

Thermochemical heat storage materials – Performance of mixed salt hydrates



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ABSTRACT

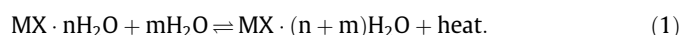
Thermochemical heat storage is highly promising, in particular with a view to long-term heat storage. For the implementation of heat storage in households, thermochemical reactions in the low temperature range below 120 °C are important. Especially salt hydrates such as MgCl₂, CaCl₂ or MgSO₄ were tested with micro gravimetric methods for their suitability. However, the cycle stability of consecutive charging (dehydration) and discharging (hydration) reactions of these materials was low and could be improved only by control of the water uptake (i.e. discharging time) to prevent overhydration. In contrast, mixtures of these salt hydrates showed significant improvements in cycle stability, mass and enthalpy balances. The experiments also showed that the cycleability of all investigated materials increased if hydration and dehydration reactions were performed under constant vapor pressure of 21 mbar. Contrary to other materials, the mixture of CaCl₂ and MgCl₂ showed good cycleability under all tested conditions. In addition, the mixture showed superior kinetic properties. Additionally, there is evidence of tachyhydrite (CaMg₂Cl₆·12H₂O) formation during cycling of the mixture by the use of XRD after the thermal analysis. Further investigations will be performed to identify further synergies, ideal mixing ratios and formed phases.

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1. Introduction

Heat storage based on thermochemical reactions is a key element in increasing energy efficiency by storing waste heat energy or solar energy for future use. Additionally, electricity production of combined-heat-and-power applications can be decoupled from heat usage (Fig. 1). This technology has the potential to store ten times more heat energy per mass or volume than latent heat storage technologies (Fisch et al., 2005). Latent heat storage, by the way of comparison only, can store five to fourteen more heat as

sensible heat storage (Hou et al., 2011). However, in real applications these numbers, compared to water storage tanks, are lower because of the additional space needed for pumps, heat exchangers and other auxiliaries. Another advantage of thermochemical heat storage is the theoretically unlimited storage time. The reason for this is the prevention of the reverse reaction by spatial separation of the reaction partners. The thermochemical reaction of a salt with water is described on the following Eq. (1):



Earlier studies had shown the dependence of pure salt hydrates on water vapor pressure, reaction progress and cycling stability (Opel et al., 2011; Rammelberg et al., 2012; N'Tsoukpoe et al., 2014). For thermochemical heat storage, cycling stability and hydration/dehydration kinetics are important material characteristics to investigate and to optimize. Cycling stability depends on chemical reversibility, whereas the kinetic of the reactions can be negatively affected by melting, agglomeration or overhydration, which is defined as overstoichiometric water uptake (Ferchaud et al., 2012). These topics frequently appear in the literature about the use of the salt hydrate magnesium chloride as a thermochemical

Abbreviations: DSC, differential scanning calorimetry; g_h , mass of hydrated form; i , cycle number; $m_{w,i}$, mass of water uptake of cycle number i , mg; $m_{w,y}$, mass of water uptake of standard cycle y , mg; $m_{\text{salt}1, \text{salt}2}$, mass of salt 1 or 2, mg; m_{mixture} , simulated, mass of mixture simulation, mg; N_m , normalized water uptake; $N_{\Delta H,R}$, normalized reaction enthalpy; n.d., not determined; p , water vapor pressure, mbar; T , temperature, °C; t , time, min; TGA, thermogravimetric analysis; $X_{\text{salt}1, \text{salt}2}$, share of salt 1 or 2 in the mixture; ΔH_e , expected reaction enthalpy of a mixed salt hydrate, kJ/mol; ΔH_R , reaction enthalpy, kJ/mol; $\Delta H_{R,i}$, reaction enthalpy of cycle number i , kJ/mol; $\Delta H_{R,y}$, reaction enthalpy of standard cycle y , kJ/mol; $\Delta H_{s1, s2}$, reaction enthalpy of pure salt hydrate 1 or 2, kJ/mol; (s), solid; (l), liquid; (g), gas; ↑, increasing value; ↓, decreasing value.

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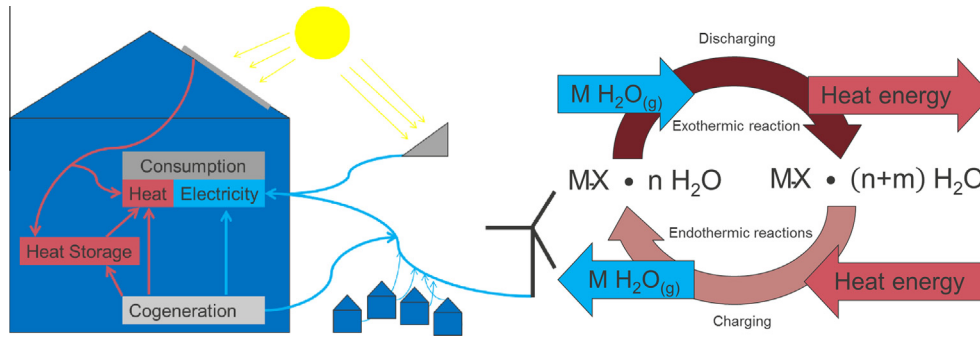
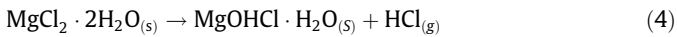
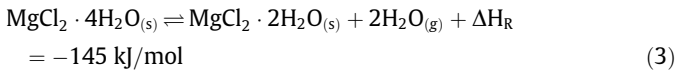
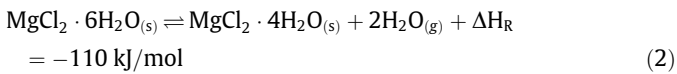
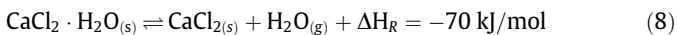
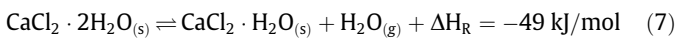
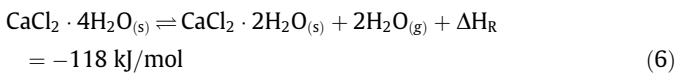
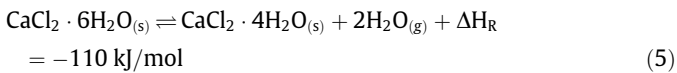


Fig. 1. Left: High-performance heat storage tank for private households. Right: scheme of thermochemical reaction for heat storage.

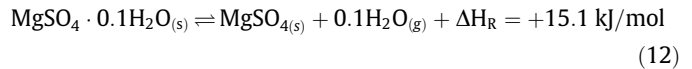
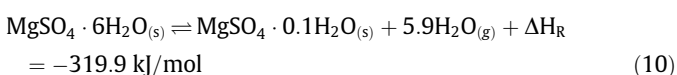
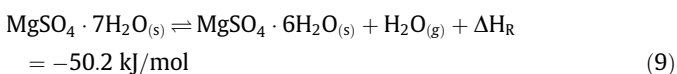
heat storage material (van Essen et al., 2010; Zondag et al., 2013; Iyimen-Schwarz and Lechner, 1983):



The dehydration and hydration of magnesium chloride hexahydrate could be useful for thermochemical storage because of its high reaction enthalpy. However, the high hygroscopy leads to (unwanted) overhydration with the appearance of deliquescence at relative humidities between 33–22% and temperatures of 20–100 °C (Ferchaud et al., 2012). Furthermore, the magnesium chloride hydrates decompose to magnesium hydroxyl chloride and hydrogen chloride as an irreversible side reaction (in non-hydrochloric atmosphere) at higher temperatures (Heide and Eichhorn, 1975; Sugimoto et al., 2007). As a result, the ongoing release of hydrogen chloride leads to a decrease of the storage density and cycle stability. The salt hydrate calcium chloride hexahydrate has also been investigated as a thermochemical heat storage material with high reaction enthalpy (Iyimen-Schwarz and Lechner, 1983):



However, it also displayed deliquescence and has a low melting point at 29.8 °C (Carlsson et al., 1979). A third highly promising salt hydrate is magnesium sulfate heptahydrate, because its potential energy storage (N'Tsoukpoe et al., 2014; van Essen et al., 2009b). Anyway, the low kinetic is an argument against the use of the pure magnesium sulfate hydrate.



Both deliquescence and melting prevent the diffusion of water vapor into a storage material during discharging and reduce useable heat storage density and power. In micro-scale measurements, the overhydration can be controlled by water vapor pressure, temperature and reaction time because of the homogeneity of the sample and the controlled reaction environment (Rammelberg et al., 2012). Macro-scale systems such as storage reactors will show a higher structural heterogeneity of the storage material. Thus, controlling the reaction will be increasingly difficult with increasing system size. Therefore, the optimization of the material itself is essential for later successful scaling-up to thermochemical heat storage applications. To overcome these disadvantages, two methods have been suggested: impregnation of carrier materials and mixing salts. Impregnations of pure and mixture salt hydrates in porous materials such as vermiculite or attapulgite showed an improved cycling stability and kinetics, with the mixtures performing better (Shkatulov et al., 2012; Jabbari-Hichri et al., 2014; Ristić and Henninger, 2014; Posern and Kaps, 2009; Posern, 2012). However, the replacement of thermochemical materials with thermochemical inactive substances decreased the energy density. The mixing of magnesium chloride and calcium chloride without a carrier also showed increased cycling stability and kinetics (Rammelberg et al., 2013). The aim of the present work is to investigate the cycle stability properties of different salt hydrates and their mixtures for the design of a thermochemical heat storage prototype (N'Tsoukpoe et al., 2014). This system enables to balance diverging supply and demand of heat and electric energy. Higher supply of electrical energy from renewable energy sources like solar or wind energy can be stored efficiently as heat energy using dehydration reactions at below 120 °C. Additionally heat storage, also using hydration reactions, from cogeneration production of electrical energy will balance electrical energy demands in household or the grid during peak load. Later off-peak heat demands can be covered as the heat storage system can be discharged by hydration of the dehydrated salt materials. This paper compares pure salt hydrates and mixed salt hydrates with respect to cycling stability, reaction enthalpy and their dependence on temperature and water vapor pressure. The influence of disturbance by overhydration is presented based on “disturbed” cycle measurements.

2. Experimental section

2.1. Materials

MgCl₂·6H₂O (p.A.), MgSO₄·6H₂O (origin: MgSO₄·7H₂O p.A.), were obtained from Merck and CaCl₂·6H₂O (reinst Ph. Eur.) was

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