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A review of salt hydrates for seasonal heat storage in domestic applications

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HIGHLIGHTS

- We report an evaluation of potential hydrate reactions for heat storage application.
- Thermodynamic data of almost 600 hydrate reactions are collected.
- A shortlist of 25 TCM hydrate reactions is identified based on thermodynamic data.
- Salt hydrates as seasonal heat storage is not realistic for large scale implementation.

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ABSTRACT

A literature review is performed in order to collect and analyse the thermodynamic data of an utmost number of salt hydrate reactions (i.e., 563 reactions are reviewed). These data allow us to evaluate the theoretical possibilities and limitations of salt hydrates as thermochemical materials (TCMs) for seasonal heat storage in the built environment (1 GJ/m^3 on system level). Two filters are used for evaluation. Filter 1 including three criteria i.e., an ideal hydration reaction with a capacity larger than 2 GJ/m^3, a hydration temperature of 65 °C (suitable for domestic hot water) or higher, a dehydration temperature below 100 °C to profit as much as possible from the solar heat that can be harvested. Only four of the studied hydrates fit with these demands. For selecting a larger number of hydrates, a second filter is introduced with less demanding constraints. It is expected that modifications on heat storage system level are needed to reach an acceptable system performance with the hydrates selected through filter 2 (hydration reaction with a capacity larger than 1.3 GJ/m^3, a hydration temperature of 50 °C or higher, a dehydration temperature below 120 °C). Based on this filter, a shortlist of 25 TCM hydrate reactions are identified, including the four of filter 1. The shortlist is analyzed by considering price, chemical stability, reaction kinetics and safety for domestic environment. Based on this additional analysis with the used constraints, K_2CO_3 is determined to be the most promising candidate for open or closed systems, but has a low energy density. Based on the review of 563 hydrate reactions, we concluded that no ideal salt exists for seasonal heat storage under the considered boundary conditions. With the current concept of seasonal heat storage, including closed and open systems, whereby only one dehydration cycle per year is performed under a system energy density of 1 GJ/m^3, it is not realistic for large scale implementation to use pure salt hydrates as heat storage material. By adjusting the constraints, such as multiple cycles per year or higher water vapor pressures, salt hydrates can still be used as TCMs. It should be mentioned that $MgSO_4{\cdot}7H_2O$, $MgSO_4{\cdot}6H_2O$ and $CaCl_2{\cdot}6H_2O$ are not listed in our shortlist of 25 TCMs, although these hydrates are commonly suggested in the literature as promising TCM for seasonal heat storage. The present study on *pT*-characteristics shows, however, that these salts are not fitting the demands of such a heat storage system.

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1. Introduction

1.1. Heat storage

Currently society is moving from carbon-based to more renewable energy sources in order to become less dependent on fossil fuels. A dominant part of the energy consumption of European residential sector (around 70% of the total consumption [1]) is related to domestic space heating and hot tap water generation. A cleaner sourcing of this part of the energy sector will have a large impact on the carbon production. For generation of carbon-free heat, new energy production techniques must be implemented, the majority of which are based on capturing solar radiation. However, solar radiation fluctuates on different time scales, i.e., hourly, daily and seasonally The power generated fluctuates, resulting in a variable and unpredictable supply of heat. For matching heat demand and supply, heat storage systems that account for the timescale of radiation fluctuations are required.

In this article, the focus is on seasonal storage in the built environment in the future, requiring a storage capacity of about 7–12 GJ in a typical West European dwelling based on the passive house standard (http://www.passivehouse.com/). This storage capacity is based on an average dwelling in the Netherlands with a floor area of 120 m^2, with the passive house standard of 15 kWh/m^2 for newly built houses and 28 kWh/m^2 in renovated houses [2,3]. A promising heat storage concept is based on a thermochemical reaction, which was suggested by Goldstein [4] in the sixties and gained interest in the last decade [5–7]. The solid materials involved in these reactions are called thermochemical materials (TCMs). Key advantages with respect to techniques like sensible heat storage and phase change materials (PCM) include nearly loss-free storage period and high energy density. In general, a gas-solid equilibrium reaction can be represented by:

$$MX \cdot nL(s) \rightleftharpoons MX \cdot mL(s) + (n - m) \cdot L(g), \quad (1)$$

wherein MX·nL(s) is a solid salt complex consisting of a salt MX·mL (s) and (n-m) mol of reactive gas L. In the current literature reactive gas L is considered to be H_2O, NH_3 or CH_3OH. As the targeted heat storage system should be used in residential areas, NH_3 and CH_3OH are not considered because of currently strict Dutch safety regulation [8]. As a result, H_2O is considered a reactive gas in this article. The amount of reactive gas L inside salt complex MX is called the loading of the salt. The formation reaction of MX·nL is exothermic, i.e. it produces energy what can be used when for heating purposes. The enthalpy of this formation reaction is $\Delta_r H_{m \to n} \equiv \sum_{reactant} \Delta H_i - \sum_{products} \Delta H_i < 0$. The reverse decomposition reaction of MX·nL is endothermic, $\Delta_r H_{m \to n} = -\Delta H_{n \to m}$ thus costs energy. This happens during summer heat storage periods. The equilibrium reaction in Eq. (1) implies that the maximum loading of a salt MX at a temperature T is determined by the vapor pressure of L(g).

1.2. Aim

During the past decade, many researchers have investigated TCM's as heat storage materials. The first generation of salt hydrates based on TCMs have already been developed, varying from labscale [9–11] to field demonstrations [12–14]. A complete overview of the systems constructed in the last decade is given by Scapino et al. [6]. A great body of research is also available on high potential salts for temperature storage below 100 °C, such as $MgSO_4$ [15–19], $MgCl_2$ [19–22], $SrBr_2$ [7,23], Na_2S [12,24] and $CaCl_2$ [22,25,26] which have been studied in detail. Storage of heat for temperature applications between 100 and 300 °C already shows some promising results with salts based on $CaO/Ca(OH)_2$ [27] and $CaC_2O_4/CaC_2O_4 \cdot H_2O$ [28]. Furthermore, some reviews have been published on TCM's [5,29–34], that use the energy density as selection criterion, with one exception focusing on applied working conditions [5] during hydration/dehydration. In the latter study three salts were selected: $MgSO_4$, $LaCl_3$ and $SrBr_2$ based on dehydration below 105 °C and rehydration at 20 mbar vapor pressure at 25 °C, which corresponds to the saturated vapor pressure in equilibrium with a water reservoir at 17 °C. However, the missing parameter for selection in this review is the generated temperature T_h during the hydration reaction, since this temperature is the highest output temperature the heat battery can deliver.

For introduction of TCMs on the market, it is important that TCMs are able to match the demands of the customers. As a first indication it is therefore necessary to determine if TCMs can theoretically match such demands. In the present work, we attempted to analyze and extend the search for pressure-temperature (pT) data on the basis of demanded working conditions of a TCM reactor in the built environment, i.e. a system that can store 10 GJ, deliver