Cyclic Assessment of Magnesium Oxide with Additives as a Thermochemical Material to Improve the Mechanical Strength and Chemical Reaction

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Abstract: Heat storage with a thermochemical reaction has the advantages of a high heat storage density and no heat loss compared to conventional methods such as the sensible and latent heat. This method is promising to use in a thermal energy network because it is an efficient solution which addresses the time mismatch problem with regard to heat production and consumption. In this paper, we investigated Magnesium oxide (MgO) with different additives as a thermochemical material (TCM) coupled with the effects of several additives in an effort to improve the structural strength and reaction rate and reduce the initiation time. As additives in an MgO composite, Bentonite, Magnesium sulfate (MgSO$_4$), and Zeolite 13X were chosen. With a cyclic scheduling experimental setup for the heat charging and discharging of the MgO composites, Bentonite as an additive improved the structural strength, and Zeolite 13X enhanced the reaction rate and led to faster reactions compared to only MgO as a TCM. With MgSO$_4$ as an additive, however, the TCM composite showed a high reactivity during the a few cycles, and then rapidly became inactive due to byproducts side reaction. The results indicated that Bentonite and Zeolite additives, in an MgO composite, as a TCM can improve the mechanical strength and chemical reaction, optimum ratio is necessary to compromise promoting the thermochemical reaction.

Keywords: thermal energy storage; thermochemical material; magnesium oxide; bentonite; zeolite 13X; composite materials

1. Introduction

Thermal energy storage is one of the major components of a thermal energy network, and it serves to offset the time mismatch problem between heat production and consumption. This approach uses short-term or long-term heat storage to minimize the heat loss from power plants or industrial processes due to distance and time inconsistencies relative to the customer [1]. Thermal energy storage methods are classified into sensible heat storage, phase-change heat storage, and thermochemical heat storage. Table 1 compares the types and performances of the heat storage materials used with each method.

Sensible heat storage is the most traditional and widely used technique, and it uses a sensible temperature increase of water or a solid below 100 °C. Although the running cost is low, the supply area is limited due to limitations such as the necessity of a piping network between the producer and consumer site, and also if there is a mismatch between the heat supply and demand, heat loss is inevitable. Phase-change heat storage is often carried out indirectly by means of a heat exchange rather than being transferred directly to the piping. The heat energy density of phase-change heat storage is higher than that of sensible heat due to the latent heat, but there are limitations related to the temperature range and heat loss [2].
1.1. Thermochemical Heat Usage

Thermochemical heat storing technology has the advantage of high heat storage density and no heat loss after the storing process given the use of the enthalpy change between material reactions. Once the thermochemical material (TCM) separates from the reactant, its enthalpy does not change before the reaction, achieving a state in which the heat is charged. Subsequently, it uses heat discharging in the form of stored energy while ensuring a stable state when the compound is created as the separated material binds [3].

In the past, various studies were carried out involving a chemical heat pump. This system uses anhydrous or adsorbate materials that adsorb and desorb in a closed loop at low temperatures [4,5], though several studies on the use of certain inorganic oxides (e.g., Calcium oxide (CaO), Magnesium oxide (MgO)) have been carried out as well [6–9]. On the other hand, thermochemical heat storage is an open system, mainly used with high-temperature solar collectors [10] or in systems that recuperate waste heat from industrial processes [11]. This approach uses chemical reactions of inorganic oxides with high reaction temperatures and high heat storage densities. Several studies involving the use of low-temperature anhydride salts [12,13] have also been conducted.

Table 1 shows the commonly used TCMs. Cobalt oxide (Co$_3$O$_4$) utilizes high reaction temperatures when reacted with an oxide. It is suited for high-temperature solar collector systems. Studies of the characteristics of Co$_3$O$_4$ powder [14] and on the development of a numerical model [15] have been conducted. CaO is suitable for use with heat sources in the temperature range of 500–700 °C. Other studies have sought to verify the safety of a repetitive cycle using a reactor [16,17], including one in which a thermogravimetric analysis was conducted [18]. Schmidt et al. [19] created a 10 kW CaO-based TCM reactor to evaluate heat charging and discharging behavior.

| Table 1. Comparison of heat storage methods and materials. |
|------------------------------------------------------------|
| Material | Co$_3$O$_4$ | CaO | MgO | MgSO$_4$ | Silicagel | Zeolite | Paraffin | Water |
| Heat storage method | TCM (Thermochemical Material) | PCM (Phase-Change Material) | Sensible |
| Heat storage density (GJ/m$^3$) | Chemical reaction | Chemical adsorption | Inorganic oxides | Anhydrate | Adsorbate | 0.2 | 0.2 ($\Delta T = 50 ^\circ C$) |
| Heat charging temperature (°C) | 925 | 550 | 350 | 125 | 85 | 220 | 60 | 0–100 |

1.2. Consideration of Magnesium Oxide as a Thermochemical Material

The selection of the TCM takes into account variables such as the heat storage temperature, operating temperature range, and heat storage density. In this study, we consider MgO rather than CaO as the TCM because it is more suitable for utilizing the waste heat generated from industrial processes such as steel production site, incineration factory and power plant. CaO has higher heat storage density than MgO, whereas the heat charging temperature of Mg(OH)$_2$ is 100 °C lower than Ca(OH)$_2$, as shown in Figure 1a. MgO is more applicable to utilize the industrial waste heat then CaO for practical aspects. Numerous studies of MgO have been conducted, including those concentrating on its thermochemical characteristics [23,24], use with chemical heat pumps [6,25], use for solar energy storage [26], and studies related to the use of additives to supplement its thermal properties. Mastronardo et al. [27–29] showed that a mixture of carbon-based materials to improve the low thermal conductivity (8–30 W/m·K [30]) of MgO can increase the thermal conductivity and improve the reaction rate. Amaral et al. [31] found that certain ions delay or accelerate the reaction in a study, which added various compounds to investigate common-ion effects on the reaction with MgO. Shktulov et al. [32] studied the thermochemical properties of MgO composites with expanded vermiculite, finding that the storage temperature of the composite material is approximately 50 °C lower than that of the bulk material.
We also considered investigating the material properties of MgO composites upon repeated exposure. As for the heat discharging, adding some heat to the reactant can help the hydration, implying that the addition of MgO reacts with water (hydration) to become Mg(OH)$_2$, causing a heat discharging reaction that generates 81 kJ/mol, after which Mg(OH)$_2$ becomes MgO through a reverse process (dehydration) at 350–500 °C. When we use MgO as a TCM, it is essential to consider the fact that MgO has different reactivity and specific surface area values depending on the calcination temperature, though it has the same chemical composition. These differences allow the classification of MgO into the light-burn (~800 °C), hard-burn (~1300 °C) and dead-burn (~1500 °C) types depending on the calcination temperature [33]. At higher calcination temperatures, it has lower reactivity because the irreversible energy portion of MgO is increased by a change in the crystal structure.

In order to understand the heat charging behavior of light-burn MgO as the TCM, we conducted preliminary experiments on the endothermic reaction of Mg(OH)$_2$ with the various time and temperature. Containers of 200 g of Mg(OH)$_2$ were placed in the electric furnace under the combination of heat charging temperatures (450 °C and 500 °C) and time (0.5/1.0/2.0/3.0/4.0/5.0 h). Figure 1b shows the relationship between the dehydration rate and elapsed time, where the rate is defined as the ratio of the weight difference before and after dehydration. Results present that the only 50 °C difference could shorten 33% of dehydration time, it is evident that a small difference in dehydration temperature expedites the heat charging. This result indicates that the appropriate selection of the heat charging temperature is very important not only enhancing the heat charging rate but also minimizing the transformation toward hard-burn MgO during the cyclic operation.

For understanding the heat discharging behavior, there are previous studies regarding the relationship between the initiation time and the reactant temperature. Thomas et al. [25] investigated the kinetics and activation energy of MgO with reactant temperatures affect the initiation time delay of the MgO as a TCM. Amaral et al. [32] studied the effect of reaction delay as ‘Time for maximum conductivity value’ in MgO. Both studies present that reactant temperature affects the rate of hydration of MgO. Their results present that a higher reactant temperature and a well distributed reactant are factors that decrease the initial reaction delay significantly. Based on the above studies, we could understand that the appropriate selection of heat charging temperature is important to reduce the processing time and prevent MgO turning into hard-burn type. As for the heat discharging, adding some heat to the reactant can help the hydration, implying that the additives can react prior to MgO and produce heat, helping to increase the TCM temperature and to speed up the MgO reaction. Therefore, we focused on examining the effects of various additives to the TCM in an effort to expedite the reaction under repetitive heat charging and discharging processes. We also considered investigating the material properties of MgO composites upon repeated exposure at different heat charging temperatures.

![Figure 1. MgO as a thermochemical material (TCM) characterization: (a) Thermogravimetry curves of Mg(OH)$_2$ and Ca(OH)$_2$; (b) Variations of the dehydration time according to the dehydration (heat charging) temperature.](image-url)
To apply MgO for practical applications, we also carried out forming MgO as a structural body rather than a powder. The honeycomb structure is a good example of a structural body popularly used in filtering applications such as automobile exhaust gas particulate filters. Recently, the honeycomb structure has seen expanded use in various applications, such as carbon absorbers, low-expansion heat exchangers, membrane-coated gas filters, and finned monolithic reactors [34]. When TCMs are used in powder form, the reaction mainly arises due to diffusion, whereas when in the honeycomb structure, the reaction can occur due to convection and the pressure drop is reduced. Convection dominant exchanges are advantageous for heat and mass transfers between the reactant and the TCM, as it means that higher heat charging and discharging rates can be expected.

Li et al. [35] found that Bentonite is useful as a lubricant because it facilitates the extrusion of the honeycomb when using a Zeolite and it avoids cracking after drying. Based on these characteristics, they studied strength improvement methods for the honeycomb structure using additives to MgO and assessed the effects of the additives on the heat storage performance of MgO.

2. Experiments

Experimental equipment for evaluating the chemical reactions with various compositions of the TCM was designed and manufactured. The proposed equipment for the TCM characteristic evaluations was considered for assessing the heat charging and discharging abilities during cyclic operations. In addition, TCMs with various compositions could be repeatedly evaluated under identical conditions, i.e., the temperature and time, among others.

2.1. System Design

The experimental equipment consists of three parts: a hot- and cold-water network, a reactor, and a control device. A schematic and the actual experimental system are shown in Figures 2 and 3, respectively. A boiler (Figure 2a (1)) makes hot water (80 °C) flow through the jacket during the heat-discharging step, and a chiller (Figure 2a (2)) forces cold water (10 °C) to flow through a jacket during the heat charging step. A motorized three-way valve (Figure 3a (4)) controls the path to change to hot or cold water. The hot- and cold-water networks serve to keep the reactor (Figure 3a (1)) ambient temperature constant during every cycle in the long-term experiment so that there are no effects of changes in the outside temperature.

The reactor is the main part of the system, and it contains TCM and the reactant (distilled water) in a closed package. Two embedded heaters (Figure 2a (3) and (4)) are installed: the upper to heat the TCM during heat charging and the lower to heat the reactant during heat discharging. Several temperature sensors monitor the status of the TCM and reactant and control the cyclic steps. The control device manages the paths in the hot- and cold-water networks according to the heat charging or discharging step; it also controls the temperature inside the reactor by controlling the embedded heaters.

Figure 2b describes the inner structure of the reactor. The reactor is enclosed in a reactor chamber such that there is no external exchange of the TCM and the reactants. The interior of the chamber is composed of upper and lower structures. The TCM is held in the upper structure container and the reactant is in the lower structure. The outside of the chamber has the form of a jacket (Figure 2b (3)) so that hot or cold water can circulate depending on the step. The upper part of the reactor chamber (Figure 2b (2)) is where the TCM is located, as noted above. The inside of the TCM is in contact with the upper heater (Figure 2b (1)) and the outside is in contact with the mesh cover (Figure 2b (6)) to prevent any loss of the TCM and to allow water vapor reactants to flow in and out. The lower part of the reactor chamber is where the reactant (Figure 2b (8)) is in contact with the lower heater (Figure 2b (10)). Therefore, during the heat discharging step, the reactant is vaporized by the lower heater and exists in a saturated vapor form while the hot water flows through the jacket. In contrast, during the heat charging step, the condensed reactant is recovered when it cascades through the wall because the cold water is at low temperatures. A thermocouple installed inside the TCM (Figure 2b (5)) measures the temperature of the TCM during the charging step and measures the reaction temperature...
of the TCM during the discharging step, while the vapor phase reactant temperature is measured with a thermocouple (Figure 2b (7)) located inside the reactor. In this way, the charging temperature, reaction temperature, and the reactant temperature of the TCM can be observed. Figure 3b,c show the method used to set the TCM to the reactor. The designed reactor holds 62 g of the TCM.

**Figure 2.** System schematic and reactor diagram: (a) Schematic of the experimental equipment: (1) boiler, (2) chiller, (3) upper heater, (4) lower heater, (5) computer, and (6) controller; (b) Inner structure of the reactor: (1) upper heater, (2) thermochemical materials, (3) heating and cooling jacket for the ambient temperature, (4) outlet for jacket to the boiler or chiller, (5) TCM temperature measurement point, (6) mesh cover, (7) vapor phase reactant temperature measurement point, (8) reactant (distilled water), (9) inlet for jacket, and (10) lower heater.

**Figure 3.** Photographs of the system setup: (a) Photograph of the experimental equipment: (1) reactor, (2) chiller, (3) boiler, (4) motorized three-way valve, (5) pump, (6) flow meter, and (7) control box; (b) View of inside of the upper structure of reactor (upside-down direction), view from the top after TCM filling; (c) View from the front ((1) mesh cover, (2) TCM, and (3) upper heater).
2.2. Experiment Procedures

In this study, the combination of heat charging and discharging is referred to as one cycle, and the experimental step involves a change of the composition of the TCM and 20 cycles repeated experiment.

Step 1 (Pre-cooling and preparing for heat charging): Before heat charging, using a cold-water network to lower the reactor temperature so as to lower the saturation vapor pressure inside the chamber and to recover the water remaining inside the TCM to the lower part of the reactor. The cold-water network holds the reactor jacket temperature at 10 °C using a chiller (Figure 2a (2) and Figure 3a (2)).

Step 2 (Heat charging-dehydration): The TCM is heated using the upper heater (Figure 2a (3) and Figure 2b (1)) to separate the TCM and the reactant. The separated reactants are released as superheated steam and are condensed by the lowered wall temperature caused by the cold-water network circulating outside of the reactor and are induced to flow in the direction of gravity. The measured temperature in Figure 2b (5) is the heat charging temperature of the TCM.

Step 3 (Reactant condensation and TCM cooling down): The upper heater (Figure 2a (3) and Figure 2b (1)) is turned off and the reactor internal temperature is lowered to recover the remaining moisture. To prepare for the heat discharging step, we wait for the TCM temperature to fall below 100 °C in order to ensure that the exothermic effect by which the TCM temperature becomes higher than the ambient temperature.

Step 4 (Stand-by after heat charging): Switching to the hot-water network and preparing for the heat discharging step.

Step 5 (Pre-heating and preparing heat discharging): Before supplying reactant as saturated steam to the TCM, the hot-water network (Figure 2a (1) and Figure 3a (3)) heat up the reactor jacket temperature as 80 °C in order to prevent any influences such as external temperature changes outside the reactor.

Step 6 (Heat discharging-hydration): The lower heater (Figure 2a (4) and Figure 2b (10)) heats the reactant to produce saturated steam. The saturated steam makes contact with the TCM through the mesh cover and the hydration reaction occurs. The thermocouple located inside the TCM in the upper chamber of the reactor measures the hydration temperature. The difference between the hydration temperature (Figure 2b (5)) and the vapor phase reactant temperature (Figure 2b (7)) is the crucial parameter for evaluating the hydration. During the discharging step, the chamber’s internal temperature is maintained at a saturated vapor temperature due to the remaining reactant in the form of a liquid.

Step 7 (Post heating and preparing for heat discharging): This process prevents any thermal shock to the lower heater from causing a sudden change to a further step (Figure 2a (4) and Figure 2b (10)).

Step 8 (Stand-by after heat discharging): Switching to the cold-water network and preparing for the heat charging step.

Table 2 shows the equipment status and operation time at each step. Figure 4a,b depict the time-series variations of the TCM temperature and vapor phase reactant temperature in a single cycle and during 20 cycles, respectively. In particular, Figure 4a shows the charging peak temperature, the discharging peak temperature defined as $T_{\text{peak}}$, the elapsed time to reach the peak temperature defined as $t_{\text{peak}}$ and the reactant temperature of vapor phase used as the reference temperature for the heat charging and discharging steps.
Yuken’s YB132A was used as an anti-cracking binder in the manufacturing of the honeycomb. To manufacture the TCM in a honeycomb structure, we added the YB132A binder and Bentonite and compared the effects of the addition or the absence of these materials. Bentonite, when used as an additive, has the effect of mixing with other materials to create a gel, but it is not chemically active and does not change even at high temperatures [34]. For this reason, it is suitable as an additive to add adequate plasticity when manufacturing the honeycomb, which is decomposed when it is exposed at 500 °C. Therefore, it does not participate in heat charging or discharging.

The experimental conditions are shown in Table 3. CASEs 1–3 were used for comparative experiments to find the optimal heat charging temperature. CASEs 4–7 observed the performance according to the mass ratio of the Zeolite. The effect of adding MgSO4 was observed in CASE 8.

We studied various compositions of MgO as a TCM with the effects of several additives to improve the structural strength, reaction rate, and reaction initiation time. As additives in the MgO composite, Bentonite for structural strength and MgSO4 and Zeolite 13X to improve the reaction were chosen. With regard to the material in this study, the Mg(OH)2 is MagShield S from Martin Marietta, and the Bentonite is Barotherm Gold, a thermally conductive grout produced by Baroid. The MgSO4 is the pure Epsom salt from Kali and the Zeolite is the Zeolum X-type F-9 from Tosoh. In addition, Yuken’s YB132A was used as an anti-cracking binder in the manufacturing of the honeycomb.

The experimental conditions are shown in Table 3. CASEs 1–3 were used for comparative experiments to find the optimal heat charging temperature. CASEs 4–7 observed the performance according to the mass ratio of the Zeolite. The effect of adding MgSO4 was observed in CASE 8.

To manufacture the TCM in a honeycomb structure, we added the YB132A binder and Bentonite and compared the effects of the addition or the absence of these materials. Bentonite, when used as an additive, has the effect of mixing with other materials to create a gel, but it is not chemically active and does not change even at high temperatures [34]. For this reason, it is suitable as an additive to increase the strength of the structural body of a TCM. YB132A is a water-based binder that is used to add adequate plasticity when manufacturing the honeycomb, which is decomposed when it is exposed at 500 °C. Therefore, it does not participate in heat charging or discharging.

In order to assess the improvement of the TCM with the effects of additives, we introduced three parameters. One is the peak temperature ($T_{peak}$) as the reaction rate within a limited time, another is the time that elapses before reaching the peak temperature ($t_{peak}$) during the discharging step. The other
is the heat storage capacity, which is measured by differential scanning calorimetry (DSC) in terms of the energy efficiency of the proposed composite MgO.

### Table 3. CASEs used in the study.

| CASE | Composition of TCM | Type of Additives | Type of Binder |
|------|--------------------|------------------|---------------|
| 1    | Mg(OH)₂ 95 wt%     | Zeolite 13X 5 wt%| -             |
| 2    | Mg(OH)₂ 100 wt%    | -                | YB132A 10 wt% |
| 3    | Mg(OH)₂ 95 wt%     | Zeolite 13X 5 wt%| -             |
| 4    | Mg(OH)₂ 90 wt%     | Zeolite 13X 10 wt%| Bentonite 5 wt% |
| 5    | Mg(OH)₂ 80 wt%     | Zeolite 13X 20 wt%| YB132A 5 wt%  |
| 6    | Mg(OH)₂ 90 wt%     | MgSO₄·nH₂O 10 wt%| -             |
| 7    | Mg(OH)₂            | -                | YB132A 10 wt% |

### 3. Results of the Experiments

#### 3.1. Determination of the Optimized Charging Temperature

Choosing the appropriate heat charging temperature is important during the multiple cycle operation. A high heat charging temperature expedites the heat storage, though that in turn generates hard-burn MgO due to the crystal structure change. Therefore, exposure to high temperatures affects the reactivity of the TCM if used repeatedly. Otherwise, a low heat charging temperature causes inefficient heat use due to the lengthy time needed to separate the reactants (see Figure 1b). Therefore, with regard to the heat charging temperature, a compromise must be found between minimizing the deformation of MgO and achieving sufficient heat storage during the cycle repetition process. In these experiments, we conducted the heat charging step with three different heat charging temperatures and then proceeded with heat discharging under identical conditions. During 20 cycles, the differences in T_{peak} were recorded to determine the optimal heat charging temperature (CASEs 1–3).

Figure 5a,b show the cyclic temperature variations of the heat charging and discharging processes. Figure 5a shows the differences in the heat charging peak temperature, whereas Figure 5b has only small differences. This indicates that there is no significant difference in the heat charging performance above a certain temperature. Therefore, it is advantageous to select a low charging temperature if T_{peak} is similar. For this reason, we used the heat charging temperature of CASE 2 (486 ± 12 °C) as the temperature condition in this study considering its efficiency and stability.

![Figure 5a](image1.png)

![Figure 5b](image2.png)

**Figure 5.** Charging and discharging peak temperatures in each cycle for CASEs 1–3: (a) Charging peak temperature; (b) Discharging peak temperature (T_{peak}).

#### 3.2. Effects of Additives: Bentonite

When Bentonite was used as an additive to maintain the shape upon the repeated use of MgO, the effects on the thermal performance and mechanical strength were compared with reference cases.
The assessment was made using the time-series $T_{\text{peak}}$ values for the thermal and the honeycomb compressive strength with regard to mechanical aspects. The results of the comparison of heat discharging with 5 wt% of Bentonite as an additive are shown in Figure 6a. CASE 5 with Bentonite had a lower $T_{\text{peak}}$ by 5 °C than CASE 2 without Bentonite. It was found that the use of Bentonite as an additive to the TCM resulted in a subtle decrease in the heat discharging performance due to the increased non-TCM proportion.

![Figure 6a: T$_{\text{peak}}$ difference with and without Bentonite](image)

**Figure 6.** Effects of Bentonite: (a) $T_{\text{peak}}$ difference with and without Bentonite; (b) Compressive strength before and after debinding.

Figure 6b shows the results of a comparison of the strength changes of the honeycomb structure when using Bentonite as an additive. The target object was a honeycomb with a diameter of 37 mm and a length of 40 mm. Two types of honeycomb structures were compared; one being only Mg(OH)$_2$ with YB132A and the other Mg(OH)$_2$ with YB132A and 5 wt% of Bentonite. Moreover, to assess the debinding effect, a comparison between the ‘as extruded/dried’ and the ‘debinded at 500 °C’ states was conducted. Following the ASTM D695-15 procedure, the compressive strength was compared with four types of honeycomb structure. These results indicated that adding Bentonite effectively led to a higher mechanical strength by several times regardless of the existence of a binder. Although Bentonite has no effect on the TCM, the results show that it is more advantageous to maintain the shape during a repetitive cycle operation even when sacrificing some portion of the heat storage performances. Figure 7 shows an image of a debinded honeycomb structure with and without Bentonite, indicating that when Bentonite is used as an additive, it prevents deformation during the debinding step. Otherwise, the honeycomb is easily broken during the drying step.

![Figure 7: Comparison of cracks after debinding](image)

**Figure 7.** Comparison of cracks after debinding: (a) With Bentonite; (b) Without Bentonite.
3.3. Effect of Additives: Magnesium Sulfate

MgSO$_4$ was tested as additives to accelerate the heat discharging step. Anhydrous MgSO$_4$ can adsorb n (up to 7) water molecules and releases heat while generating a substance referred to as MgSO$_4$·nH$_2$O. It adsorbs moisture at room temperature via an exothermic reaction and desorbs at 125 °C as an endothermic reaction. As shown in Figure 8a, when MgSO$_4$ was used as an additive, it exhibited a higher $T_{\text{peak}}$ up to seven cycles as compared to when MgSO$_4$ was not added. However, $T_{\text{peak}}$ then continued to decline and was lower than in CASE 4 afterward. At the beginning of the cycle, it was found that CASE 8 had a high $T_{\text{peak}}$ value because MgSO$_4$ acted as an additive to cause more MgO to participate in the discharge process. Figure 8b shows an X-ray diffraction (XRD) analysis of the material after 20 cycles to determine the degree of degradation. As shown in the figure, 20 cycles of heat charging and discharging created the new material (Mg$_3$[SO$_4$]$_2$(OH)$_2$) due to a side reaction between the decomposition of MgSO$_4$ and the combination with Mg(OH)$_2$. Unlike MgO and MgSO$_4$, the byproduct became inactive and did not participate in the chemical reaction or adsorption processes. Therefore, it is thought that $T_{\text{peak}}$ was continuously lowered because a portion of the byproduct increased and was no longer involved in the heat charging and heat discharging processes as TCM. Thus, MgSO$_4$ is not suitable as an additive for promoting an exothermic reaction given because it forms an irreversible material by bonding with MgO.

![Figure 8. Effects of using MgSO$_4$ as an additive: (a) Differences in $T_{\text{peak}}$ with the additive of MgSO$_4$, and without this additive; (b) XRD patterns for CASE 8 after 20 cycles.](image)

3.4. Effect of Additives: Zeolite

Zeolite 13X undergoes an exothermic reaction while adsorbing water at room temperature and an endothermic reaction while desorbing water at 180 to 250 °C. Similar to MgSO$_4$, it generates heat at a low temperature and can serve to promote the chemical reaction of MgO. In the experiments of CASEs 4 through 7, the weight contents of Zeolite varied from 0 wt% to 20 wt%. Figure 9 shows comparisons of $T_{\text{peak}}$ and $t_{\text{peak}}$ over time at the 15th heat discharging cycle. In addition, Figure 10a,b depict time-series comparisons of $T_{\text{peak}}$ and $t_{\text{peak}}$ for each case during cyclic heat discharging. A higher value of $T_{\text{peak}}$ means that a certain amount of MgO participated throughout the chemical reaction. A shorter $t_{\text{peak}}$ means that a certain amount of MgO participated within a limited time. In Figure 10a, the trend of $T_{\text{peak}}$ in CASEs 5–7 is higher than in CASE 4, and it remained stable after five or six cycles to the end. Also, Figure 10b shown, $t_{\text{peak}}$ showed behavior similar to that of $T_{\text{peak}}$, and the values in CASEs 5–7 were smaller than in CASE 4 with stable values starting at five or six cycles, indicating that Zeolite as an additive assisted the MgO reaction and that Zeolite did not react with MgO throughout the multiple heat charging and discharging cycles.
those containing 20 wt% (CASE 7), suggesting that adding an appropriate ratio of Zeolite is a good approach.

The cases containing 5 wt% (CASE 5) and 10 wt% (CASE 6) of Zeolite showed higher thermal behavior and heat storage capacity. Therefore, we carried out further analysis to find the best composition. Because the higher contents of sulfate (MgSO₄) and Zeolite 13X were chosen. During 20 cycles of heat charging and discharging, we observed the various effects of additives in the TCM on the thermal behavior and heat storage efficiency due to the low heat storage density of additives.

Despite CASE 6 (10 wt% of Zeolite 13X) presenting the best result of peak temperature (Tpeak) and peak time (tpeak), it is appropriate to use 5 wt% of Zeolite (CASE 5) considering that heat storage capacity has 55% higher than CASE 6.

Table 4 compares Tpeak, tpeak, and heat storage capacity. It presents that adding Zeolite 13X can result in lower total heat storage capacity. Therefore, we carried out further analysis to find the best composition. Because the higher contents of sulfate (MgSO₄) and Zeolite 13X were chosen. During 20 cycles of heat charging and discharging, we observed the various effects of additives in the TCM on the thermal behavior and heat storage efficiency due to the low heat storage density of additives.

Table 4 shows the average of Tpeak, tpeak, and heat storage capacity of CASE 4 through CASE 7. It presents that adding Zeolite 13X can result in lower total heat storage capacity. Therefore, we carried out further analysis to find the best composition. Because the higher contents of sulfate (MgSO₄) and Zeolite 13X were chosen. During 20 cycles of heat charging and discharging, we observed the various effects of additives in the TCM on the thermal behavior and heat storage efficiency due to the low heat storage density of additives.

Figure 9. Examples of the temperature profiles, Tpeak and tpeak values at the 15th heat discharging step.

Figure 10. Comparisons of Zeolite 13X contents: (a) Tpeak; (b) tpeak.

Figure 11 shows box plots of Tpeak and tpeak for CASE 4 through 7, we considered the values after six cycles when calculating the pertinent values (i.e., the average, variance, box plot).

Figure 11. Box plots of Tpeak and tpeak for each case: (a) Tpeak; (b) tpeak.

The average value in each case for Tpeak shows the trend of CASE 4 < CASE 7 < CASE 5 < CASE 6, and the average values of tpeak are in order of CASE 4 > CASE 5 > CASE 7 > CASE 6. Specifically, the cases containing 5 wt% (CASE 5) and 10 wt% (CASE 6) of Zeolite showed higher Tpeak values than those containing 20 wt% (CASE 7), suggesting that adding an appropriate ratio of Zeolite is a good approach.
way to optimize the reaction rate. Results presented that MgO as a TCM with 10 wt% of Zeolite was
the best only if $T_{\text{peak}}$ and $t_{\text{peak}}$ were considered.

However, as for the heat storage system, it may not be sufficient to use $T_{\text{peak}}$ and $t_{\text{peak}}$ for assessing
the TCM with different additives for finding the best composition. Because the higher contents of
additives can result in lower total heat storage capacity. Therefore, we carried out further analysis
including the heat storage capacity in terms of energy efficiency from DSC results of CASE 4 through
CASE 7. Figure 12a is the heat flow curves and figure 12b represent the heat storage capacities,
which were derived from the cumulative result of heat flow from 200 °C to 400 °C.

Table 4 compares $T_{\text{peak}}$, $t_{\text{peak}}$, and heat storage capacity. It presents that adding Zeolite 13X can
assist chemical reaction faster, whereas the larger portion of additives makes the lower the energy
efficiency due to the low heat storage density of additives.

Table 4. Average of $T_{\text{peak}}$, $t_{\text{peak}}$ and heat storage capacity of CASE 4 through CASE 7.

| CASE   | Average of $T_{\text{peak}}$ (°C) | Average of $t_{\text{peak}}$ (s) | Heat Storage Capacity (J/g) |
|--------|----------------------------------|---------------------------------|-----------------------------|
| CASE 4 | 103 ± 0.6                        | 1046 ± 146                      | 905.5                       |
| CASE 5 | 113 ± 0.8                        | 779 ± 78                        | 787.2                       |
| CASE 6 | 114 ± 0.7                        | 622 ± 135                       | 507.5                       |
| CASE 7 | 110 ± 0.5                        | 687 ± 97                        | 444.4                       |

In the case of CASE 7 (20 wt% of Zeolite 13X), additive helped to expedite $t_{\text{peak}}$, but it made $T_{\text{peak}}$
lower than CASE 5 and CASE 6 because Zeolite contents made the heat storage capacity lower. Despite
CASE 6 (10 wt% of Zeolite 13X) presented the best result of $T_{\text{peak}}$ and $t_{\text{peak}}$, it is appropriate to use
5 wt% of Zeolite (CASE 5) considering that heat storage capacity has 55% higher than CASE 6.

4. Conclusions

In this study, we investigated the feasibility of adding additives with Magnesium oxide (MgO) as a
thermochemical material (TCM) in an effort to improve the structural strength, heat discharge reaction
rate and reaction initiation time. To do this, various contents of MgO composite were assessed in an
experimental setup of the cyclic scheduling of heat charging and discharging steps under identical
boundary conditions. As additives in an MgO composite, Bentonite, Magnesium sulfate (MgSO$_4$)
and Zeolite 13X were chosen. During 20 cycles of heat charging and discharging, we assessed the
various effects of additives in the TCM on the thermal behavior and heat storage capacity. Regarding
the thermal behavior, three parameters were considered. One is the peak temperature ($T_{\text{peak}}$) as
the reaction rate within a limited time, another is the time that elapses before reaching the peak
temperature ($t_{\text{peak}}$) during the discharging step. The other is the heat storage capacity, which is
measured by differential scanning calorimetry (DSC) in terms of the energy efficiency of the proposed composite MgO.

Bentonite was found to be effective given its higher mechanical strength by several times despite the associated subtle decrease in the heat discharging performance due to the increased non-TCM proportion. Considering heat storage applications, however, it is more advantageous to maintain the shape during a repetitive cycle operation, sacrificing some portion of heat storage performance. When adding MgSO₄ as an additive, the MgO composite exhibited a higher T_peak during the initial cycles compared to when MgSO₄ was not added. However, T_peak then continued to decline and was lower than that of pure MgO afterwards. This is why the side reaction produced the new material of Mg₃[SO₄]₂(OH)₂, which it did not participate in the chemical reaction or adsorption process. Thus, MgSO₄ is not suitable as an additive to promote an exothermic reaction given that it forms an irreversible material by bonding with Mg(OH)₂. Zeolite 13X as an additive showed stable cyclic operation, indicating that Zeolite as an additive serves to assist the MgO reaction and that it does not react with MgO throughout the multiple heat charging and discharging cycles. In order to maximize the performance of a TCM with an additive, however, it is necessary to find the optimal portion of Zeolite because higher contents of Zeolite lead to lower total heat storage capacity.

The results of a comparison in a cyclic experiment using various Zeolite contents showed that T_peak and t_peak improved up to 10 wt%, but decreased at higher Zeolite contents due to the reduction of heat storage capacity. When we consider the perspective of reactivity, 10 wt% of Zeolite is the best to use, but considering the perspective on energy efficiency, TCM with 5 wt% of Zeolite is more applicable to use because the heat storage capacity is 55% higher than that of 10 wt% of Zeolite. These results indicate that the optimum ratio of Bentonite and Zeolite additives in an MgO composite as a TCM can improve the mechanical strength and chemical reaction capabilities, while minimizing the loss of heat storage capacity.

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