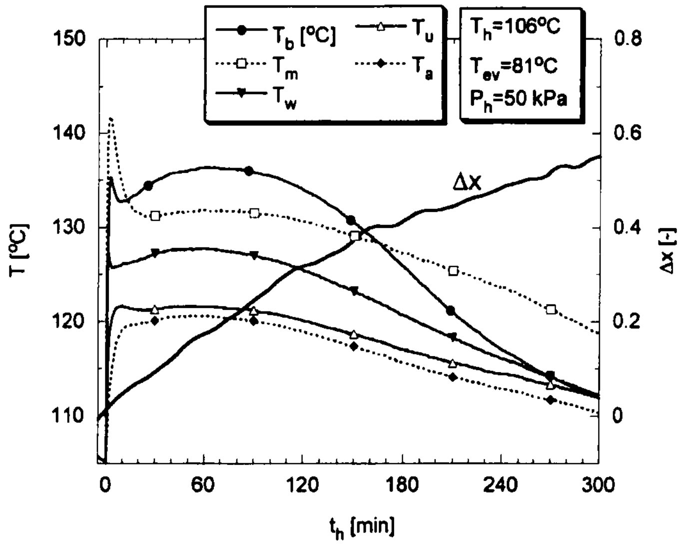

Figure 6. Experiment results of magnesium oxide hydration (heat output) operation at an evaporation temperature of 81°C and a vapour pressure of 50kPa.

change was slowed during the period of 30 to 70 min because the rate of reaction at the inner bed was constrained by heat conduction. After the completion of the dehydration reactor, the inner bed temperature rose higher than the temperature at the upper bed surface atmosphere (T_a), and the reaction was terminated.

The effect of the dehydration temperature, T_d, on the dehydration reactivity under the same condensation temperature of 30°C is shown in Figure 5. Δx change is faster at a higher dehydration temperature, because the dehydration reactivity becomes higher at higher temperatures. As shown in Figure 4, the dehydration is capable of proceeding at less than 300°C. The reactivity difference in Figure 5 results from low heat conductivity in the reactor bed. A higher dehydration temperature ensures a high enough temperature distribution in the whole of the bed for dehydration. On the other hand, a lower T_d is insufficient to maintain a sufficient dehydration temperature in the whole region because of the low heat conductivity of the bed, and the dehydration proceeds slowly. Therefore, the heat conductivity enhancement in the bed is effective in lowering the dehydration temperature.

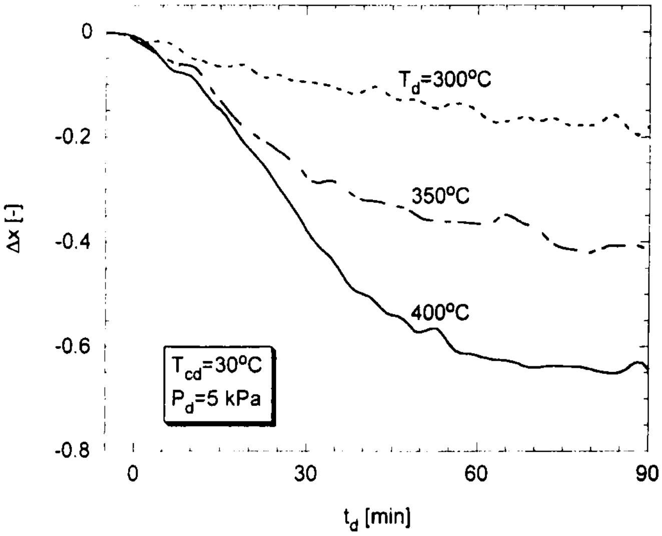

Figure 5. Effect of dehydration temperature on dehydration reactivity under a pressure of 5 kPa.

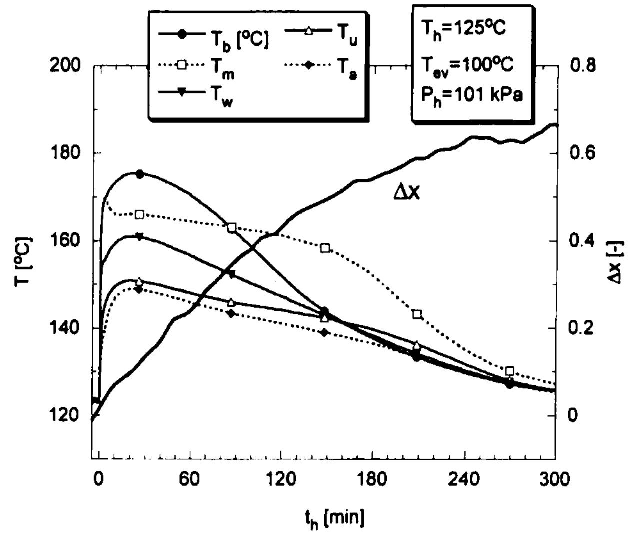

Figure 7. Hydration operation results at T_{ev} = 100°C and P_h = 101 kPa.

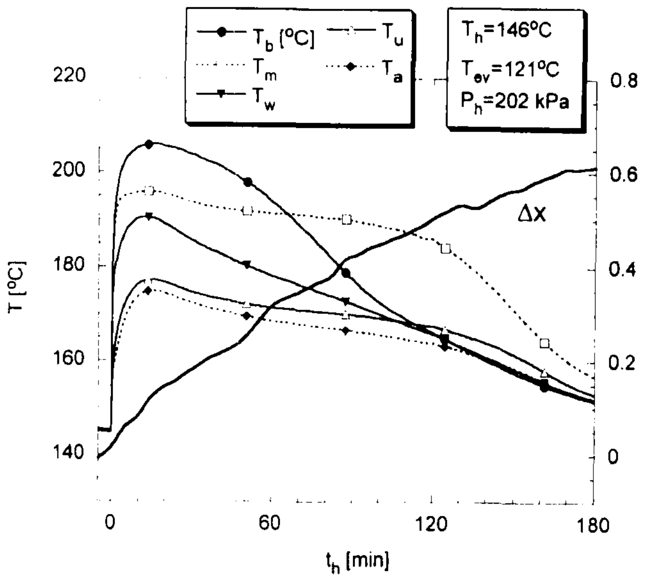

Figure 8. Hydration operation results at T_{ev} = 121°C and P_h = 202 kPa.

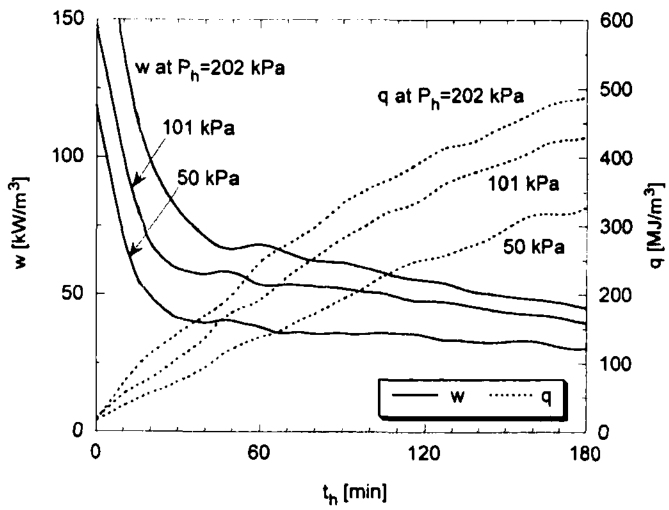

Figure 9. Hydration output performance of the heat pump.

Hydration Operation

A hydration result under an evaporation temperature (T_{ev}) of 81°C at the water reservoir, a vapour pressure (P_h) of 50 kPa, and the initial bed temperature (T_h) of 106°C is shown in Figure 6. In the hydration experiment, the initial temperature of the inner wall of the reactor (T_w) was controlled at T_h. The chamber inner atmosphere temperature was kept also at T_h. In the initial hydration period, the vapour diffuses into the bed rapidly by the large pressure driving force between P_d and P_h. Physical absorption of vapour on the reactant particle surface proceeds in advance of the hydration. The adsorption heat is released rapidly, so the bed temperature rises quickly in the beginning of hydration. The chemical hydration proceeds subsequently after the bed temperature distributions become lower and appropriate for the hydration. Because the vapour that is relatively colder than the bed enters from the top of the bed, and the thermal insulation at the bottom of the bed is better than that at the top, the bottom temperature (T_b) tends to be higher than the upper temperature (T_u). On the other hand, the middle point (T_m) was kept at a similar temperature during more than 3 h, a longer duration than for other points. It was presumed that the middle point was controlled most strongly by the vapour diffusion and heat conduction through the packed bed. Since T_b was higher than T_m during the initial 2 h, it was thought that the vapour diffusion resistance through the reactant particles in the bed was higher than the resistance between the inner wall of the reactor and the circumference of the bulk reactant bed. Moreover, the temperature at the middle point was controlled by heat conduction in the bed because of the low heat conductivity of the reactant. Thus the hydration at the middle point proceeded more slowly than at other points, and the point maintained a similar bed temperature during longer period of hydration.

The hydration result at under T_{ev} = 100°C and P_h = 101 kPa, and T_{ev} = 121°C and P_h = 202 kPa are shown Figures 7 and 8, respectively. A higher-pressure reaction shows a higher bed temperature attainment and a higher reaction rate. Since the chemical hydration proceeds more rapidly under the higher pressure, the physical adsorption effect becomes indiscernible at higher reaction pressures. The bottom temperature attained 207°C under 202 kPa. A higher pressure vapour generation requires higher evaporation temperature. Such an evaporation heat could be supplied by utilizing waste heat from the heat pump output itself, that is generated secondarily after the use of the original hydration output heat between the original output temperature and the evaporation temperature.

Thermal Output Performance of the Bed

The thermal output performance of the heat pump based on this reactor bed measurement was evaluated. An output heat from the reactor per unit volume of initial charged $Mg(OH)_2$ (q (kJ/m³)) is defined as follows:

$$q = \frac{\Delta x \Delta H_1^{\circ} \rho}{M} \tag{6}$$

A mean heat output rate (w [W/m³]) is defined as follows:

$$w = \frac{q}{t_h} \tag{7}$$

Temporal changes of q and w under conditions in Figures 6 to 8 are shown in Figure 9. An output rate of 58 kW/m³ and a gross output of 245 MJ/m³ were expected during the initial 60 min at a pressure of 202 kPa. When the same amount of heat is stored by a conventional, sensible heat water storage system between 70°C and 90°C, the heat output amount from water is around 83 MJ/m³. The heat storage density of the heat pump is about three times than that of the water storage system. An output temperature of the heat pump of around 170°C to 200°C is high enough over that of the water system. The heat pump also can store heat for a longer period as chemical reactants, and can supply heat at various temperatures. This heat pump performance is an advantage over conventional heat storage systems. Thus, the heat pump has the potential to develop new heat utilization market.

The heat transformation ability of the reactant is large enough compared to conventional heat pump systems. On the other hand, the solid reactants of MgO and $Mg(OH)_2$ have poor heat conductivity compared to a liquid/gas system. Enhancement of thermal conductivity in the reactor bed would be major subject technically in the next stage of research. Then, the development of a new reactor design having higher heat transfer ability would be required. The cost competitiveness to a conventional system, especially to a sensible heat water storage system, also needs to be considered. The cost of the reactant magnesium oxide would control the total system cost. Then, more economical material production process, in which seawater is used as a precursor, is being discussed now.

Conclusions

It was demonstrated experimentally that a magnesium oxide/water chemical heat pump was capable of being driven thermally. Under reaction pressures that are higher than those of the previous study, the hydration process was examined. The hydration output above 200°C was measured under a pressure of 202 kPa. A higher temperature output was expected to be obtained under higher vapour pressure. Hydration heat that is generated secondarily after the use of the original hydration output can be used for the high pressure vapour production. The thermal storage performance of the heat pump is sufficient for practical use compared to a conventional heat storage system. The heat pump can cover the temperature range of cogeneration engines' exhaust gases. The heat pump is expected to be applicable as a chemical heat storage system for load levelling of a common cogeneration system by chemically storing, at 300°C to 400°C, waste heat generated from an engine during low heat demand, and for supplying hydration heat above 200°C during peak load periods under thermally driven operation. The bed reaction process depends on heat and mass transfer phenomena. The enhancement of the thermal conductivity and mass diffusivity in the particle bed reactor are important factors in the upgrade of the thermal performance of the heat pump.

Acknowledgements

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Nomenclature

C	specific heat of gas, (kJ/kmol·K)
L_i	initial loaded magnesium hydroxide weight, (kg)
m	material weight, (kg)
M	molecular weight of magnesium hydroxide, (kg/kmol)
P	reaction pressure, (kPa)
q	hydration heat output, (kJ/m^3)
t	reaction time, (s)
T	temperature, (°C)
w	hydration heat output rate, (W/m^3)
x	mole reacted fraction

Greek Symbols

ΔH°	standard enthalpy change of a reaction, (kJ/kmol)
Δx	mole reacted fraction change amount
ρ	density of magnesium hydroxide, (kg/m^3)

Subscripts

1	magnesium oxide/water reaction system
2	water liquid/gas phase change
a	bed upper surface atmosphere
b	the bottom centre of the bed
cd	condensation
d	dehydration of $Mg(OH)_2$
ev	evaporation
g	gas
H_2O	water
h	hydration of MgO
ini	the initial state of the reaction cycle
MgO	magnesium oxide
m	middle centre of the bed
rc	inner reaction chamber
u	upper centre of the bed
w	inner wall of the reactor at the middle in height

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