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Research Paper

Development of thermal storage material using vermiculite and calcium hydroxide

Jun Kariya^a, Junichi Ryu^b, Yukitaka Kato^{c,*}^a Department of Nuclear Engineering, Tokyo Institute of Technology, 2-12-1-N1-22 Ookayama, Meguro-ku, Tokyo 152-8550, Japan^b Department of Urban Environment Systems, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba-ken 263-8522, Japan^c Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1-N1-22 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

HIGHLIGHTS

- A chemical heat storage (CHS) material that utilizes waste heat is proposed.
- This material can be used in industrial plants and nuclear power plants.
- Vermiculite is used as a support for calcium hydroxide.
- The vermiculite is highly porous, chemically stable, and low cost.
- The composite CHS material exhibits an enhanced reaction rate.

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ABSTRACT

A chemical heat storage (CHS) material that utilizes waste heat (with temperatures over 450 °C) from industrial plants, thermal generation plants, and nuclear power plants was developed. Calcium hydroxide (Ca(OH)₂) was selected as the CHS material because it decomposes at temperatures over 450 °C under atmospheric pressure. A support that holds the CHS material dispersed in micrometer-sized clusters was needed to prohibit Ca(OH)₂ agglomeration; this support also permitted the moldability of the Ca(OH)₂ material for loading into practical heat-exchange reactors. Vermiculite was selected as the support for Ca(OH)₂ because of its high porosity, chemical stability, and low cost. Using the impregnation method, composite materials were developed, which consisted of Ca(OH)₂ and vermiculite. The reaction performance was then studied with thermal gravimetric analysis (TGA). It was confirmed that, in comparison with the original Ca(OH)₂, the reaction rate of the composite material was enhanced because of the incorporated vermiculite.

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1. Introduction

Over the past hundred years, energy consumption has steadily increased because of population growth and technological development. As a result, our energy and environmental problems have become serious. Technologies to increase energy efficiency are therefore necessary for realizing a sustainable society. Chemical heat storage (CHS) could potentially increase energy efficiency worldwide. It is therefore expected that CHS will utilize waste heat for the purpose of heat storage.

CHS that uses a calcium oxide/water/calcium hydroxide (CaO/H₂O/Ca(OH)₂) reaction has been researched for the purpose of utilizing unused heat (with temperatures over 450 °C) because it has high material volumetric energy density; moreover, the reaction

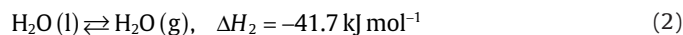
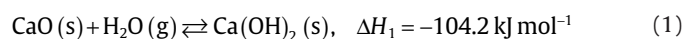
exhibits impressive reversibility. More specifically, the CHS system based on the CaO/H₂O/Ca(OH)₂ reaction has been examined for applications in solar thermal energy storage [1], iron making processes [2], and preheating automobile engines to reduce exhaust gas [3]. Thermal storage is crucial in allowing solar thermal energy systems to supply electricity stably. There is a time lag between the peak heat obtained from the sun and the peak windows of demand. Excess solar heat collected during the daytime can be stored and utilized during the night with the aid of CHS.

Notably, CHS systems can store energy for long periods of time with energy densities that are higher than those of conventional heat storage systems based on sensible and latent heat. For example, organic phase change materials (PCMs) are popular technologies for solar thermal storage. However, the energy density of organic PCMs is 180–200 kJ kg⁻¹ [4], which is lower than that of the CHS system based on CaO/H₂O/Ca(OH)₂ (i.e., 1300 kJ kg⁻¹). Therefore, CHS is an especially promising thermal storage system for solar energy utilization [1].

* Corresponding author. Tel.: +81357342964.

E-mail address: yukitaka@nr.titech.ac.jp (Y. Kato).

The dehydration of $\text{Ca}(\text{OH})_2$ and the hydration of CaO shown in Eq. (1) correspond to the heat storage and heat output operating modes, respectively.



CHS systems based on $\text{CaO}/\text{H}_2\text{O}$ have been examined previously. Most studies have focused on clarifying the reaction mechanisms [5,6]; that is to say, studies exploring the practical applications of such systems are few. For example, Ogura tried to enhance heat transfer in the packed bed reactor by inserting a metal mesh [7]. P. Pardo et al. evaluated the CHS performance using fluidized bed [1]. Moreover, Linder et al. evaluated the physical bulk properties and their impact on the operation characteristics of storage systems [8]. Generally, CHS materials must have high reaction performance and moldability because they are loaded between the fins of heat-exchange reactors in practical use. Thus, a support that holds the CHS material dispersed in micrometer-sized clusters is needed for prohibiting $\text{Ca}(\text{OH})_2$ agglomeration, maintaining paths for vapor diffusion through materials, and offering $\text{Ca}(\text{OH})_2$ moldability for ease of loading in practical heat-exchange reactors. However, there are only a few studies that focus on developing composite materials of CHS based on $\text{CaO}/\text{H}_2\text{O}$ with supports. Therefore, a support for $\text{Ca}(\text{OH})_2$ was selected, and composite materials were developed in this work.

Vermiculite was selected as a support for $\text{Ca}(\text{OH})_2$. The merits of vermiculite include chemical stability, low cost, and large pore volume [9]. The chemical formula of vermiculite is given as $\text{Mg}_{1.8}\text{Fe}^{2+}_{0.9}\text{Al}_{4.3}\text{Si}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$. Aristov et al. used vermiculite as the support for adsorption heat pump materials such as lithium, calcium, and barium halides [10], as well as the CHS material magnesium hydroxide [11]. They tried to divide the bulk reagents into tiny particles to avoid particle agglomeration, and showed that the compound with vermiculite enhanced reaction performance. The main reason to select vermiculite as a support for $\text{Ca}(\text{OH})_2$ is the chemical stability it offers, in light of the fact that the operating conditions represent a harsh environment for supports. Supports are exposed to vapor under high temperature (over 400 °C) and to $\text{Ca}(\text{OH})_2$ particles, which constitute a strong base. Carbon materials and metal forms are typical supports for chemical storage materials [12]. However, carbon materials react with vapor and generate hydrogen, carbon monoxide, and methane at temperatures over 400 °C [13]. The vapor also corrodes porous metal forms under the same conditions. Therefore, in terms of durability, vermiculite is superior to the other supports under such harsh conditions. Moreover, vermiculite has a large pore volume, which allows particle swelling during reaction and helps to maintain its structure as a host material [10].

In this work, composite materials consisting of vermiculite and $\text{Ca}(\text{OH})_2$ were developed. The effect of vermiculite on the hydration of the CaO was evaluated using thermogravimetric analysis (TGA).

2. Experiment

2.1. Sample preparation

Vermiculite particles with the length of the particles, 1–2 mm, were heated at 900 °C for 1 h as a pretreatment (heating rate to target temperature: 30 K·min⁻¹). Then, the mass of vermiculite was mixed with pure water in a 50 mL beaker. In order to remove air that existed in the vermiculite pores, the beaker was placed into a desiccator, which was vacuumed for 12 h at room temperature. After that, a constant mass of calcium acetate mono hydroxide (Wako Pure Chem-

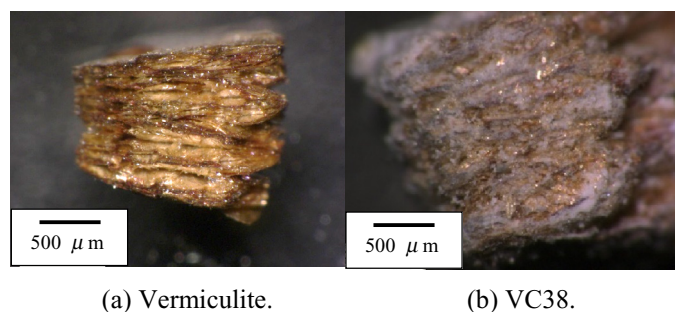


Fig. 1. Photos of samples.

ical Industries) was resolved to the mixture and dried on a heater at 220 °C. The obtained material was loaded in a crucible and heated from room temperature to 900 °C in 20 min under atmospheric pressure using an electric muffle furnace. Finally, the mixed material was exposed to saturated vapor for 30 min at a temperature of 200 °C with an autoclave. The obtained composite material was named $\text{VC}\alpha$, wherein α indicates the weight ratio of $\text{Ca}(\text{OH})_2$ to vermiculite. For example, the weight ratio of $\text{Ca}(\text{OH})_2$ in VC37 is 38 wt% (mass of $\text{Ca}(\text{OH})_2$:mass of vermiculite = 38:62). On the other hand, pure $\text{Ca}(\text{OH})_2$ was synthesized using the same method without vermiculite. Photos of two samples are shown in Fig. 1.

2.2. Experimental apparatus

TGA was performed to measure the changes in the sample mass with respect to temperature; the apparatus is shown in Fig. 2. A sample placed in a cell was set in a thermobalance (TG-9600, ULVAC Riko, Inc.). The cell was made of platinum, and the volume was 628 μL . After the pretreatment, the temperature was maintained constant in the thermobalance. Materials were dehydrated in a flow of dry argon at a rate of 100 mL min⁻¹ at 450 °C. Hydration was carried out at a partial vapor pressure of 57.8 kPa, which was achieved by mixing argon with vapor generated in a glass-bead bed reactor. Scanning electron microscopy (SEM) images were obtained with a SM-200 TOPCON microscope.

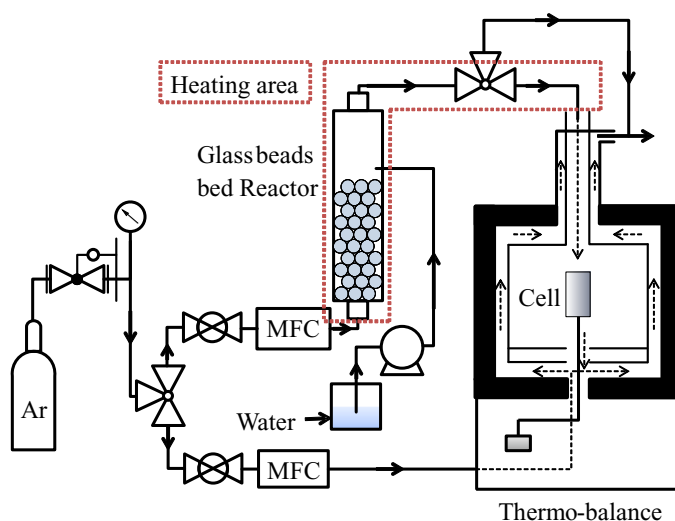


Fig. 2. Schematic diagram of thermal gravimetric (TG) apparatus.

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