



Development of low-cost inorganic salt hydrate as a thermochemical energy storage material



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ABSTRACT

Thermochemical storage is based on a reversible chemical reaction; energy can be stored when an endothermic chemical reaction occurs and then, energy is released when it is reversed in an exothermic reaction. According to literature and based on the energy storage density (*esd*), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is a promising candidate material for thermochemical energy storage. Bischofite is an inorganic salt obtained as a by-product material from extraction processes of non-metallic minerals, from Salar de Atacama in Chile, containing approximately 95% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Thus, the purpose of this study was to characterize the dehydration reaction of bischofite ore, studied as a low-cost thermochemical storage material. Thermogravimetric data for bischofite were obtained using a TGA instrument coupled to a DSC, at four different isotherms 70 °C, 80 °C, 90 °C and 100 °C. The results of conversion reaction (α -t) from the thermal dehydration experiments, demonstrated the first phase of dehydration with the loss of two water molecules. The study showed a typical sigmoid curve with a significant acceleration in the conversion at the beginning of the reaction until it reaches a maximum rate, where the curve keeps constant. The same behavior was observed for all the temperatures used. The kinetics of bischofite dehydration model was determined using the isothermal kinetics method. For this, the thermogravimetric data were fitted to the most used kinetic models (D, F, R, A) and then their respective correlation coefficients R were evaluated. The results indicated that the dehydration reaction of bischofite was described by the kinetics of chemical reaction of cylindrical particles R_2 . The rate of dehydration reaction and *esd* of bischofite are lower as compared to synthetic $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, at temperatures higher than 80 °C. However, the cost of materials to store 1 MJ of energy is three times lower for bischofite, which is an evident advantage to promote the reuse of this material left as waste by the non-metallic industry.

1. Introduction

Thermal energy storage (TES) is an available technology, where energy in the form of heat or cold is stored in materials (charging process) for a specific time, to be released in the form of heat (discharge process), which can be transformed into other forms of energy or simply used as heat, depending on energy demand. The incorporation of TES systems increases efficiency in solar energy use throughout 24 h of the day, reduces loss of useful thermal energy and consequently favors the reduction of greenhouse gas emissions considerably [1].

The amount of thermal energy that can be stored and discharged depends on the characteristics of the storage material and the associated temperature effects between the storage medium and the energy source. Thermal energy can be stored by virtue of the internal energy change of a material caused by sensible heat, latent heat, and chemical

reactions [1]. Sensible heat TES systems store energy through temperature change in the storage materials, where thermal energy is stored by raising the temperature of a material [2]. Latent heat is heat absorbed or released by a material, while changing its phase at constant temperature [3]. Latent heat is released when the phase change material (PCM) is cooled again and solidifies. However, the main disadvantages of these two, sensible and latent, heat storage forms are low energy density and considerable heat loss during storage. These disadvantages are overcome by the heat storage type occurring by means of a chemical reaction, also called thermochemical storage, since it keeps high energy density, which becomes 5 and 10 times greater, compared to latent heat and sensible heat storage systems, respectively. This thermochemical storage type is mainly based on obtaining heat by means of a reversible chemical reaction (See Fig. 1 [4]). In this reaction, a thermochemical energy storage material (C) absorbs external heat

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Nomenclature

<i>esd</i>	energy storage density (J/cm ³)
ρ	density (kg/m ³)
TES	thermal energy storage
α	fraction reacted
THS	thermochemical heat storage
LHS	latent heat storage
SHS	sensible heat storage
PCM	phase change material
TCM	thermochemical material
CHP	chemical heat pump
DTA	differential thermal analysis
DTG	derivative thermogravimetric
IR	infrared spectroscopy
SEM	scanning electron microscope
STA	simultaneous thermal analysis
EDX	energy dispersive X-ray

TG	thermogravimetry
MS	mass spectrometer
DSC	differential scanning calorimetry
LM	mean size (μm)
LD	mode size (μm)
XRD	X-ray diffraction
$t/t_{0.5}$	time/time $\alpha = 0.5$
E_a	energy activation (J/mol)
A	frequency factor (s ⁻¹)
R	correlation coefficient
T	temperature (°C)
t	time (min)
b	slope
a	intercept
ΔH_D	dehydration enthalpy (kJ/kg)
$\Delta_r H$	reaction enthalpy (kJ/mol)
k	rate constant
% wt	percentage of weight loss (%)

(e.g. solar energy) through an endothermic reaction, decomposing into A and B. Products (A and B) are separated by physical means and stored in separate containers. When materials A and B are combined again, exothermic reverse reaction, generation of C and release of stored thermal energy occur [5].

Storage and transport times are theoretically unlimited because there is no heat loss during storage of materials A, B and C; thus, products can be stored at room temperature. Therefore, these are promising systems for long-term heat storage (as seasonal storage) [6,7]. Recent studies also show advances in applications of thermochemical storage systems at high temperature in CSP plants [8].

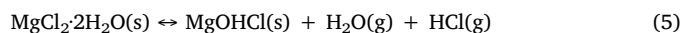
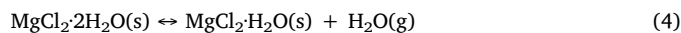
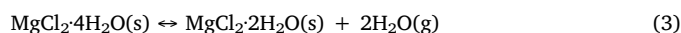
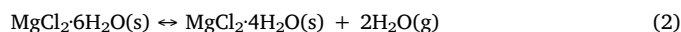
However, there is still little experience in the development of materials and systems for thermochemical storage. [9].

Reversible chemical reactions occurring between reactive components or pairs of reagents are largely responsible for thermal energy charge and discharge. The different reactions that have been studied for thermochemical storage are classified in the systems illustrated in Fig. 2. Of these, salt hydrate pairs are potential candidates for thermal energy storage as, during the energy storage phase, when heated, they are converted into partially or completely anhydrous salts, through water release. These hydrophilic anhydrous salts can readily react with water to release stored heat during the discharge step. On the other hand, it is feasible to achieve long-term thermal energy storage by separating the anhydrous salt and water at room temperature (Eq. (1)).



The Chilean Salar de Atacama brines, which are in a territory with very high solar radiation, are rich in salt hydrates. Due to their high availability and low cost, these salts can be studied and used to store thermal energy. In fact, since they are obtained as waste or by-products during brine concentration or during chemical conversion for production of lithium carbonate, among other compounds [12], it proves attractive to carry out studies for reusing these large quantities of salts as TES materials. One of the natural minerals precipitating at the evaporation ponds, during the brine concentration process at Salar de Atacama, is bischofite, composed mainly of MgCl₂·6H₂O (> 95 wt%) with some impurities, such as KCl, NaCl, Li₂SO₄·H₂O and others [13].

Previous studies [14–21] of synthetic MgCl₂·6H₂O salt indicate that it has a hydration/dehydration reaction suitable for thermochemical energy storage. In researches [15–21], the decomposition of pure magnesium chloride hexahydrate has been extensively studied. The studies determined four stages of MgCl₂·6H₂O dehydration (Eqs. (2)–(5)) under different dehydration conditions (Table 1). Eq. (5) shows that a hydrolysis reaction occurs at the same time as the dehydration reaction of Eq. (4).



More recent studies propose the application of synthetic MgCl₂·6H₂O salt as phase change material (PCM) for latent heat storage. Thus, several works focused on properties characterization, such as heat capacity and melting temperature [22–29], obtaining promising results to utilize this material for latent heat storage. On these grounds, studies by Ushak et al. [13] have been conducted with bischofite, natural mineral from Salar de Atacama, which characterized the physical and thermal properties of this material for use as PCM. Results indicated that bischofite exhibits thermal properties similar to synthetic salt hydrate.

Recent studies have focused on the use of synthetic MgCl₂·6H₂O as a thermochemical material (TCM) because the thermal decomposition of this salt occurs by means of a chemical dehydration reaction and stores a high energy density. MgCl₂·6H₂O dehydration/hydration reactions were described by some authors [14,21,30–32], and it was possible to determine the different charging and discharging operating temperatures of the material and the energy storage density *eds* (see Table 2).

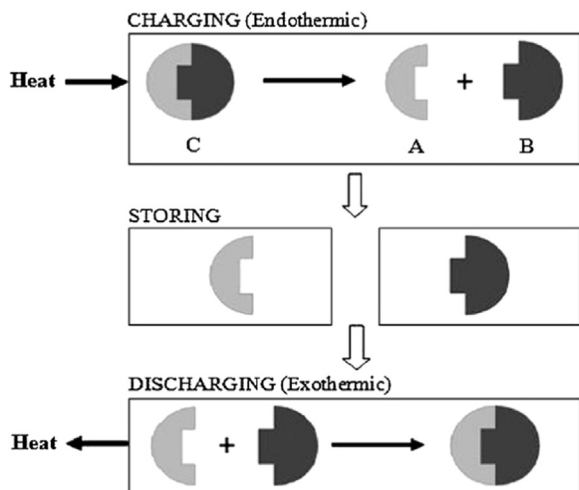


Fig. 1. Thermochemical storage process cycle: charge, storage and discharge [4].

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