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Composite block of magnesium hydroxide – Expanded graphite for chemical heat storage and heat pump

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HIGHLIGHTS

- A composite material of expanded graphite and $Mg(OH)_2$ has been developed (EM8).
- Thermal conductivity of EM8 was measured, resulting higher than that of $Mg(OH)_2$.
- An EM8 cylindrical block was manufactured for utilization in a packed bed reactor.
- EM8 block had superior thermochemical performances than a bed of $Mg(OH)_2$ pellets.
- Hydration in EM8 block is controlled by mass transfer for $P_h < 101$ kPa.

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ABSTRACT

The chemical heat storage/chemical heat pump technology (CHS/CHP) based on the reversible gas–solid chemical reactions between magnesium oxide, water, and magnesium hydroxide ($MgO/H_2O/Mg(OH)_2$) requires enhanced thermal conductivity for the packed bed reactors. A composite material of expanded graphite (EG) and $Mg(OH)_2$, EM8, was prepared. $Mg(OH)_2$ and EG, used in the preparation of EM8, were mixed at the optimal mass mixing ratio of 8:1. EM8 was then compressed into a cylindrical block with dimensions matching that of the reactor of a CHP apparatus (diameter $\phi_{reactor} = 48$ mm, height $z_{reactor} = 48$ mm). The dehydration and hydration reactions, corresponding to the heat storage and heat output mode of the CHP, were carried out using the apparatus by inserting the EM8 block directly into the reactor. The results were compared with those obtained under the same reaction conditions by filling the reactor with a packed bed of $Mg(OH)_2$ pellets. The results show that after 120 min of dehydration at 400 °C, the EM8 block had a volumetric heat storage ($q_{d,v}$) of 747 MJ m_{bed}^{-3}, while that for the bed of $Mg(OH)_2$ pellets was 502 MJ m_{bed}^{-3}. After 60 min of hydration at water vapor pressure of 361 kPa, the EM8 block had a gross heat output ($q_{h,v}$) of 911 MJ m_{bed}^{-3}, while that for the bed of $Mg(OH)_2$ pellets was 497 MJ m_{bed}^{-3}. Kinetic analysis for the hydration reaction indicated that in the EM8 block, the hydration rate was controlled by mass transfer for $P_h < 101$ kPa, while it was controlled by heat transfer for $P_h > 101$ kPa.

1. Introduction

Chemical heat storage and chemical heat pump (CHS/CHP) systems are based on solid–gas reversible reactions, and are candidates for storing and reutilizing heat from a large variety of sources characterized by different temperature levels. They can therefore be useful for a large variety of applications such as deep freezing, residential space heating and cooling, storage of solar energy, and storage of industrial waste heat. Reversible chemical reactions have, in general, a larger heat storage capacity than phase changing materials [1–4]. The materials commonly used for the chemical reactions are hygroscopic salts [5,6], zeolite [7,8] or oxide/hydroxides [9,10]. In this work, a magnesium oxide (MgO) water (H_2O) CHP system was analyzed. Its principle is based on a reversible chemical reaction, as demonstrated by Y. Kato et al. [11,12]. The reversible chemical reaction can be expressed as follows:

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s) \quad \Delta H_r^\circ = -81.0 \text{kJ mol}^{-1} \qquad (1)$$

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$$H_2O(g) \leftrightarrow H_2O(l) \quad \Delta H^{\circ}_{pc} = -41.0 \text{kJ mol}^{-1} \tag{2}$$

The forward in (1) is that of MgO hydration; it is an exothermic reaction and corresponds to the heat output (or heat pump) mode. The backward reaction in (1) is that of $Mg(OH)_2$ dehydration; it is an endothermic reaction and corresponds to the heat storage mode. In general, CHS/CHP materials are characterized by low values of thermal conductivity. To overcome this issue, new composites were developed by mixing CHS/CHP materials with another material characterized by higher thermal conductivity. Expanded Graphite (EG) is a well know material used as heat transfer enhancer for CHS/CHP materials. S. Mauran et al. developed an impregnation method for $MnCl_2$ with EG [13] and succeeded in the operation of a prototype machine for solar heating and cooling [14]. K. Fujioka et al. [15] utilized EG for the preparation of a composite of $CaCl_2$, while L.G. Gordeeva et al. investigated a composite of EG and LiBr [16]. In a previous work [17], a new composite material, named EM, was prepared by mixing expanded graphite (EG) with $Mg(OH)_2$ powder in water. It was observed experimentally that EM pellets (diameter $\phi = 7$ mm, average thickness $l = 3.5$ mm) accelerated the dehydration and hydration reactions in a packed bed reactor of a CHP apparatus. It was also determined in a previous study [18] that the optimal mass mixing ratio $Mg(OH)_2$: EG [g : g] for the preparation of EM was 8:1, compared to other mixing ratios reported previously (16:1 and 4:1). This particular EM (referred to EM8 hereafter) ensured large thermal conductivity in the packed bed reactor and a sufficient volumetric heat storage capacity, $q_{d,v}$ [MJ m^{-3}_{bed}], which was, however, still lower than the $q_{d,v}$ achievable by filling the reactor with a packed bed of $Mg(OH)_2$ pellets (diameter $\phi_{pellet} = 2$ mm, average length $l_{pellet} = 10$ mm). By increasing the density of the packed bed of EM8 tablets, it was possible to achieve a $q_{d,v}$ comparable to that of a packed bed of $Mg(OH)_2$ pellets [19]. However, thermal conductivity in the packed bed reactor can be increased further and the contact between the bed materials and surface for heat exchange can be improved. This allows maximizing the benefits achievable with the utilization of EG as a thermal conductivity enhancer and take advantage of the moldability of EG. The objective of this work was to manufacture and operate an EM8 composite block that fit within the reactor of the CHP apparatus. In these experiments, the packed bed corresponded to an EM8 block that completely filled the reactor (diameter $\phi_{reactor} = 48$ mm, height $z_{reactor} = 48$ mm). The rate of dehydration and hydration were determined experimentally by measuring the change in the mass of the reactor as a function of reaction time. The thermochemical performance parameters (volumetric heat storage capacity $q_{d,v}$ [MJ m^{-3}_{bed}], volumetric gross heat output $q_{h,v}$ [MJ m^{-3}_{bed}], and mean heat output rate, $w_{mean,v}$ [kW m^{-3}_{bed}]) were calculated from the experimental results and compared with the performance of a packed bed of $Mg(OH)_2$ pellets. In addition, the thermal conductivities of a slab specimen of EM8 were measured and compared with those of $Mg(OH)_2$ (as a slab specimen and as a bed of pellets). Those measurements were useful in quantifying the enhancement in thermal conductivity achieved with the direct utilization of the EM8 block in the packed bed reactor apparatus.

2. Experimental

2.1. Preparation of EM composite material

$Mg(OH)_2$ pellets (diameter $\phi_{pellet} = 2$ mm, average length $l_{pellet} = 10$ mm, MH-V05G, UBE Material Industries, Japan) [20,21] were used as precursors for preparing the EM composite. EG was obtained from graphite flakes (SS-3, Air Water, Inc., Japan) after thermal treatment (700 °C for 10 min) in an electric muffle furnace under atmospheric conditions. The EM8 composite was prepared as follows:

1. $Mg(OH)_2$ pellets (64.83 g) were loaded in a plastic bottle (1 L) and crushed by rotating in a mill for 24 h. Demineralized water (approx. 500 mL) was added to the bottle to obtain a $Mg(OH)_2$ slurry.
2. To aid the milling and stirring process, a pestle (ceramic, length $l = 10$ cm, diameter $d = 2$ cm) was inserted into the bottle. A milling time of 24 h was found to be sufficient for crushing all the $Mg(OH)_2$ pellets.
3. The amount of EG (8.09 g) was added to the bottle containing the $Mg(OH)_2$ slurry to make EM8.
4. To homogenize the EM8 slurry, the bottle was rotated at the minimum speed in the mill for 3 min.
5. The homogeneous EM8 slurry was then placed inside a Pyrex beaker and dried in an electric oven at 95 °C for 2 days.

From a total initial weight of $Mg(OH)_2$ and EG, corresponding to 72.92 g, the final amount of EM8 obtained was 70.93 g. In other words, 1.99 g of EM8 was lost during the preparation (by attaching to either the beaker or the mold's surface). As the EM8 is homogeneously mixed, it is considered that the amount of lost EM8 was characterized by the original mass mixing ratio used for the EM8 preparation. In particular the ratio between the mass of $Mg(OH)_2$ and the total amount of EM is $r_{mix} = 8.01$. Therefore, as the mass of the EM8 block is 70.93 g, the amount of $Mg(OH)_2$ in the block corresponds to $8.01/(8.01+1) \times 70.93\,g = 63.05$ g. The preparation of the EM8 block is shown in Fig. 1. After loading the dried EM8 into the mold pipe (diameter 48 mm), it was compressed with a piston by using a pneumatic press. The final dimensions of the EM8 block were diameter ($\phi_{EM8\ block}$) = 48 mm and height ($z_{EM8\ block}$) = 40 mm. The density ($\rho_{EM8\ block}$) was found to be 1.022 g cm^{-3}. The EM8 block was then loaded into the reactor, as shown in Fig. 1(c). A screwdriver was used to make a hole through the EM8 block for inserting the thermocouple (Fig. 1(d)).

Experiments comprised 27 cycles of dehydration at 400 °C and hydration at a certain pressure P_h [kPa]. The results obtained for the EM8 block were compared with those obtained from experiments on a packed bed of $Mg(OH)_2$ pellets. Table 1 shows the properties of a packed bed of $Mg(OH)_2$ pellets and those of the EM8 block fitted within the experimental reactor.

2.2. Experimental apparatus and procedure

Fig. 2 shows a schematic diagram of the CHP experimental apparatus. It is an assembly of a reaction chamber and a water reservoir, connected by heated tubes and stop valves. The reactor containing the packed bed of $Mg(OH)_2$ pellets (or the EM8 block) was placed at the center of the vacuum chamber, as shown in Fig. 3. Temperature at the center of the reactor and on its internal wall surface was monitored by two thermocouples, T_{center} and T_{wall}, lying on the horizontal barycentric plane of the packed bed, respectively. Heat for $Mg(OH)_2$ dehydration was supplied through a sheath heater surrounding the reactor's external wall surface. The chamber was mounted on an electric balance: the reactor's weight changed because of the movement of water vapor from the packed bed to the water reservoir and vice versa during the reactions. The experiment consisted of two chemical reactions operated cyclically, starting with dehydration. In the dehydration experiment, the apparatus (including piping, reaction chamber, and packed bed) was at first preheated at a temperature of 120 °C. The condensation temperature in the water reservoir was maintained at 20 °C using a water chiller. In this manner, the dehydration pressure P_d was fixed at 2.3 kPa. During dehydration, the water reservoir was used for