

Thermochemical seasonal solar heat storage in salt hydrates for residential applications - Influence of the water vapor pressure on the desorption kinetics of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Citation for published version (APA):

Ferchaud, C., Scherpenborg, R. A. A., Zondag, H. A., & Boer, de, R. (2013). Thermochemical seasonal solar heat storage in salt hydrates for residential applications - Influence of the water vapor pressure on the desorption kinetics of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. In *Proceeding ISES Solar World Congress, 3-7 November 2013, Cancun, Mexico* (pp. 2436-2440). (Energy Procedia; Vol. 57). <https://doi.org/10.1016/j.egypro.2014.10.252>

DOI:

[10.1016/j.egypro.2014.10.252](https://doi.org/10.1016/j.egypro.2014.10.252)

Document status and date:

Published: 01/01/2013

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.



2013 ISES Solar World Congress

Thermochemical seasonal solar heat storage in salt hydrates for residential applications - Influence of the water vapor pressure on the desorption kinetics of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Claire J. Ferchaud ^{a*}, Robbert A.A. Scherpenborg ^{a,b}, Herbert A. Zondag ^{a,b} and Robert de Boer ^a

^a ECN, Energy Research Centre of the Netherlands, Petten, The Netherlands

^b Eindhoven University of Technology, Eindhoven, The Netherlands

Abstract

An interesting thermochemical material for compact seasonal heat storage is magnesium sulfate heptahydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Previous studies in the field showed that this material presents a storage energy density of 1 GJ/m^3 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, improving the performance of the material.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Selection and/or peer-review under responsibility of ISES.

Keywords : seasonal solar heat storage ; sorption process ; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; water vapor pressure ; 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

* Claire Ferchaud. Tel.: +31 224 564454; fax: +31 224 568615.

E-mail address: ferchaud@ecn.nl.

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 ($MgSO_4 \cdot 7H_2O$). 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/m³ 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 $MgSO_4 \cdot 7H_2O$ 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 μm 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 $p(\text{H}_2\text{O})$ 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ until 150°C mainly proceeds in two reaction steps for every $p(\text{H}_2\text{O})$ studied, characterized by two endothermic peaks. By analogy with previous studies [2], the first endothermic peak corresponds to the dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ into $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. The second endothermic peak with the abnormal long tail corresponds to the dehydration of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ show an increase of the reaction rate with increasing $p(\text{H}_2\text{O})$ until 50 mbar. The reaction rate decreases again for $p(\text{H}_2\text{O})$ 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, this maximum was found in this study for a $p(\text{H}_2\text{O})$ of 50 mbar. The use of this $p(\text{H}_2\text{O})$ in a seasonal heat storage system would optimize the kinetics of the dehydration process of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

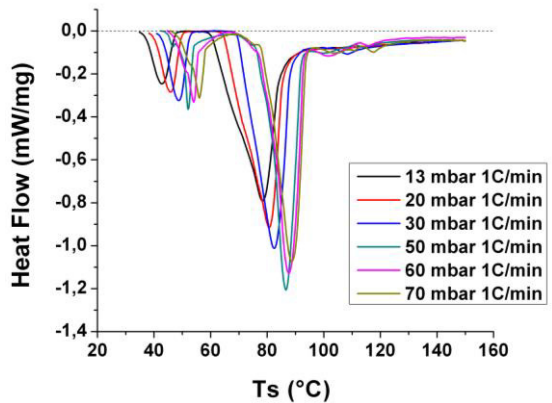


Fig. 1. DSC measurements of the dehydration reaction of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ performed at $1^\circ\text{C}/\text{min}$ in function of $p(\text{H}_2\text{O})$

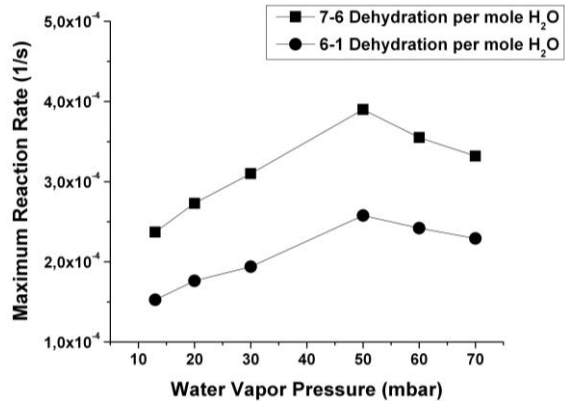


Fig. 2. Reaction rate da/dt of the dehydration reactions of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ performed at $1^\circ\text{C}/\text{min}$ in function of $p(\text{H}_2\text{O})$

4. Conclusions

The dehydration process of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 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 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Acknowledgements

This research has been carried out in cooperation between the Energy research Centre of the Netherlands (ECN) and the Mechanical Engineering department of the Eindhoven University of Technology TU/e. The project has received financial support from the Advanced Dutch Energy Materials (ADEM) program.

References

- [1] Ferchaud CJ, Zondag HA, de Boer R and Rindt CCM, Characterization of the sorption process in thermochemical materials for seasonal solar heat storage application. *Proc Int Conf 12th on Energy Storage, Innostock*, 2012; INNO-ST-08
- [2] Ferchaud, CJ, Zondag HA, Veldhuis JBJ and de Boer R, Study of the reversible water vapour sorption process of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ under the conditions of seasonal solar heat storage. *J. Phys.: Conf. Ser.* 2012;**395**:012069
- [3] Bevers ERT, Onnk HAJ, Haije WG and van Ekeren PJ, Investigation of thermodynamic properties of magnesium chloride amines by HPDSC and TG. *J Therm Anal Calorim* 2007;**90**:3, p. 923–929

- [4] van Essen VM, Zondag HA, Cot Gores J, Bleijendaal LPJ, Bakker M, Schuitema R, van Helden WGJ, Characterization of MgSO_4 hydrate for Thermochemical seasonal heat storage, *J Sol Energy Engineering* 2009;**131**:041014
- [5] L'vov BV, Brown ME, Thermal Decomposition of solids and melts – New thermodynamical approach of the mechanism, kinetics and methodology. In: Ed Springer Science Business Media BV; 2007, p. 87-109