Durable Reaction Material Development for Magnesium Oxide/Water Chemical Heat Pump

Yukitaka KATO, Tomofumi SAITO, Tsutomu SOGA,
Junichi RYU and Yoshio YOSHIZAWA
*Research Laboratory for Nuclear Reactors,
Tokyo Institute of Technology,
2-12-1-N1-22, Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

Keywords: Chemical Heat Pump, Repetitive Operation, Reaction Material Durability, Magnesium Oxide, Magnesium Hydroxide

Durable reaction material for repetitive reaction operation of a chemical heat pump that used a reversible magnesium oxide/water reaction system was discussed to enhance the heat pump performance. Because a material for the heat pump use was required to fit multi-production process, a molding method was introduced for material preparation. Some molded samples under different preparation conditions were evaluated kinetically by a thermo-balance analysis. Magnesium hydroxide prepared from ultra fine particle magnesium oxide and purified water showed enough reactivity, and also stable durability to 70 of repetitive reaction cycles. Removal of impurity was effective for durability enhancement of magnesium hydroxide made from seawater precipitated precursor. The cost of the precipitated hydroxide was less than one several tenths of the ultra fine particle material. It was demonstrated that the molded reactant made from precipitated hydroxide was applicable for multi production and cost reduction of magnesium hydroxide material for the heat pump. The thermal performance of magnesium oxide/water chemical heat pump was evaluated from experimental results.

Introduction

Chemical heat pumps have possibility to develop a new thermal energy conversion market. The thermal performance of a chemical heat pump depends on the reaction system used in it. Solid–gas reaction system is expected as candidate for thermal utilization because of high-energy storage density, reaction reversibility with no side reaction, and small work for reactant separation.

Magnesium oxide has possibility for thermal utilization also as an inorganic oxide (Ervin, 1977). A chemical heat pump using a reversible magnesium oxide/water reaction system has been examined to promote thermal energy utilization (Bauerle and Chung, 1980; Bhatti and Dollimore, 1984). The heat pump examined in this study is based on the following chemical reactions:

This heat pump makes it possible to store and transform thermal energy on demand using both the hydration of magnesium oxide (MgO) and the dehydration of magnesium hydroxide (Mg(OH)₂). A previous study showed that the heat pump could be used as a heat amplifier to transform a heat source at 70–90°C to one at 100–150°C by storing heat at a temperature of 350°C (Kato *et al.*, 1993). The pump is expected to contribute to load leveling in electrical power generation systems by storing surplus electricity generated during the night as heat energy and re-supplying it to users during peak-demand periods. The heat pump is also effective for co-generation system by utilizing surplus heat in the exhaust gas generated from a co-generation engine.

Previous studies demonstrated that the hydration of MgO controlled the overall rate of heat pump operation. A rate equation was proposed for hydration based on an experimental kinetic study using a thermo-balance (Kato *et al.*, 1996), and the feasibility of the heat pump was discussed. Heat pump operation was demonstrated using a laboratory-scale heat pump with a packed reactor bed (Kato *et al.*, 2001, 2003). The pump had a heat output of up to 100 W/kg. The results showed that the heat pump had practical possibility.

Both hydration of MgO and dehydration of Mg(OH)₂ are achieved during one cycle of operation. For practical utilization of the heat pump, more than 100 repetitions of the cycle are required. Therefore,

Received on July 13, 2007; accepted on August 23, 2007.
Correspondence concerning this article should be addressed to Y. Kato (E-mail address: yukitaka@nr.titech.ac.jp).
Presented at International Symposium on Innovative Materials for Processes in Energy Systems, IMPRES, Kyoto, October, 2007.

Table 1 Physical properties of V05Gs

Sample	Pre-cursor	Moisture of precursor paste [%]	BET specific surface area [m ² ·g ⁻¹]	Apparent particle diameter [μm]
V05G-40	UFP MgO	40	29.4	5.8
V05G-45		45	27.1	5.8
V05G-50		50	32.4	5.8

the reaction material chosen for the heat pump must be capable of enduring repetitive reaction. The reaction cycles for both hydration and dehydration of some MgO materials has been examined. MgO material using ultra fine powder (UFP) of magnesium oxide as the precursor showed durability to repetitive reaction of 24 cycles was expected as one of appropriate materials for the heat pump (Kato *et al.*, 1998). Reactant for the heat pump is preferred to be produced from mass production process for conventional use. However, the ultra fine material had been prepared by handmade and complicated processes, that is, produce of dried solid mass Mg(OH)₂, crash of the mass into particles, and passing materials into sieve for obtaining of desired diameter fraction particles with low-yield. It was required to develop production process matching with mass-production for market development of the heat pump with high-yield and stable production. Then, a molding method using an extruder was introduced in the material preparation because the method was expected to be suitable for mass production and realize homogeneous quality of product. Molded materials were prepared in some production conditions and examined durability under repetitive cycles longer than previous experiment in a thermo-balance in this study.

Cost reduction of material is also one of important terms for the heat pump material. UFP of magnesium oxide needs special vacuum chamber for production and fairly large energy consumptions for raw metal magnesium and UFP production processes, and the cost is generally 10,000 JPY/kg (=80–90 USD/kg). Change from expensive material of the UFP MgO into lower cost one of conventional MgO was preferable because market price of the latter is less one several tenths of the former. It had been concluded that impurity reduction from row material was effective for durability enhancement of MgO (Kato *et al.*, 1999). Then, a material made by removal of impurity from conventional MgO was examined for durability enhancement to repetitive cycle operation. Contribution of the developed materials to the chemical heat pump was evaluated from measured experimental results.

1. Experimental

1.1 Materials

UFP and seawater precipitated MgO materials were used as precursors of experimental reactant of

Fig. 1 V05G-40 of molded reactant of Mg(OH)₂ (diameter of 1.9 mm and length of 5–10 mm)

Mg(OH)₂, respectively. The sample materials of the Mg(OH)₂ were prepared by the cooperation with UBE Material Industries, Ltd.

1.1.1 UFP Mg(OH)₂ UFP MgO (primary particle diameter of 50 nm, UBE Material Industries, Ltd.) was used as high purity material of precursor. The precursor was hydrated with purified water. After hydration, the pasty products of Mg(OH)₂ were dried to a level of some moisture and were molded in a cylindrical shape by an extruder. The moldings were dried completely later. The cylindrical molded materials of Mg(OH)₂ had a diameter of 1.9 mm and lengths of 5–10 mm. Degree of moisture of the pasty products was effective for the reactivity of the molded material and load of the extruder. Pasty products having water concentration of 40, 45 and 50 wt% were used for the molding reactant preparation. The moldings were named as V05G-40, V05G-45 and V05G-50, respectively. Physical properties of them are shown in **Table 1**. **Figure 1** shows appearance of sample of the V05G-40. Apparent particle diameter was measured by laser diffraction.

1.1.2 Seawater precipitated Mg(OH)₂ A conventional Mg(OH)₂ (L3G_{raw}, UBE Material Industries, Ltd.) extracted from seawater by precipitation method was used for another precursor. Because the material is made from plentiful seawater, the price of around 100 JPY/kg (=less 1 USD/kg) is clearly more cost-effective than UFP one. The chemical heat pump would convert waste heat into value added thermal energy.

Table 2 Impurity concentrations of Mg(OH)₂ materials

Sample	Purity of MgO [%]	Concentration [ppm]							BET specific surface area [m ² ·g ⁻¹]	Apparent particle diameter [μm]
		Ca	Si	Fe	Al	B	Cl	S		
L3G _{raw}	97.5	1100	610	200	200	42	600	2800	13	1.8
L3G _{treat}		640	330	140	140	43	70	633	5	1.9
V05G-40	>99.98	2	7	13	<1	<1	15	4	29.4	5.8

The heat pump itself is required to be low-cost. The cost reduction of charged reaction materials for the heat pump is a keen point for practical market development of the heat pump. Then, durability improvement of conventional material of L3G_{raw} was examined in this study as following. Impurity in L3G_{raw} was removed by calcination treatment.

Resulted MgO material was hydrated into Mg(OH)₂ and molded into a cylindrical form in the same size and manners of V05Gs, and named as L3G_{treat}. Molded L3G_{raw} in the same cylindrical form was also prepared as reference material to compare with L3G_{treat}. Impurity concentrations of L3G_{raw}, L3G_{treat} and V05G-40 are shown in **Table 2**.

1.2 Kinetic measurement experiment

The material reaction durability was measures by a thermo-balance (TGD-9600, ULVAC-RIKO, Inc.) under a flow system. A material sample, which was just molded raw material, of about 15 mg placed in a platinum cell was installed in the reactor of the balance. The temperature at the bottom of the cell, which was considered to be the reaction temperature, was measured by a thermocouple and controlled by an electric furnace. Each repetitive experiment was proceeded as following sequence.

During dehydration of Mg(OH)₂, argon gas of 100 mL-STP·min⁻¹ was flown in the balance to remove generated vapor at a temperature of 350°C (*T_d*). During hydration of MgO, argon gas of 45 mL-STP·min⁻¹ as a carrier gas was passed into a water evaporator in which constant amount of 33.4 μL·min⁻¹ of purified water was supplied from a micro-feeder. The water vapor and gas mixture under a partial vapor pressure (*P_h*) of 48 kPa, which corresponds to a saturated vapor pressure at a temperature (*T_s*) of 80°C, was supplied in the balance for the hydration at a temperature (*T_h*).

The reactor's mass change due to the reaction, Δ*m* [g], was caused by the movement of vapor. Thus, the mole reacted fraction, *x* [—], is defined as follows.

$$x = 1 + \frac{(\Delta m / M_{\text{H}_2\text{O}})}{(m_{\text{Mg(OH)}_2} / M_{\text{Mg(OH)}_2})} \quad (3)$$

where *m*_{Mg(OH)₂} [g], *M*_{Mg(OH)₂} [g·mol⁻¹] are initial charged mass of Mg(OH)₂ in the cell and the molecu-

Table 3 Hydration performances of V05Gs in the first cycle

Sample	Δ <i>x</i> ₁₂₀ [mol%]	ρ [g·cm ⁻³]	ρΔ <i>x</i> ₁₂₀
V05G-40	65.7	0.485	0.319
V05G-45	64.2	0.458	0.294
V05G-50	66.1	0.434	0.287

lar mass of Mg(OH)₂. 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* = 0.1. Hydration saturated at around *x* = 0.7. In order to obtain an objective comparison of the reaction reactivity, the mole reacted fraction change, Δ*x* [mol%], is defined as follows.

$$\Delta x = x - x_{\text{ini}} \quad (4)$$

where *x*_{ini} is the initial reacted fraction of hydration in a reaction cycle.

2. Results and Discussion

2.1 Ultra fine particle materials

The first hydration reactivities of V05Gs were compared by a thermo-balance measurement under condition of *T_h* = 110°C, *P_h* = 48 kPa and *T_s* = 80°C. Attained reacted fraction changes in hydration after 120 min, Δ*x*₁₂₀, and reaction densities, ρΔ*x*₁₂₀ [g·cm⁻³], are shown in **Table 3**. The result indicated that lower moisture would be applicable for higher reaction density. However, the extruder had lower limitation for moisture, because higher viscosity at lower moisture paste made difficulty for stable extrusion operation. Then, the V05G-40 was chosen as the most applicable reactant in the materials because it had the highest reaction density and the moisture value was the lowest limitation for stable extrusion process in the process.

The durability to the repetitive cycle of V05G-40 was examined for 70 cycles under *T_h* = 110°C, *P_h* = 48 kPa and cyclic hydration time (*t_h*) of 60 min. It was presumed that the chemical heat pump was operated once a day storing co-generation exhaust gas in winter season and for two months, then, the cycle times was

Fig. 2 Hydration reactivity change during repetitive cycle of 70 times for V05G-40

targeted. The result of the hydration of the material in the cyclic operation is shown in **Figure 2**. The reactivity decreased during initial less than 5 cycles, but remained constant from 10th to 70th cycle. SEM photographs of the hydrated materials are shown in **Figure 3**. Agglomeration between primary particles was developed gradually from original material in Figure 3(a) to 70th cycle in Figure 3(c). However, from the result of Figure 2, it was supposed that reaction in primary particle limited overall reaction and the agglomeration did not effect on the hydration reaction rate during repetitive cycle. The bulk shape of the molded particle was kept well after the cyclic operation. V05G-40 was expected to have some extent of repetitive operation durability. On the other hand, a methodology for protection to the agglomeration still is needed for longer repetitive operation.

2.2 Precipitated materials

The hydration reactivity of materials of $L3G_{\text{raw}}$, $L3G_{\text{treat}}$ and V05G-40 in repetitive cycle were compared under $T_h = 120^\circ\text{C}$, $P_h = 48 \text{ kPa}$ as shown in **Figure 4**. $L3G_{\text{treat}}$ had higher reactivity compared with $L3G_{\text{raw}}$ in all over cycles, and similar durability with V05G-40 in the initial 11 cycles. $L3G_{\text{treat}}$ was eliminated well chloride and sulfur ions from precursor of $L3G_{\text{raw}}$. Chloride ion tends to form magnesium chloride, MgCl_2 , with magnesium ion.

$\text{Mg}(\text{OH})_2$ and MgO have a hexagonal and square crystal structure, respectively (Itatani, 1988). The reactive nuclei production by the structure change from $\text{Mg}(\text{OH})_2$ to MgO has positive effect to hydration reactivity enhancement (Kato *et al.*, 1999). Stable material formations from magnesium ion and chloride or sulfur ions had possibility to inhibit the nuclei production, to enhance the agglomeration and to reduce re-

Fig. 3 SEM photographs of hydrated materials of V05G-40 after cyclic pperations: (a) original material; (b) after 2nd cycle; (c) after 70th cycle

petitive durability. V05G-40 was superior to $L3G_{\text{treat}}$ after larger cycle times. It showed that agglomeration of particles in V05G-40 was more moderate than $L3G_{\text{treat}}$. However, the figure shows that impurity elimination is effective for durability enhancement. Cost of the precipitated material precursor is less than one several tenths of one of UFP. Although the $L3G_{\text{treat}}$ tended to be inferior to V05G-40 in repetitive durability, the

Fig. 4 Hydration reactivity in repetitive cycle of $\text{Mg}(\text{OH})_2$ made from precursors of precipitated and UFP MgO

former had obviously cost-effectiveness compared with later. It was prospected that durability improvement of the former material by impurity control was more cost-effective for practical market development of the heat pump. Identification of impurities which inhibited repetitive durability and removal of them from precipitated material were useful methodologies for the development of cost effective and durable materials.

2.3 Effect of dehydration on durability

High temperature process of dehydration has also possibility to affect reduction of durability. The effect of dehydration duration time ($t_{\text{d-dura}}$) on repetitive durability was measured for $\text{L3G}_{\text{treat}}$. Repetitive operations of 15 cycles each were measured under $t_{\text{d-dura}} = 15, 25, 35$ and 55 min, respectively. Dehydration of a sample was observed until almost initial 10 min, and the sample was left under the dehydration condition until the end of the duration time. Hydration reactivity changes of every cycle are shown in **Figure 5**. After initial 3 cycles, existence of optimum dehydration duration time was observed. Enhancement of reactivity between $t_{\text{d-dura}} = 15$ min and 25 min means that reaction duration time extension has positive effect on dehydration in the period. Decrease of reactivity from $t_{\text{d-dura}} = 35$ min to 55 min was caused by progress of agglomeration of primary particles.

As mentioned in the Section 2.2, the reactive nuclei production by the structure change from $\text{Mg}(\text{OH})_2$ to MgO is effective for hydration reactivity enhancement. In the dehydration process, it was presumed that the reactive nuclei were produced until initial 10 min by the dehydration, and the agglomeration accompanying the nuclei disappearance was proceeded mainly after 35 min. The time period between $t_{\text{d-dura}} = 15$ and 25 min was assumed to be some transient time for structure change from dehydrated raw structure state to agglomeration state. It was assumed that the structure

Fig. 5 Effect of dehydration time on repetitive durability for $\text{L3G}_{\text{treat}}$

change at the transient time was positive for the hydration reactivity enhancement, and then Δx was enlarged between $t_{\text{d-dura}} = 15$ min and 25 min. It was inferred that structural water relocation in the material was one of reasons for the structure change in the period.

Figure 5 depicted the effect of dehydration duration time on repetitive heat pump operation and the existence of the optimal dehydration time. The specification of the structure change mechanism needed much more detailed analysis for temporal structure change in the dehydration.

2.4 Thermal performance of the materials

At hydration after 70 cycles in the condition of Figure 2, it was estimated from the experimental result that V05G-40 had a gross output of 725 kJ/kg and 315 kJ/L for 60 min operations. 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 and 90°C , the heat output amount from water is around 83 kJ/kg . The heat storage density of the heat pump is estimated as 9 times that of the water storage system. The chemical heat pump would have a possibility to develop a new market on heat storage utilization and to contribute load leveling of cogeneration system.

Conclusions

Durable reaction materials for repetitive reaction operation of a chemical heat pump that used a reversible magnesium oxide/water reaction system were discussed to enhance the heat pump performance. Molded

process for materials was expected to be suitable for multi-production method. A molded material made from ultra fine particle MgO which contains high-purity MgO over 99.8% of concentration had repetitive durability on 70 cycle repetitive operation. Impurity reduction from seawater precipitated $\text{Mg}(\text{OH})_2$ was effective on enhancement of repetitive durability operation. The cost of the precipitated hydroxide reduced impurities was less than one several tenths of the ultra fine particle material. A molded reactant made from the precipitated hydroxide was applicable for multi production and cost reduction of magnesium hydroxide material for the practical development of the heat pump. The thermal performance of magnesium oxide/water chemical heat pump assumed to use the material based on the ultra fine particle was sufficiently competitive with a conventional sensible heat water storage system in terms of heat storage density and output temperature.

Acknowledgements

Authors greatly thank to Mr. Yuzo Kato, UBE Material Industries, Ltd. and the company itself for technical supports on the preparation of the materials.

Nomenclature

M	=	molecular mass	[g/mol]
$m_{\text{Mg}(\text{OH})_2}$	=	initial charged mass of $\text{Mg}(\text{OH})_2$ in the cell	[g]
P	=	pressure	[Pa]
T	=	temperature	[°C]
t	=	reaction time	[min]
x	=	mole reacted fraction change	[—]
x_{ini}	=	initial reacted fraction of hydration in a reaction cycle	[—]
Δm	=	mass change of measured sample	[g]
Δx	=	reacted fraction change	[mol%]

Δx_{120}	=	attained reacted fraction change in hydration after 120 min	[mol/mol]
ρ	=	apparent material density	[g·cm ⁻³]

<Subscript>

h	=	hydration
d	=	dehydration
d-dura	=	duration of dehydration
s	=	saturated vapor

Literature Cited

- Bauerle, G. and D. K. Chung; "Storage of Thermal Energy in Inorganic/Hydroxide," Proc. of Int. Seminar on Thermochemical Energy Storage, pp. 205–246, Stockholm, Sweden (1980)
- Bhatti, A. S. and D. Dollimore; "The Rates of Hydration of Sea Water Magnesias," *Surf. Technol.*, **22**, 181–188 (1984)
- Ervin, G.; "Solar Heat Storage Using Chemical Reactions," *J. Solid State Chem.*, **22**, 51–61 (1977)
- Itatani, K., K. Koizumi, F. S. Howell, A. Kishioka and M. Kinoshita; "Agglomeration of Magnesium Oxide Particles Formed by the Decomposition of Magnesium Hydroxide," *J. Mater. Sci.*, **23**, 3405–3412 (1988)
- Kato, Y., N. Yamashita and Y. Yoshizawa; "Study of Chemical Heat Pump with Reaction System of Magnesium Oxide/Water," *Kagaku Kogaku Ronbunshu*, **19**, 1213–1216 (1993)
- Kato, Y., N. Yamashita, K. Kobayashi and Y. Yoshizawa; "Kinetic Study of the Hydration of Magnesium Oxide for a Chemical Heat Pump," *Appl. Therm. Eng.*, **16**, 853–862 (1996)
- Kato, Y., K. Kobayashi and Y. Yoshizawa; "Durability to Repetitive Reaction of Magnesium Oxide/Water Reaction System for a Heat Pump," *Appl. Therm. Eng.*, **18**, 85–92 (1998)
- Kato, Y., J. Nakahata and Y. Yoshizawa; "Durability Characteristics of the Hydration of Magnesium Oxide under Repetitive Reaction," *J. Mater. Sci.*, **34**, 475–480 (1999)
- Kato, Y., A. Minakami, G. Li and Y. Yoshizawa; "Operability of a Thermally Driven Magnesium Oxide/Water Chemical Heat Pump," *Can. J. Chem. Eng.*, **79**, 536–541 (2001)
- Kato, Y., K. Sasaki and Y. Yoshizawa; "Thermal Performance Measurement of a Packed Bed Reactor of a Magnesium Oxide/Water Chemical Heat Pump," *J. Chem. Eng. Japan*, **36**, 833–839 (2003)