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Thermochemical performance of magnesium hydroxide–expanded graphite pellets for chemical heat pump

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HIGHLIGHTS

- Composite EM was developed by mixing expanded graphite and $Mg(OH)_2$.
- EM pellets had higher dehydration and hydration reactivity than pure $Mg(OH)_2$ pellets.
- Homogeneous temperatures were measured in EM-packed beds.
- EM achieved a higher final reaction conversion than pure $Mg(OH)_2$ pellets.
- Dehydration rates were a function of EM mass mixing ratio.

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ABSTRACT

Expanded graphite (EG) was used to enhance the thermal conductivity in the packed bed reactors of magnesium oxide–water (MgO–H_2O) chemical heat pumps (CHP). An expanded graphite–magnesium hydroxide composite (EM) was obtained by mixing a precursor CHP material of magnesium hydroxide ($Mg(OH)_2$) powder and EG. The composite was pelletized to achieve a diameter (ϕ) of 7.1 mm and thickness (l) ranging of 3.5–4.5 mm. $Mg(OH)_2$ dehydration and MgO hydration in the EM pellets were investigated on the packed bed reactor of a 100-W-scale CHP experimental apparatus. The temperatures measured in the packed beds of the EM pellets, as well as the dehydration and hydration kinetics, were compared with the results obtained using a packed bed of pure $Mg(OH)_2$ pellets ($\phi = 1.9$ mm, $l = 5$–10 mm). The thermochemical performances of the EM pellets were analyzed as a function of the mass mixing ratio of $Mg(OH)_2$ to EG (4:1, 8:1, and 16:1) used for preparing the EM. In both dehydration and hydration, the EM pellets showed a higher reaction rate and more homogeneous temperature distribution in the packed bed than did the pure $Mg(OH)_2$ pellets. Consequently, a greater final material conversion was achieved. A higher reactivity enhancement was measured with the addition of a greater quantity of EG in the EM preparation. From the experimental results, it was calculated that the bed comprising EM pellets (having a mass mixing ratio of 8:1) had a heat-storage capacity of 881 $kJ/kg_{Mg(OH)_2}$, gross heat output of 714 kJ $kg_{Mg(OH)_2}$, and mean power output rate of 132 $W/kg_{Mg(OH)_2}$. These values were higher correspondingly than the 755, 505, and 94 $W/kg_{Mg(OH)_2}$ values calculated for the bed comprising pure $Mg(OH)_2$ pellets. It was demonstrated that the EM pellets had higher reactivity than pure $Mg(OH)_2$ pellets because of their higher thermal conductivity.

1. Introduction

Over the past few decades, there have been many discussions on improving waste heat-recovery technologies by using thermochemical processes such as a chemical heat pump (CHP) [1]. These systems consist of solid–gas equilibrium reactions, for instance, $CoCl_2$–NH_3 [2] and CaO–H_2O [3] among the many available couples. A major difficulty faced during the operation of such reactions is the result of the low thermal conductivity of the employed materials. In order to efficiently supply or remove the heat of reaction, a material with high thermal conductivity and a tight contact between the material and the surface of the heat exchanger are required. This means that even if such materials can, in principle, recover and reuse waste heat, the design of the packed bed reactor for the corresponding CHP could be large and impractical. Therefore, improving the thermal conductivity of the materials is crucial

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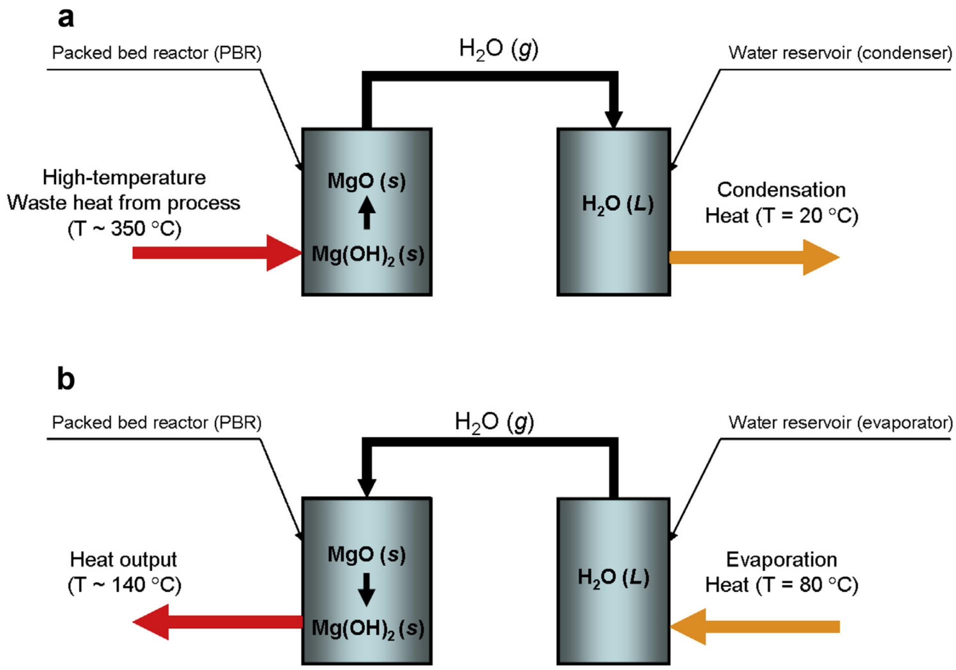

Fig. 1. $MgO-H_2O$ chemical heat pump cycle: a) dehydration and b) hydration. a): Dehydration (heat-storage mode): $Mg(OH)_2$ (s) → MgO (s) + H_2O (g). b): Hydration (heat-output mode): MgO (s) + H_2O (g) → $Mg(OH)_2$ (s).

for enhancing reactor performance. To this end, carbon-based materials have been revealed as good candidates [4]. Several mixing methods and impregnation techniques have been developed for using carbon fibers and [5] and expanded graphite (EG) [6] as thermal conductivity enhancers for CHP materials. In particular, composites of EG and CHP materials have already been investigated in the compressed state; they have exhibited high values of thermal conductivity similar to that shown by Fujioka et al. [7] and Critoph et al. [8]. Another important property of a composite material with EG is its moldability. It is possible to shape the composite and minimize the heat-transfer resistance through contact between the composite material and the heat-exchanger surfaces in a CHP reactor.

In this work, EG was used to improve the thermochemical performance of a magnesium oxide (MgO) and water (H_2O) CHP. Its principle is based on a reversible chemical reaction, as demonstrated by Kato et al. [9]. The equilibria are expressed as follows:

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

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

The leftward reaction in (1) is **$Mg(OH)_2$ dehydration**. It is an *endothermic* reaction and corresponds to the heat-storage mode of the CHP system, as shown in Fig. 1(a).

The rightward reaction in (1) is **MgO hydration**. It is an *exothermic* reaction and corresponds to the heat-output mode of the CHP system, as shown in Fig. 1(b).

The dehydration reaction occurs at temperature higher than 350 °C. Therefore, its application is attractive for the recovery of waste heat in industrial processes such as steel making [10], or for the storage of thermal energy and load leveling in thermal power stations, whether fueled by fossil fuels [11], nuclear [12], or solar energies [13,14]. Another possible application on a smaller scale involves the use of this material for thermal storage to simultaneously minimize the energy consumption and pollutants from automobile engines during cold starts [15].

A new composite material called EM was prepared by mixing $Mg(OH)_2$ powder and EG with pure water. The mixture was then dried and compressed into pellets. These EM pellets were examined for the packed bed reactor of a 100-W-scale CHP, which was developed to demonstrate the applicability of pure $Mg(OH)_2$ pellets [16].

The objective of this work was to experimentally observe the benefits of using EG as a heat-transfer enhancer for the dehydration and hydration reactions. Three types of pellets with different $Mg(OH)_2$ to EG mass mixing ratios were compared. The progress of the chemical reaction as a function of time was observed experimentally by measuring the mass change in the packed bed reactor. The effect of the EM mixing ratio on its reactivity was examined. Thermochemical performance parameters such as the heat-storage capacity, gross heat output, and mean heat-output rate were calculated from the experimental results and compared with the performance of pure $Mg(OH)_2$ pellets. Finally, the apparent thermal conductivities of the packed beds were measured using a thermal conductivity meter.

2. Experimental

2.1. Preparation of expanded graphite–magnesium hydroxide composite

$Mg(OH)_2$ pellets (MH-V05G, UBE Material Industries, Japan) [17] were used as the 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 EM composite was prepared as follows:

1. Pure $Mg(OH)_2$ pellets were crushed with a mortar and pestle and sieved (average particle size < 150 μm).
2. The sieved $Mg(OH)_2$ powder and EG were placed on a glass dish; then, purified water was added (approx. 30 ml) to the powder mixture, and the resulting slurry was mixed gently using a spatula.