OPERABILITY ANALYSIS OF A THERMALLY DRIVEN MAGNESIUM OXIDE/WATER CHEMICAL HEAT PUMP

Y. Kato, A. Minakami and Y. Yoshizawa

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152-8550, Japan

ABSTRACT

The operability of a chemical heat pump using magnesium oxide/water reaction system was discussed experimentally under hydration operation pressures between 30 kPa and 203 kPa. The heat pump was expected to be applicable in cogeneration systems using gas and diesel engine, or fuel cell and micro gas turbine. In the experiment, a reactant having high durability for repetitive operation was packed in a cylindrical reactor. The heat pump was operated thermally with no mechanical work. The operation of a unit cycle consisted of the endothermic dehydration of magnesium hydroxide for heat storage, and the exothermic hydration of magnesium oxide for heat release. The cycle of operation was repeated under various thermally driven operation conditions. The forward and reverse reactions were studied by measuring the reactor bed temperature distribution and the reacted fraction changes. The reactor bed could store heat around 300-400^{o}C by the dehydration reaction and release heat around 100-200^{o}C by the hydration reaction under heat amplification mode operation. The practical possibility of the reactor bed was discussed based on the experimental results. The heat pump was expected to be applicable for a load leveling in a cogeneration system by chemical storage of surplus heat at low heat demand and by supplying heat in the peak load period.

KEYWORDS

Chemical Heat Pump, Heat Storage, Magnesium Oxide, Water, Bed Reactor

Nomenclature

C = specific heat of gas, (kJ/kmol.K), ΔH^{o} = standard enthalpy change of a reaction, (kJ/kmol), L_{i} = initial loaded magnesium hydroxide weight, (kg), M = molecular weight of magnesium hydroxide, (kg/kmol), m = initial charged material weight, (kg), P = reaction pressure, (kPa), q = hydration heat output, (kJ/kg), q_{H2O} = heat output amount of a sensible heat water storage, (kJ/kg), T = temperature, (^{o}C), t = reaction time, (s), w_{mean} = mean hydration heat output rate, (W/kg), x = mole reacted fraction, Δx = mole reacted fraction change amount

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, $Mg(OH)_2$ = magnesium hydroxide, m = middle part of the bed, rc = inner reaction chamber, u = upper centre of the bed, w = inner wall of the reactor at the middle in height

1. INTRODUCTION

The present study attempts to show 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. A chemical heat pump, which manages heat transformation via a chemical reaction, is one type of heat storage and utilisation system. A decentralized cogeneration system using a chemical heat pump could be a practical application. A chemical heat pump that uses reversible inorganic metal oxide/water reaction system has 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. [1] as a heat storage system for utilization of surplus electricity energy, and examined experimentally by Ogura et al. [2] as a drying system. A magnesium oxide/water chemical heat pump has been described previously, in terms of reaction kinetics using a thermobalance [3], and also in terms of thermal performance of the packed bed reactor using a laboratory scale heat pump [4, 5]. A three phase reactor in which magnesium oxide particle is suspended in tri-ethylene glycol has been discussed by Matsumura et al. [6] in due to enhance heat conductivity of the solid/gas reaction system. The thermobalance experiment showed that the magnesium oxide/water heat pump was capable of storing waste heat at around 300^{o}C and amplifying the stored heat at a heat delivery temperature between 100 and 150 ^{o}C at subatmospheric pressure. A new reactant made from an ultra fine powder of magnesium oxide and purified water was found the durability to repetitive reaction [7, 8]. A laboratory scale heat pump was examined to observe a heat storage ability of the heat pump using a particulate type of the reactant in a bed reactor. Detailed bed reactor experiment is necessary in order to evaluate the practical performance of the heat pump in the next step, because the reactor bed is complex system in which chemical reactions, vapor diffusion and thermal conduction proceed simultaneously. Experimental heat pump apparatus in a previous study required mechanical

Y. Kato, yukitaka@nr.titech.ac.jp

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. Moreover, 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. Therefore, in the present work a new heat pump system that was thermally driven and capable of being operated under high pressure was examined.

2. HEAT STORAGE FOR COGENERATION

The chemical heat pump is being developed for energy efficiency enhancement of a cogeneration by using its chemical heat storage ability. A conventional cogeneration system shown in Figure 1 (a) uses a shaft work and exhaust heat of a gas, diesel engine or micro gas turbine for electrical and heat output, respectively. The high temperature exhaust gas of the engine is generally used to generate steam at an exhaust gas boiler. 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 as shown. Chemical heat storage has a possibility to enhance the energy use efficiency of a cogeneration. The proposed system is shown in Figure 1(b). The system consists of a cogeneration engine and a chemical heat storage system. The heat storage system is operated in batch mode between a heat storage mode and a heat output mode. In the heat storage mode, an endothermic reaction process of the chemical heat storage system proceeds by consuming surplus waste heat generated from the engine. In the heat output mode, an exothermic reaction process of the storage system proceeds generating a reaction heat output. Because the heat storage system could store heat for longer period as chemical reactants, and the heat output temperature could be variable by choosing reaction conditions, then the heat output would be supplied at various temperatures, when it is required. In consequence, the surplus heat is utilized more efficiently than a conventional heat storage system.

2. 1 Heat storage using reversible chemical reaction

Although there are a lot of ways for heat storage, the thermal performance of a heat storage system depends on thermodynamic properties of the used heat storage materials. Higher-heat storage density and reaction reversibility are required on the materials for heat storage. Figure 2 shows energy densities of physical and chemical changes for heat storage. Heat density of chemical changes is relatively higher than one of physical changes. Sensible heat and phase changes in physical changes are popular system for conventional heat storage technologies because of well reversibility of their changes. On the other hand, chemical changes such as oxidation are irreversible and hard to apply for repetitive heat storage operation. Then, reversible chemical reaction is expected to have potential for heat storage and energy utilization process in the next generation because of its relative high-energy density and reversibility.

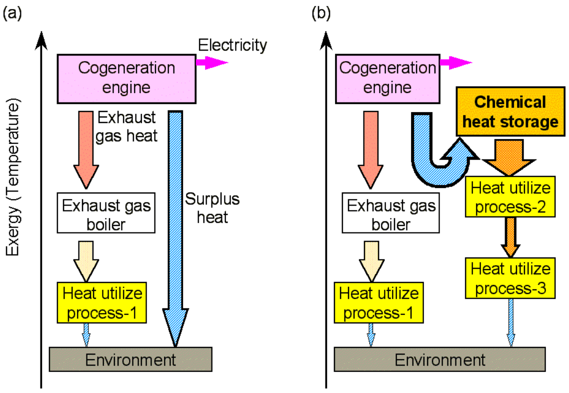

Fig. 1 Application of a chemical heat storage system on a cogeneration sys tem (a) thermal flow of a conventional cogeneration, (b) thermal flow of combined system of a chemical heat storage and cogeneration.

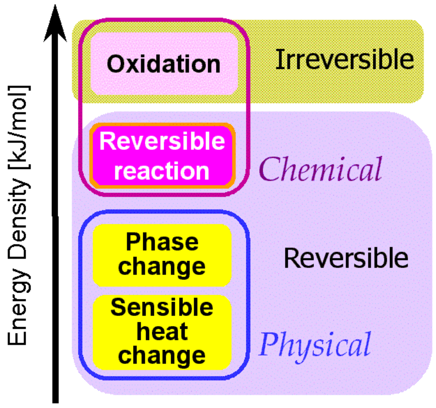

Fig. 2 Comparison of heat density of chemical and physical changes for heat storage.

2. 2 Magnesium oxide/water chemical heat pump

A chemical heat pump that uses a reversible magnesium oxide/water reaction system to promote heat storage and energy utilisation has been examined by Bhatti and Dollimore [9], Ervin [10] and Kato et al. [3]. This heat pump is based on the following equilibria:

$$MgO(s)+H_2O(g)\leftrightarrow Mg(OH)_2(s),\ \Delta H^\circ_1 = -81.0\ \text{kJ/mol} \quad (1)$$
$$H_2O(g)\leftrightarrow H_2O(l),\ \Delta H^\circ_2 = -40.0\ \text{kJ/mol} \quad (2)$$

This heat pump enables thermal energy to be stored via the dehydration of magnesium hydroxide (the right direction of 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 3. 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 (Fig. 3 (a)), magnesium hydroxide ($Mg(OH)_2$) is dehydrated by surplus heat at T_d. Generated vapor is condensed at the reservoir at T_{cd}. In heat output mode (Fig. 3 (b)), 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 vapor, and hydration heat at T_h is generated.

The heat pump would be a unique system that can store a heat at around 300 °C and amplify the heat into a heat at around 100°C. The advantageous of the heat pump are that exhaust or surplus heat generated from a cogeneration process can be stored by the heat pump, the reactant materials are safety, economical and environmentally friendly and longer-term heat storage is possible compared with conventional heat storage.

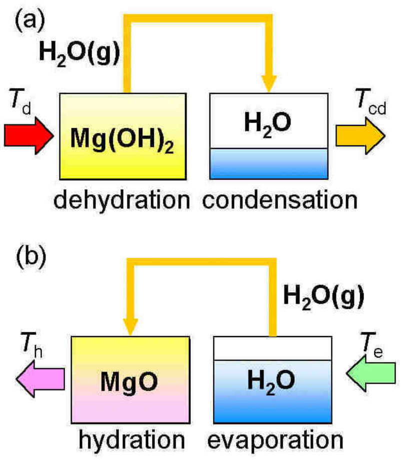

Fig. 3 Principle of the chemical heat pump: (a) heat storage mode, (b) heat output mode.

3. EXPERIMENT

A schematic diagram of the experimental apparatus of the thermally driven chemical heat pump is shown in Figure 4. 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 vapor was moved between the chambers through the stop valve by pressure difference alone. Figure 5 shows detail of the cylindrical packed bed reactor, (2) which appears in Figure 4, in the reaction chamber. The reactor is made of stainless steel having inside diameter of 50 mm and height of 50 mm. 53 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 Fig. 5) 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. The positions and notations of the thermocouples are depicted in Figure 5. A cap (4) was installed for enhancement of thermal insulation at the upper bed surface. The reaction pressure was generated by the introduction of the vapor from the water reservoir, and the pressure of the vapor was maintained by the reservoir water temperature control using a heating tube and joule heater, (11) and (12) in Fig. 4. The pressure was monitored by a pressure gauge. The weight change of the reactor during reactions was measured directly by a balance, (5) in Fig. 4. 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.

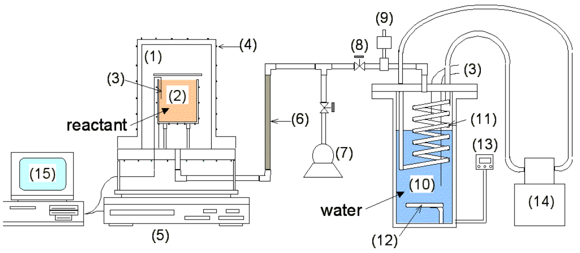

Fig. 4 Schematic diagram of thermally driven magnesium oxide/water chemical heat pump system: (1) reaction chamber, (2) packed bed reactor, (3) thermocouples, (4) joule heater, (5) balance, (6) flexible tube, (7) vacuum pump, (8) stop valve, (9) safety valve, (10) water reservoir, (11) heating tube,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

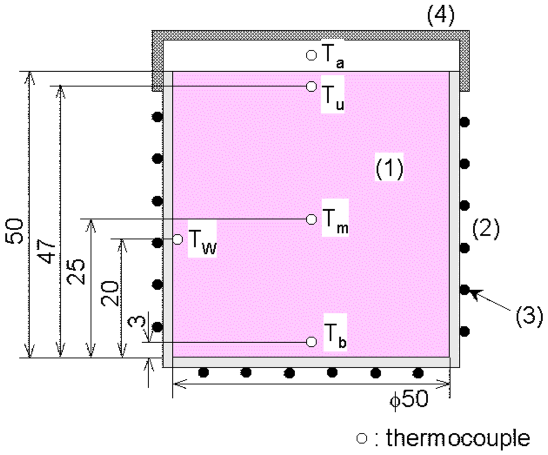

Fig. 5 The packed bed reactor: (1) reactant, (2) reactor, (3) joule heater, (4) insulation cap.

3. 1 Experimental procedure

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

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

The stable reactivity to the repetitive cycle of the reactant has been demonstrated [8]. 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 Fig. 4, was closed initially. A water coolant was circulated in a heating tube in the water reservoir. The dehydration pressure was controlled by the vapor pressure of water in the reservoir. The vapor 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 vapor 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 vapor pressure. The reactor and reaction chamber temperatures were maintained at predetermined hydration temperature, which is 25°C higher than the vapor temperature in order to avoid vapor 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 vapor. Thus, the mole reacted fraction, x [-], is defined as follows.

$$x = 1 + \frac{\left(\Delta m / M_{\mathrm{H2O}}\right)}{\left(m_{\mathrm{Mg(OH)2}} / M_{\mathrm{Mg(OH)2}}\right)} \quad (4)$$

where $m_{\mathrm{Mg(OH)2}}$ is the initial charged weight of magnesium hydroxide 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 follows.

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

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

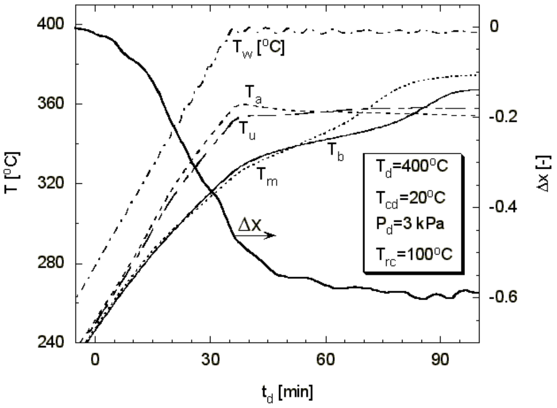

Fig. 6 Experimental result of magnesium hydroxide dehydration (heat storage) operation at a bed temperature of 400 °C and a condensation temperature of 20 °C and a vapor pressure of 3 kPa.

4. RESULTS AND DISCUSSION

4. 1 Dehydration operation

The inner wall temperature (T_w) was controlled as the dehydration bed temperature (T_d) by the heater at dehydration operation. Figure 6 gives sample dehydration result: temperature and reacted fraction changes of the bed at a dehydration temperature of 400°C, a water reservoir temperature for vapor condensation (T_{cd}) of 20°C and a reaction chamber inner temperature (T_{rc}) of 100°C are shown. Each notation of temperature in Fig. 6 corresponds to the same one in Fig. 5. The reaction pressure (P_d) was kept below 3 kPa by the vapor 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 change was slowed during the period of 20 - 60 min because heat consumption by the dehydration was balanced with the joule heating from the reactor wall in the period. As the dehydration approached completion, the joule heating was relatively greater than the dehydration heat consumption, then the inner bed temperature rose and finally became higher than the upper bed temperatures (T_a and T_u), and the dehydration was terminated. This result showed that the dehydration was controlled by heat conduction in the reactor bed. As shown in previous work using thermobalance [8], the dehydration is capable of proceeding at around 300°C. Relatively

Y. Kato, yukitaka@nr.titech.ac.jp

higher temperature of 400°C was required in the case of Fig. 6 to realize a high enough temperature distribution in the whole of the bed for the reaction. Then, heat conductivity enhancement in the bed is needed for lowering of the dehydration temperature.

The effect of condensation temperature, T_{cd}, on the dehydration reactivity under the same dehydration temperature of 400°C is shown in Figure 7. Dehydration pressure, P_{cd} is corresponding to T_{cd}. Δx change is faster at a lower T_{cd}, because a lower pressure enhances dehydration reactivity. However, the dehydration completion times of both pressures are similar and the reactivity difference between them is small enough for practical use. A higher condensation temperature is more advantageous for practical operation. Then, a higher condensation temperature than 30°C would be expected to be possible for more practical operation.

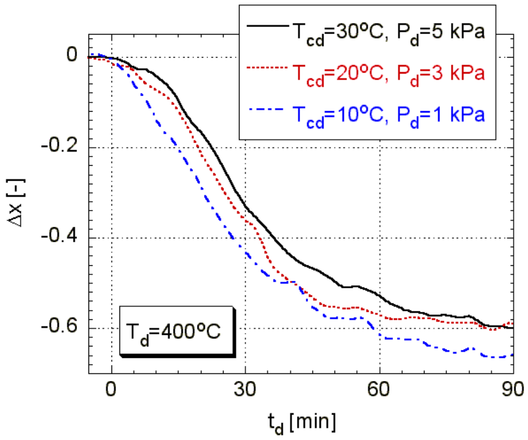

Fig. 7 Effect of dehydration pressure on dehydration reactivity under a dehydration temperature of 400 °C.

4. 2 Hydration operation

A hydration result under an evaporation temperature (T_{ev}) of 100°C at the water reservoir, a vapor pressure (P_h) of 101 kPa, and the initial bed temperature (T_h) of 125°C is shown in Figure 8. In the hydration experiment, the initial temperature of the inner wall of the reactor (T_w) was controlled at T_h. The inner atmospheric temperature in the reaction chamber was kept also at T_h. In the initial hydration period, the vapor diffuses into the bed rapidly by the large pressure driving force between P_d and P_h. Physical absorption of vapor 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, and the chemical hydration proceeds subsequently. Because the vapor 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 inner bed temperatures (T_b and T_m) tends to be higher than the upper temperature (T_u). The middle temperature of the bed (T_m) was kept at a similar temperature during more than 2 h, a longer time than for other points. It was presumed that the middle point was controlled most strongly by the vapor diffusion and heat conduction through the packed bed. Since T_b was higher than T_m during the initial 80 min, it was thought that the vapor 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 effect of hydration pressure on the reactivity under the same dehydration condition is shown in Figure 9. A higher pressure hydration shows a higher reacted fraction change. Figure 10 shows the dependency of the representative bed temperature (T_m) on the hydration pressure. A higher temperature is attained at a higher pressure. Since the chemical hydration proceeds more rapidly under the higher pressure, the physical adsorption effect becomes indiscernible at higher reaction pressures. A heat over 190°C is generated at 203 kPa of the pressure. The heat output can be used as a heat source for cooling by an absorption heat pump. A heat output at 100°C is produced at 30 kPa. The heat output is possible to be re-used for the next vapor production, which is higher than the initial vapor pressure, and then subsequent hydration using the higher vapor pressure generates higher output temperature as a self catalytic reaction. Therefore, when hydration heat output is used for the next vapor production in cascade, for example, a high output temperature over 190°C could be realized using a low temperature vapor around 69°C.

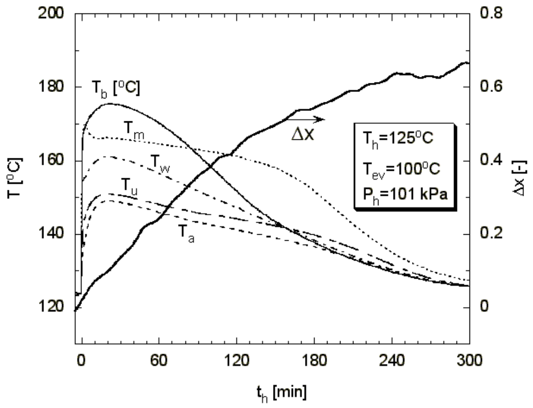

Fig. 8 Experiment results of magnesium oxide hydration (heat output) operation at an evaporation temperature of 100 °C and a vapor pressure of 101 kPa

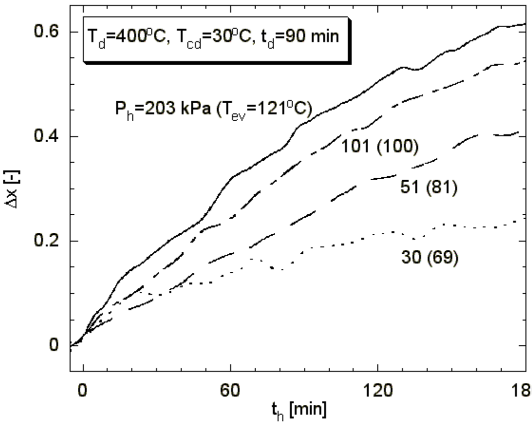

Fig. 9 Effect of hydration pressure on the reactivity under the same dehydration condition.

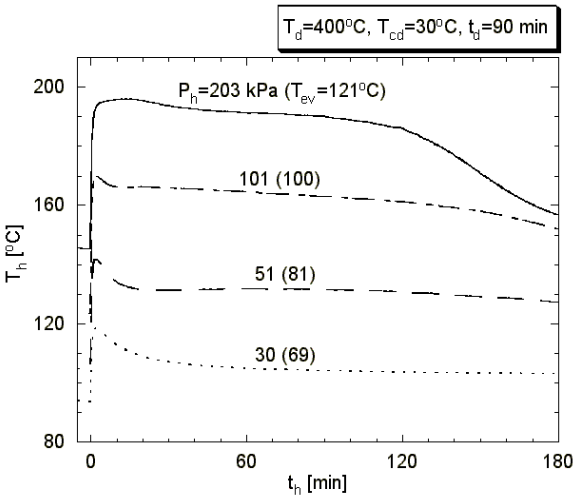

Fig. 10 Effect of hydration pressure on hydration temperature, measured at the middle part of the reactor bed, under the same dehydration condition.

4. 3 Thermal output performance of the bed

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

$$q = (\Delta H_1^\circ / M)\int_0^{t_h} x\,dt_h \qquad (6)$$

The mean heat output rate (w [W/kg]) is defined as follows.

$$w_{mean} = \frac{q}{t_h} \qquad (7)$$

Temporal changes of q and w_{mean} under conditions are shown in Figure 11. At a pressure of 203 kPa, an output rate of 119 W/kg and a gross output of 430 kJ/kg were expected during the initial 60 min. 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 (q_{H2O} [kJ/kg]) is around 83kJ/kg shown in a dashed line in Fig. 11. The heat storage density of the heat pump is about five times of the water storage system at hydration time of 60 min. Output temperature of the heat pump of around 170 °C to 200°C is enough higher than one of the water system. The heat pump also can store heat for longer period as chemical reactants, and supply heats at various temperatures. Those performances of the heat pump are advantages over conventional heat storage systems. Then, the heat pump has a potential to develop new heat utilization market.

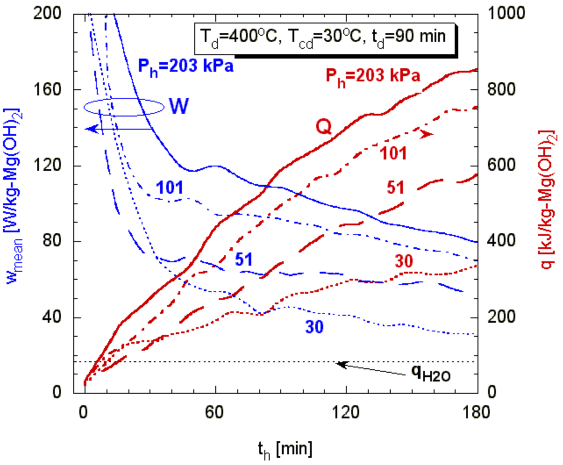

Fig. 11 Hydration output performances of the heat pump.

5. CONCLUSIONS

The thermally driven heat pump operability was demonstrated experimentally. The heat pump was expected to widen heat utilization ways of surplus heat generated from cogeneration system. Heat output above 190°C by the hydration operation was measured experimentally under a pressure of 203 kPa. A higher temperature output was expected to be obtained when hydration output could be used for higher vapor production for the next hydration in cascade. The heat storage performance of the heat pump was competitive enough to a conventional sensible heat water storage system in terms of heat storage density and output temperature. The heat pump can cover the temperature range of cogeneration engines' exhaust gas. The heat pump is expected to be applicable as a heat storage system for load leveling of a common cogeneration system by chemically storing of surplus waste heat, at 300°C to 400°C, generated from an engine during low heat demand; and supplying hydration heat about 200°C during peak load periods under thermally driven operation.

Acknowledgements

The research was granted by the grant-in-aid for scientific research of Japan Society for the Promotion of

Science. Authors thank for the research support of DMW Corporation, Japan.

References

[1] Kanamori M., Matsuda H. and Hasatani M., Heat storing/releasing characteristics of a chemical heat storage unit of electricity using a $Ca(OH)_2/CaO$ reaction, Heat Transfer - Japanese Research, **25**(6), pp 400-409, ISSN 0096-0802 (1996)

[2] Ogura H., Shimojyo R., Kage H., Matsuno Y. and Mujumdar A. S., Simulation of hydration/dehydration of $CaO/Ca(OH)_2$ chemical heat pump reactor for cold/hot heat generation, Drying Technology, **17**(7), pp 1579-1592, ISSN 0737-3937 (1999)

[3] Kato Y., Yamashita N. and Yoshizawa Y., Study of Chemical Heat Pump with Reaction System of Magnesium Oxide/Water, Kagaku Kogaku Ronbunshu **19**, pp 1213-1216, ISSN 0386-216X (in Japanese) (1993)

[4] Kato Y., Inoue S., Nanmoku W. and Yoshizawa Y., Kinetic study of the hydration of magnesium oxide/water chemical heat pump, Proc. 30th Intersociety Energy Conversion, vol. 3, pp 17-22, Orlando (1995)

[5] Kato Y., Takahashi F., Nanmoku W. and Yoshizawa Y., Heat Output Performance Study of Magnesium Oxide/Water Chemical Heat Pump, Kagaku Kogaku Ronbunsyu **24**, pp 840-844, ISSN 0386-216X (in Japanese) (1998)

[6] Matsumura Y., Nakahara Y., Morita H. and Yoshida K., Chemical heat pump using hydration of MgO particles in a three-phase reactor, International Journal of Energy Research, **19**(3), pp 263-273, ISSN 0363-907X (1995)

[7] Kato Y., Nakahata J. and Yoshizawa Y., Durability Characteristics of the Hydration of Magnesium Oxide under Repetitive Reaction, J. of Materials Science. **34**, pp 475-780, ISSN 0022-2461 (1999)

[8] Kato Y., Kobayashi K. and Yoshizawa Y., Durability to Repetitive Reaction of Magnesium Oxide/Water Reaction System for a Heat Pump, Applied Therm. Eng. **18**, pp 85-92, ISSN 1359-4311 (1998)

[9] Bhatti A. S. and Dollimore D., The rates of hydration of sea water magnesias, Surface Technology **22**, pp 181-188, ISSN 0376-4583 (1984)

[10] Ervin G., Solar heat storage using chemical reactions, J. Solid State Chem. **22**, pp 51-61, ISSN 0022-4596 (1977)

Y. Kato, yukitaka@nr.titech.ac.jp