PACKED BED REACTOR DEMONSTRATION OF MAGNESIUM OXIDE/WATER CHEMICAL HEAT PUMP

Y. Kato, T. Sekiguchi, J. Ryu

Tokyo Institute of Technology
2-12-1-N1-22, O-okayama, Meguro-ku, Tokyo, 152-8550 JAPAN
Tel: 81-3-5734-2967
yukitaka@nr.titech.ac.jp

1. INTRODUCTION

Heat utilization system for low temperature waste heat at less than 100 ^{o}C has been well developed for conventional process waste heat. Because of the recent spread of decentralized cogeneration system using diesel engine, gas engine and fuel cells, a large amount of surplus exhaust heat at middle temperatures between 100 ^{o}C to 400 ^{o}C is emitted occasionally from cogeneration systems. The utilization of the middle temperature heat would be one of new valuable subjects in the energy use market. To enhance the actual total energy efficiency adding up electrical and thermal output uses for a cogeneration system, heat storage and transformation systems would be required.
The present study attempts to show the applicability of a magnesium oxide/water chemical heat pump as a means of utilizing surplus heat, enhancing the actual energy efficiency of cogeneration, and in turn reducing global carbon dioxide emissions. A chemical heat pump, which manages heat transformation via a chemical reaction, is one of system type for storing and utilizing heat energy. A decentralized cogeneration system using a chemical heat pump could be a practical application.
Chemical heat pumps that use a reversible magnesium oxide/water reaction system have been examined by Ervin (1977), Bhatti and Dollimore (1984) and Kato *et al.* (1993) to promote heat storage and energy utilization. A magnesium oxide/water chemical heat pump has been described previously, in terms of reaction kinetics using a thermo-balance (Kato *et al.*, 1993), and also in terms of thermal performance of the packed bed reactor using a laboratory-scale heat pump with reactant amount of less 2 kg (Kato *et al.*, 1995, Kato *et al.*, 1998a).
The thermo-balance experiment showed that the magnesium oxide/water chemical 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 200 ^{o}C under sub-atmospheric pressure. A new reactant made from an ultra-fine powder of magnesium oxide and purified water was found to be durable against repetitive reactions (Kato *et al.*,1998b; Kato *et al.*,1999) . A study in operating heat output under a higher pressure was also discussed using 10-100 W class output reactor and a particulate type of the new reactant (Kato *et al.*, 2003a). It was shown that a higher-pressure operation enhanced the output quality, that is, temperature of the heat pump.
In the next step, the study of a heat pump system having a practical size reactor bed would be required to demonstrate practical performance of the heat pump. Enhancement of thermal conductivity in the bed is one of the key points. Enhancement of thermal transportation performance being consistent with high-reactivity and reduction of construction cost of the heat pump system would be required for the development of commercial heat pump system. Impregnation of reactant salt into carbon expanded graphite or carbon fiber is showing good result for enhancement of thermal conductivity (Cerkvenik *et al.*, 1999, Hirata *et al.*, 2003, Critoph and Tamainot-Telto, 1997, Vasiliev, 2002, Spinner, 1992). To install high-heat conductivity material in the bed is one of the techniques. Study the use of a cupper fin for thermal conductivity enhancement in the bed had demonstrated effectiveness for the heat pump performance (Kato et al. 2003b). The cupper fin has good material for the enhancement, however, the corrosion of the material under high-temperature vapor and a difficulty of construction of heating fin structure still need improvement. Then, a carbon fiber sheet was examined for heating fin because of its high-chemical durability under vapor atmosphere, high-thermal conductivity and ease construction handling. 500 W class bench-scale heat pump installed carbon fiber sheet fin was discussed to evaluate practical thermal performance of the heat pump in this study.

2. HEAT STORAGE FOR COGENERATION

Chemical heat pump that uses a reversible magnesium oxide/water reaction system is based on the following equilibria:

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

$$H_2O(g) \Leftrightarrow H_2O(l), \qquad \Delta H^\circ_2 = -40.0\ kJ\cdot mol^{-1} \qquad (2)$$

The operation principle of the heat pump has been proposed in a previous study (Kato, *et al*., 1996). The heat pump enables thermal energy to be stored via the dehydration of magnesium hydroxide (the left direction of Eq. (1)) and releases the stored energy on demand via the hydration of magnesium oxide. The heat pump would be a unique system that can store heat at around 250-400 ^{o}C and amplify it into heats around 100-250^{o}C under a reaction pressure less 400 kPa. The advantages of the heat pump are that it can store exhaust or surplus heat generated from a cogeneration process, the reactant materials are safe, economical and environmentally friendly, and the heat can be stored for longer periods than with conventional heat storage.

3. HEAT PUMP EXPERIMENT

A bench-scale heat pump that was packed with a practical amount of reactant was examined under various operation conditions. Figure 1 shows the heat pump system. The heat pump consisted of a reaction chamber (3), water reservoir (9) and heat exchanging system (6). Both chambers were connected by a tube and stop valve. A reactor bed (1) packed in a basket vessel which was made of stainless steel mesh, with an inside diameter of 360 mm and a height of 140 mm was installed in the chamber. 6.8 kg of particle reactant of $Mg(OH)_2$ (avg. diameter 1.5 mm) was used in the bed. A spiral heating tube and carbon fiber sheet fins were set in the reactor bed. Layout of both parts in the bed is shown in Fig. 2. The heating tube was stainless steal of length of 2.1 m. The tube had 5 cm interval between a spiral turn and the next turn. A sheath heater was attached along with the tube. Quadrilateral carbon fiber fin (12 cm of height x 16 or 11 cm of width x 0.2 mm of thickness) of 28 sheets were set crossing at right angles to the tube in the bed. Heating tube cross section part in a sheet was removed previously, and the fin was set around the tubes. Averaged interval between the fins was 2cm. The reactor temperature was maintained by the sheath heater. Heat output at hydration operation was recovered by the tube circulated water in the tube as coolant media. Thermocouples were installed at some points in the reactor bed in order to measure the bed temperature change. The temperature at the middle position between fins and at the middle height (T_{m1}) was used as a representative bed temperature. The temperature on the surface of the tube (T_{ex}) was used as reference temperature of the heating at dehydration and heat exchanging at hydration.

Water vapor passed through the mesh wall of the basket and top bed surface during both reactions. The vapor was moved between the chambers through the stop valve by pressure difference alone. 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. The water level change of the reservoir during reactions was measured.

The magnesium hydroxide of the initial reactant was produced from an ultra-fine magnesium oxide powder (avg. primary particle diameter: 10 nm, Ube Material Industries, Ltd.) and purified water. The repetitive cycle operation was carried out during each experiment using the same reactant. Stable reactivity to the repetitive cycle of the reactant has been demonstrated (Kato *et al.*, 1998b). After initial removal of residual gas from the chambers using a vacuum pump, the system was driven thermally with no mechanical pump work. In the heat storage (dehydration) mode, the $Mg(OH)_2$ in the bed was dehydrated. The stop valve was closed initially. The reactor temperature was raised for dehydration by using the heater on the tube. Then, MgO and water vapor were generated by the reaction. When the stop valve was opened, the generated vapor was condensed in the water reservoir using a condenser (8) depicted in Fig. 1. The reaction progress was measured by the level meter and by the thermocouples. The stop valve was closed at the end of the reaction.

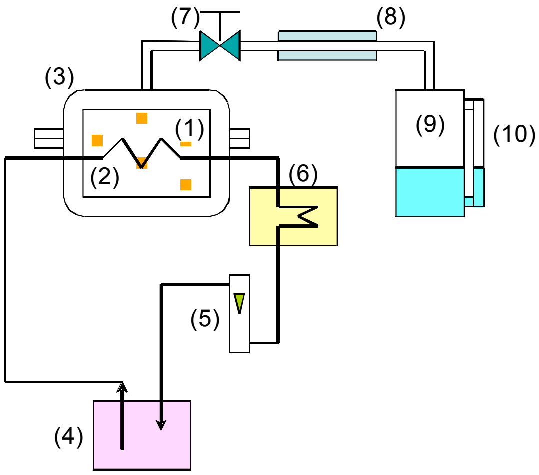


Figure 1: Laboratory-scale MgO/H_2O chemical heat pump: (1) packed bed reactor, (2) heating tube, (3) reactor chamber, (4) thermostat, (5) flow meter, (6) radiator, (7) stop valve, (8) condenser, (9) water reservoir, (10) water level meter.

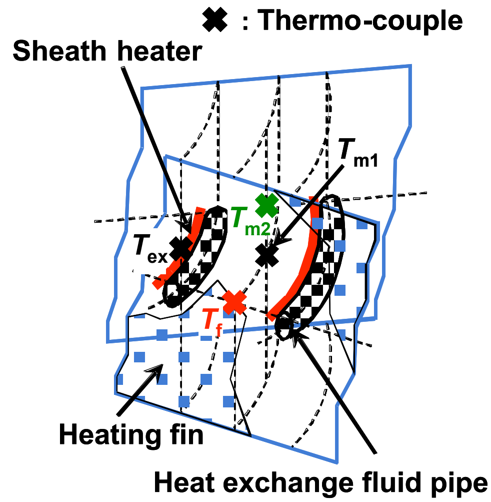


Figure 2: Cross section of reactor bed cut vertically to the radius direction

In the heat output (hydration) mode, the water reservoir was heated to generate a specified reaction vapor pressure. The reactor was maintained at a predetermined hydration temperature. After the reactor and the reservoir attained the steady state, steam generated by the reservoir was introduced into the reactor via the valve. The magnesium oxide reacted with the steam, and heat output was generated. The heat output was recovered by the heating tube circulated water coolant.
Reacted water change amount (Δm [kg]) due to the reactions was measured by the level meter. Thus, the mole reacted fraction, x [-], is defined as follows.

$$x = 1 + \frac{\left(\Delta m / M_{\mathrm{H_2O}}\right)}{\left(m_{\mathrm{Mg(OH)_2}} / M_{\mathrm{Mg(OH)_2}}\right)} \tag{3}$$

where $m_{\mathrm{Mg(OH)2}}$ [kg] and M [kg·kmol^{-1}] are the initial charged weight of magnesium hydroxide in the reactor bed and the molecular weight, respectively. The hydration experiments started from the dehydrated state. Both dehydration and hydration saturated before reaching completion under the reaction conditions (Kato *et al*., 1996). In order to obtain an objective comparison of the reaction reactivity, the mole reacted fraction change, Δx [-], is defined as follows.

$$\Delta x = x - x_{\mathrm{ini}} \tag{4}$$

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

4. RESULTS AND DISCUSSION

Heat pump operation
In dehydration operations, the heating tube surface temperature (T_{ex} [^{o}C]) was controlled as the dehydration bed temperature (T_d [^{o}C]) by the heater during dehydration operation. All of dehydration operation was proceeded at a subjective dehydration temperature of 430^{o}C under the reaction pressure (P_d [kPa]) under 20 kPa, for 5 h.
Hydration operations were examined under various conditions. The hydration results under the conditions shown in Table 1 was presented in the following discussion. $T_{ex\text{-}ini}$ [^{o}C], T_s [^{o}C] and T_{cool} [^{o}C] show the reactor bed initial

temperature measured at the point for T_{ex}, saturated temperature of supplied steam and coolant temperature at the inlet of the heating tube, respectively.

Table 1 Hydration operation conditions

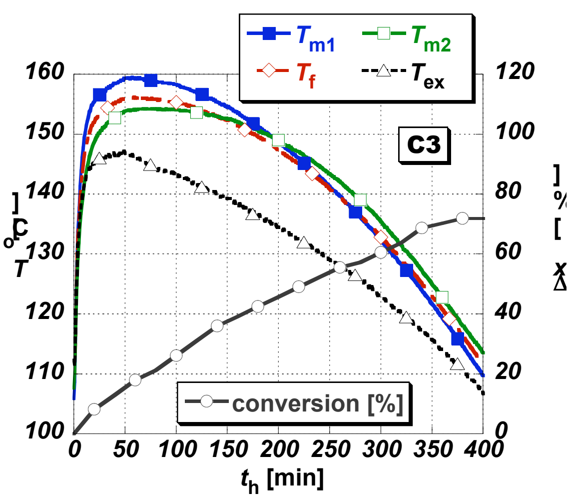
Operation conditions	$T_{ex\text{-}ini}$ [°C]	T_s [°C]	P_s [kPa]	T_{cool} [°C]
C1	120	85	58	75
C2	120	80	47	75
C3	110	85	58	75
C4	110	80	47	75

At the beginning of the hydration period, the sheath heater input of the packed bed was switched off, and the vapor was introduced into the bed rapidly from the reservoir, then hydration process was measured. Hydration output was measured till that outlet coolant temperature attained below the T_s or the bed temperature attained below 100 °C to prohibit any vapor condensation in the bed. Figure 3 shows an example of hydration operation under the C3. Bed temperatures (T_{m1} ,T_{m2}) raised rapidly around 160°C by hydration. The fin temperature (T_f) was middle between the bed temperatures and heating tube temperature (T_{ex}) in initial period, the fin would be available as a heat conduction enhancer in the period. The reacted fraction change (_x) raised almost monotonously. These changes showed that the bed was limited by thermal conduction between reactant bed and the fin.

The inner bed was kept at over 150 °C for 3 h. The exothermic hydration at the inner part proceeded slowly because of the relatively high-temperature, and the heat production rate balanced with heat dissipation by heat conduction in the inner part. Thus the inner part maintained a similar bed temperature during the period. The constancy of heat output temperature is one of the character and advantage of chemical heat storage.

Figure 4 shows the effect of hydration condition on the hydration reactivity. A higher pressure of steam a higher hydration reactivity was observed. Bed initial temperature had small effect on the reactivity in these conditions. All of the reaction conversion rose monotonously. These changes showed also that the bed was limited by thermal conduction under all conditions. Figure 5 shows bed temperature profiles of T_{m1} at hydration. The profiles have similar tendency with results in Fig. 4. The saturated steam temperature was dominant effect on the temperature change. A higher bed temperature was attained at a higher pressure, since the chemical hydration proceeded more rapidly under the higher pressure. Maximum attained temperature at 159°C was measured under the C3.

T_{m1}, which is the recoverable maximum temperature, is possible to rise at a higher vapor pressure (Kato *et al.*, 2003a). The hydration temperature is possible to be higher than one of dehydration at a high pressure. It indicates that higher-pressure reaction would realize a heat transformation operation of the heat pump. When the hydration output is used for the water reservoir heating, subsequent hydration output temperature will be higher than one of the original hydration output. For example, a hydration output over 150°C is produced by saturated vapor at 85°C in Fig. 5. When the heat output is used for water reservoir heating again, a higher pressure vapor is generated from the reservoir, and a higher heat output is produced by the vapor.



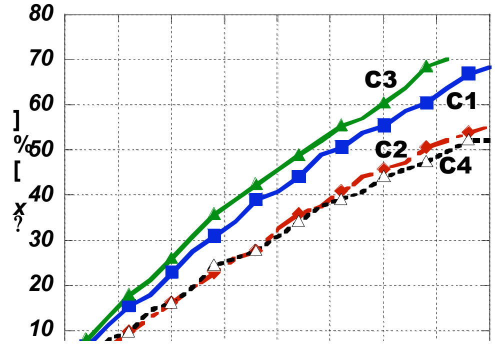


Figure 3: Hydration operation example result: C3, $T_{ex\text{-}ini}$=120°C, T_s=85°C, T_{cool}=75°C

Figure 4: Effect of reaction conditions on hydration reactivity

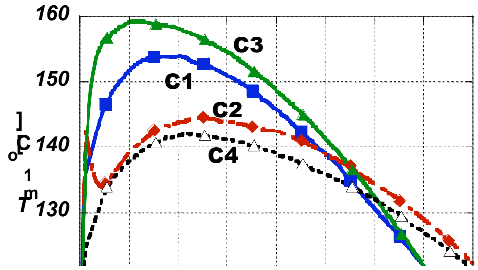


Figure 5: Bed temperature profiles at hydration

Thermal performance evaluation

The recovered heat by the heating tube was shown in Figure 6. For 100 min operation under C3 and C1, recovered heat output rate (w_{output}) of 49 and 43 W/kg-$Mg(OH)_2$ and gross heat output (q_{output}) of 296 and 244 kJ/kg-$Mg(OH)_2$ and were measured, respectively. For 200 min operation under the same conditions, q_{output} of 569 and 477 kJ/kg-$Mg(OH)_2$ and were measured, respectively. When the same amount of heat is stored by a conventional sensible heat water storage system using a temperature difference of 20°C between 70°C and 90°C, the heat output amount from water is around 83 kJ/kg. The heat storage density of the heat pump is 3-7 times that of the water storage system. The heat pump would have a possibility to develop a new market on heat storage utilization and to contribute load leveling of cogeneration system. Comparison with bed reactor performance experiment using cupper heating fin in the same reactor basket, the heat output performance of the carbon fiber fin was evaluated about 70 % of the cupper fin's one. Although the carbon fiber fin has smaller effect on thermal conductivity than the cupper fin, however, the carbon fiber sheet has high-chemical durability to the vapor atmosphere, ease character for construction handling with low-cost. Then, to use the carbon fiber sheet for thermal conductivity enhancement in the packed bed would have merit in practical use.

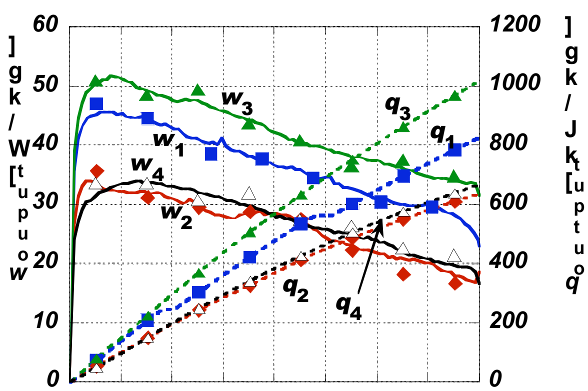


Figure 6: Heat output performance of the heat pump

5. CONCLUSION

The thermally operability of a chemical heat pump using a magnesium oxide/water system was demonstrated experimentally by a laboratory-scale heat pump installed carbon fiber sheet heating fins. Heat output above 150^{o}C by the hydration operation was measured experimentally. It was expected that the higher temperature output would be realized by a higher-pressure hydration operation and enhancement of the heat conductivity in the bed. The heat storage performance of the heat pump was sufficiently competitive with a conventional sensible heat water storage system in terms of heat storage density and output temperature. To use the fiber fin instead of cupper fin for thermal conductivity enhancement in the bed had practical merit because of its low-cost and easy handling.

REFERENCES

Aidoun, A., Ternan, M. (2002). A $CoCl_2 \cdot NH_3$ Chemical Heat Pump for Refrigeration and Heating. Proc. of Int. Sorption Heat Pump Conf., Shanghai, P. R. China, 450-456

Bhatti A. S., Dollimore D. (1984). The Rates of Hydration of Sea Water Magnesias. Surface Technology, **22**, 181-188

Cerkvenik B. A., Satzger P., Ziegler F., Poredos A. (1999). High Efficient Cycles Using CaO/H_2O and $LiBr/H_2O$ for Gas Cooling. Proc. of 6th ASME Conf. On Renewable and Advanced Energy System for the 21st Century, Hawaii, USA

Critoph R.E., Tamainot-Telto Z. (1997). Adsorption Refrigeration Using Monolithic Carbon - Ammonia Pair. Int. J. Refrigeration **20**, 2, 146-155

Ervin G. (1977). Solar Heat Storage Using Chemical Reactions. J. Solid State Chem., **22**, 51-61

Fujioka K., Sasaki K., Hirata Y.(2001). Promotion of Gas-Solid Reaction for Chemical Heat Pump by Use of Composite Particles Prepared with Expanded Graphite. Proc. of World Cong. of Chem. Eng., Melbourne, Australia, paper number 471

Hirata Y., Fujioka K., Fujiki S.(2003). Preparation of Fine Particles of Calcium Chloride with Expanded Graphite for Enhancement of the Driving Reaction for Chemical Heat Pump. J. Chem. Eng. Japan, 36(7), 827-832

Kato Y., Yamashita N., Yoshizawa Y. (1993). Study of Chemical Heat Pump with Reaction System of Magnesium Oxide/Water. Kagaku Kogaku Ronbunshu, 19, 1213-1216

Kato Y., Inoue S., Nanmoku W. and Yoshizawa Y. (1995). Kinetic Study of the Hydration of Magnesium Oxide/Water Chemical Heat Pump. Proc. of 30th Intersociety Energy Conversion, Orlando, USA, vol. 3, 17-22

Kato Y., Yamashita N., Kobayashi K., Yoshizawa Y. (1996). Kinetic Study of the Hydration of Magnesium Oxide for a Chemical Heat Pump. Applied Thermal Engineering, 16, 853-862

Kato Y., Takahashi F., Nanmoku W., Yoshizawa Y. (1998a). Heat Output Performance Study of Magnesium Oxide/Water Chemical Heat Pump. Kagaku Kogaku Ronbunshu, **24**, 840-844

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

Kato Y., Nakahata J., Yoshizawa Y.(1999). Durability Characteristics of the Hydration of Magnesium Oxide Under Repetitive Reaction. J. Materials Science, 34, 475-480

Kato Y., Sasaki K., Yoshizawa Y.(2003a). Thermal Performance Measurement of a Packed Bed Reactor of a Magnesium Oxide/Water Chemical Heat Pump. J. Chem. Eng. Japan, 36(7), 833-839

Kato, Y. (2003b). Development of a Magnesium Oxide/Water Chemical Heat Pump for Efficient Energy Storage and Utilization. Proc. of the 5th Minsk International Seminar "Heat pipes, heat pumps, refrigerators", Minsk, Belarus, 129-140

Spinner, B. (1992). Les Transformateurs Thermochimiques a Ammoniac. Proc. Symp. Solid Sorption Refrigeration, Paris, France, 145-152

Vasiliev, L. L. (2002). Solar Sorption Refrigerators with Dual Sources of Energy. Proc. of Sorption Heat Pump Conf. (ISHPC '02) , Shanghai, P. R. China, 26-33