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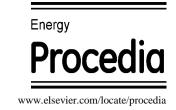
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Thermochemical seasonal solar heat storage in salt hydrates for residential applications - Influence of the water vapor pressure on the desorption kinetics of MgSO₄.7H₂O

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Abstract

An interesting thermochemical material for compact seasonal heat storage is magnesium sulfate heptahydrate MgSO₄·7H₂O. Previous studies in the field showed that this material presents a storage energy density of 1 GJ/m³ when the material is built in a TC storage system with a 50% porosity packed bed reactor. However, the material has slow reaction kinetics under the low vapor pressure typically occurring in a seasonal heat storage (13 mbar). The kinetic study presented in this paper shows that a higher water vapor pressure of 50 mbar increases the reaction kinetics of the dehydration process of MgSO₄•7H₂O, improving the performance of the material.

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 $\textit{Keywords}: seasonal\ solar\ heat\ storage\ ;\ sorption\ process\ ;\ MgSO_4.7H_2O\ ;\ water\ vapor\ presssure\ ;\ kinetic\ study.$

1. Introduction

In Europe, the main part of the energy demand in residential buildings is used for heating purposes (tap water and space heating). In order to reduce the consumption of fossil fuels, a larger contribution of solar heating systems has been proposed to fulfil this heating demand. However, solar energy requires a seasonal storage in order to be distributed according to the heat demand over a year. Thermochemical (TC) heat storage in salt hydrate materials is a very promising means for long-term, compact, low energy loss, heat storage adapted to this application. These materials can take up and release heat under operating conditions set in an open sorption TC storage system. During summer, the salt hydrate can store

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heat by dehydration of the material with an ambient air flow heated up by vacuum tube solar collectors to a maximum temperature of 150° C. During winter, the dried salt can release the stored heat by hydration with a moist air stream at 13 mbar water vapour pressure $p(H_2O)$, corresponding to a saturated evaporation of water from a borehole at 10° C [1]. An interesting salt hydrate is magnesium sulphate heptahydrate (MgSO₄·7H₂O). Previous experimental studies performed at the Energy research Centre of the Netherlands (ECN) showed that this material presents a storage energy density of 1 GJ/m^3 when the material is used in a TC storage system with a 50% porosity packed bed reactor [2]. This energy storage density is around 4-5 times higher than sensible heat storage in water tank. However, the material has slow reaction kinetics under the operating conditions applied for a seasonal heat storage. The slow kinetics of reaction may be related to the amorphization of this material [2], which occurs when the process is performed under a $p(H_2O)$ at 13 mbar, corresponding to the average $p(H_2O)$ value found for north European climate. In order to improve the performance of MgSO₄·7H₂O as TC material for seasonal heat storage, the dehydration reaction was studied at different $p(H_2O)$ to determine the optimal conditions that should be set in a TC storage system increasing the kinetics of reaction. The results of this study are presented below.

Nomenclature

 $p(H_2O)$ water vapour pressure (mbar)

α fractional conversion of the reaction

 $d\alpha/dt$ reaction rate (s⁻¹)

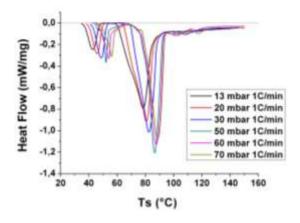
2. Material and methods

The kinetic investigation presented in this paper was carried out by Differential Scanning Calorimetry (DSC) measurements and kinetic calculations. DSC measurements were performed with a Mettler DSC apparatus on commercial powder samples of magnesium sulphate heptahydrate (VWR BDH Prolabo, CAS 10034-99-8, NORMAPUR, 99.5% pure). Samples of 10 mg sieved at 100-200 μ m were used in the different measurements in order to avoid effects of layer thickness and particle size on vapour transport as shown in previous studies [2, 4]. The dehydration was carried out between 30°C and 150°C with a heating rate of 1°C/min and left for 15 minutes at 150°C to stabilise the composition of the dehydrated material. The water vapour pressure $p(H_2O)$ applied into the system during the dehydration was controlled by an external humidification system [2]. Six water vapour pressure values were investigated between 13 and 70 mbar. The reaction rate $d\alpha/dt$ of each reaction step in the dehydration reaction was calculated from the DSC measurements for each water vapour pressure, with α corresponding to the fractional conversion of a reaction calculated by integration of the DSC peaks of each reaction.

3. Results and discussion

DSC measurements in fig.1 show that the dehydration reaction of MgSO₄·7H₂O until 150°C mainly proceeds in two reaction steps for every $p(H_2O)$ studied, characterized by two endothermic peaks. By analogy with previous studies [2], the first endothermic peak corresponds to the dehydration of MgSO₄·7H₂O into MgSO₄·6H₂O. The second endothermic peak with the abnormal long tail corresponds to the dehydration of MgSO₄·6H₂O into a monohydrated phase of magnesium sulfate.

For each phase transition, the reaction rate per mole of water was calculated and plotted for different water vapor pressures in fig.2. The two consecutive reactions taking place during the dehydration of MgSO₄·7H₂O show an increase of the reaction rate with increasing $p(H_2O)$ until 50 mbar. The reaction rate decreases again for $p(H_2O)$ above 50 mbar. This phenomenon is known as the Topley-Smith effect found in many salt hydrates. In the literature, this effect is often explained by assuming that the increasing water vapor pressure promotes the formation of additional structural defects (additional channels, cracks and pores) which increase the water vapor removal out of the material and thereby facilitate the formation of a new lower hydrated phase [5]. However, for larger vapor pressures the direct effect of the water vapor on the dehydration becomes dominant, reducing again the driving pressure difference and thereby the rate of the dehydration reaction. A maximum reaction rate can therefore be identified for each salt hydrate, depending on the lattice reorganization of the material during the dehydration reaction. For MgSO₄·7H₂O, this maximum was found in this study for a $p(H_2O)$ of 50 mbar. The use of this $p(H_2O)$ in a seasonal heat storage system would optimize the kinetics of the dehydration process of MgSO₄·7H₂O.



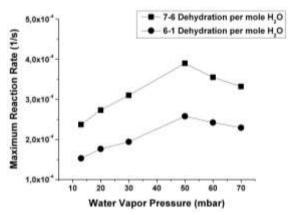


Fig. 1. DSC measurements of the dehydration reaction of MgSO₄·7H₂O performed at 1°C/min in function of $p(H_2O)$

Fig. 2. Reaction rate $d\alpha/dt$ of the dehydration reactions of MgSO₄·7H₂O performed at 1°C/min in function of $p(H_2O)$

4. Conclusions

The dehydration process of $MgSO_4 \cdot 7H_2O$ is directly influenced by the water vapor pressure applied in a seasonal heat storage system. It was shown in this paper that the kinetics of the two consecutive dehydration reactions of $MgSO_4 \cdot 7H_2O$ increases when the water vapor pressure is increased until 50 mbar. The kinetics of these reactions decreases again for water vapor pressures above 50 mbar. This phenomenon is directly related to the intrinsic properties of the material. The water vapor seems to promote the formation of structural defects (additional channels, cracks and pores) which facilitate the water vapor removal of the material and the formation of a new lower hydrated phase. Above 50 mbar, a saturation of the material surface in water vapor reduces the removal of the water vapor in the material. Therefore, the use of water vapor pressure of 50 mbar in a seasonal heat storage system would improve the reaction kinetics in the dehydration process of $MgSO_4 \cdot 7H_2O$.

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