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A review on the properties of salt hydrates for thermochemical storage

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Abstract

Solar energy is capable of supplying enough energy to answer the total demand of energy in dwellings. However, because of the discrepancy between energy supply and energy demand, an efficient way of storing thermal energy is crucial. Thermochemical storage of heat in salt hydrates provides an efficient and compact way of storing solar energy. The properties of the salt hydrates determine the storage capacity, operating conditions and cost of the thermochemical storage system. In this paper an overview of the properties of the most promising candidates for thermochemical storage for our purposes is given.

1. Introduction

Solar energy is more abundant during summer than in winter. The total solar energy supply is sufficient to answer the total demand of energy in dwellings [1]. However, in order to be able to rely completely on sustainable energy sources an efficient method to store energy is required. One of the oldest and simplest way to store thermal energy is in water, for example by using a boiler. For short timeslots this is an efficient and cheap way to store heat [2]. A disadvantage is that a large volume of water is needed and that in spite of insulation, heat will be lost. In phase change materials (PCMs) heat can be stored by using a phase transition in the material. PCMs have a larger storage capacity than water [3]. A disadvantage is that phase change materials are expensive and still suffer from heat loss

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during storage, as storage needs to take place at temperature levels that prevent the phase change. In thermochemical materials (TCMs) heat is stored by performing a chemical reaction. TCMs have a large storage capacity and therefore they only require a small volume to store a large amount of heat. As the heat is stored by performing a chemical reaction, there is no loss of heat during storage. The storage volumes required for the annual thermal energy demand of an average household stored in water, PCM and TCM are shown in Fig. 1.
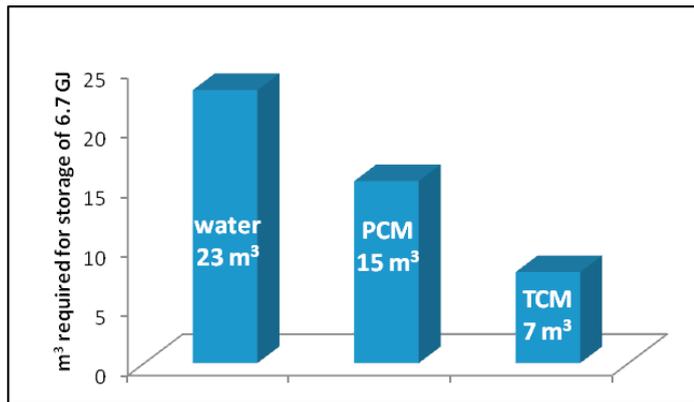

Fig. 1. An indication of the volume of storage material needed to store the 6.7 GJ/year of thermal energy for an average household, after [3]. The value for TCM used to calculate this figure is a conservative average based on Table 1 and with the auxiliary system taking a conservatively estimated 50% of volume.

The most commonly used TCMs are salt hydrates in which thermal energy is stored by drying the salt hydrate and storing the dry salt and the water separately. The reversible reaction of hydration and dehydration of a salt hydrate is shown in Eq. 1.

$$salt + xH_2O \leftrightarrow salt \cdot xH_2O + heat \tag{1}$$

Salt hydrates for thermal energy storage have a minimum storage density of 1 GJ/m^3 (depending on operating conditions) and no loss of heat occurs during storage. Using salt hydrates, a storage volume of 4 – 8 m^3 would be sufficient for the storage of the energy needed for an average household for one year. The energy density of the TCM will determine the precise volume of the storage system, the cost and the storage capacity. A large variety of prices and energy densities for different salt hydrates was found.

2. Methods

2.1. Calculation of the energy densities of selected salt hydrates

The volumetric energy densities of salt hydrates were calculated using the enthalpies of formation (at 298.15 K, 1 bar) obtained from the Handbook of Chemistry and Physics [4] and the NBS tables of Chemical Thermodynamic Properties [5]. The reaction enthalpy of hydration per mole salt Δh_r (kJ/mol) was calculated using the enthalpies of formation of the hydrated salt Δh_{fh}, the dehydrated salt Δh_{fd} and of water vapor Δh_{fw}, as shown in Eq. 2 with x the number of moles water absorbed.

$$\Delta h_r = \Delta h_{fd} + x \cdot \Delta h_{fw} - \Delta h_{fh} \tag{2}$$

The enthalpy per kilogram Δh_m (kJ/kg) was calculated by dividing the enthalpy per mole through the molecular weight of the hydrated salt. The energy density Δh_v (GJ/m^3) was calculated by multiplying the enthalpy per kilogram Δh_m with the density of the hydrated salt (least profitable, but realistic in contrast to using the density of the dry salt). It is important to note that the calculated energy densities are theoretical; they will only be reached in

an ideal process. The prices for the salt hydrates were obtained from the world wide web [6]: for each salt the cheapest bulk price for a reasonable purity was chosen. The price per gigajoule (€/GJ) was calculated by multiplying the price per kilogram with the density and dividing this by the volumetric energy density. It should be emphasized that the prices mentioned in this work are just a rough indication for bulk applications.

In order to gain insight in the dehydration and hydration temperatures of the salt hydrates, a few available phase-diagrams were studied. The dehydration and hydration take place at a certain temperature and a certain relative humidity, however, usually only a dehydration and hydration temperature is given. For a detailed investigation about phase diagrams of salt hydrates and their implications for thermochemical storage applications, the reader is referred to De Jong *et al.* [7].

3. Results & Discussion

3.1. Energy densities of selected salt hydrates

An overview on the volumetric energy densities and the prices of selected salt hydrates is given in Table 1. The salt with the highest theoretical volumetric energy density shown here is Na_2S. Because only the Na_2S anhydrate is commercially available, the prices mentioned here are the same regardless whether the pentahydrate or the nonahydrate was used. A disadvantage in the use of this salt is the formation of toxic H_2S gas during hydration. For the reaction from the pentahydrate to the 'hemihydrate', the hydration temperature of Na_2S is 73 °C and the dehydration temperature is 80 °C. It should be noted that the 'hemihydrate' mentioned here consists of a mixture of the anhydrate and the dihydrate in a (3:1) ratio [8]. $MgCl_2$ has a volumetric energy density almost as high. A disadvantage of this salt is the slow hydration and dehydration rate. The hydration temperature of the $MgCl_2 \cdot H_2O$ to the $MgCl_2 \cdot 6H_2O$ is 70 °C and the dehydration temperature of the hexahydrate back to the monohydrate is 130 °C [9]. The cheapest salt hydrate with a reasonable energy density is Na_2SO_4. A disadvantage of this salt is the low melting point (30 °C) of the hydrate and the salt needs high relative humidities (>75%) to hydrate [10]. $MgSO_4$ is also relatively cheap with a reasonable volumetric energy density. A disadvantage of this salt is that it melts during dehydration as the melting point of the salt is lower than the dehydration temperature [11].

Table 1. The energy densities and prices of selected salt hydrates for the mentioned reactions.[a]

Reaction	M (kg/mol)	ρ (kg/m³)	Δh_r (kJ/mol hyd. salt)	Δh_m (kJ/kg hyd. salt)	Δh_v (GJ/m³ hyd. salt)	Price (€/1000kg)	Price (€/GJ)
$CaCl_2 \cdot 6H_2O \leftrightarrow CaCl_2 \cdot 2\,H_2O + 4\,H_2O$	0.2190	1710	236.9	1082	1.85	116	107
$CaCl_2 \cdot 6H_2O \leftrightarrow CaCl_2 + 6\,H_2O$	0.2190	1710	361.2	1649	2.82	116	70
$MgCl_2 \cdot 6H_2O \leftrightarrow MgCl_2 + 6\,H_2O$	0.2033	1569	406.7	2001	3.14	154	77
$MgCl_2 \cdot 6H_2O \leftrightarrow MgCl_2 \cdot 1H_2O + 5\,H_2O$	0.2033	1569	360.9	1775	2.79	154	87
$MgCl_2 \cdot 6H_2O \leftrightarrow MgCl_2 \cdot 2H_2O + 4\,H_2O$	0.2033	1569	252.0	1239	1.94	154	125
$Na_2S \cdot 5H_2O \leftrightarrow Na_2S + 5\,H_2O$	0.1681	1580	312.2	1857	2.93	348	220
$Na_2S \cdot 5H_2O$[b] $\leftrightarrow Na_2S \cdot 0.5H_2O + 4.5\,H_2O$	0.1681	1580	283.3	1685	2.66	348	242
$Na_2S \cdot 9H_2O \leftrightarrow Na_2S + 9\,H_2O$	0.2402	1430	532.7	2218	3.17	348	203
$MgSO_4 \cdot 7H_2O \leftrightarrow MgSO_4 + 7\,H_2O$	0.2465	1680	411.8	1671	2.81	77	73
$Na_2SO_4 \cdot 10H_2O \leftrightarrow Na_2SO_4 + 10\,H_2O$	0.3222	1464	563.4	1749	2.56	54	56
$SrBr_2 \cdot 6H_2O$[c] $\leftrightarrow SrBr_2 \cdot 1H_2O + 5\,H_2O$	0.3555	2386	300.6	814.4	2.02	2400	2838

[a]The average was taken from the enthalpy values calculated with the handbook of Chemistry and Physics [4] and from the NBS tables [5].
[b]Articles by de Boer *et al.* [8] and Bach *et al.* [12] were used to calculate the energy density for this reaction.
[c]The pricing information was obtained from Mauran *et al.* [13], on the web [6], prices which were more than 10 times higher were found.

$SrBr_2$ is by far the most expensive salt and is probably not a good storage candidate because of the moderate energy density and high cost. The operating conditions of this salt are, however, promising with a hydration and

dehydration temperature of 52 °C [13]. The calcium chloride hexahydrate melts at 30 °C and the salt is highly deliquescent. Another major problem with the use of calcium chloride in a thermochemical storage system is the high corrosivity of the salt [14].

The properties shown in Table 1 give important information about salt hydrates for thermochemical storage. Based on these data $MgCl_2$, Na_2S, $CaCl_2$ and $MgSO_4$ are the most promising candidates because of their combined properties compared to others (energy density, price, workability). However, in order to make a solid decision in the choice of thermochemical material, more studies have to be done. Very important are the Clausius-Clapeyron diagrams to investigate the dehydration temperature and humidity and to determine for which process conditions the salts are suitable. To avoid problems during storing and releasing of energy it is necessary to know the melting and deliquescence points. Salt hydrates which seem unsuitable for thermochemical storage because of a high dehydration temperature, a low melting- or deliquescence point, or extensive corrosivity, may make an excellent material for thermochemical storage when they are encapsulated [15]. For the sake of safety the toxicity of the salt hydrates and possible by-products will have to be investigated.

3.2. Thermogravimetric analysis under controlled humidity

Only a small number of Clausius-Clapeyron diagrams or phase diagrams are known for an even smaller number of salt hydrates. An efficient way to gain insight in the Clausius-Clapeyron diagram of a salt hydrate is by thermogravimetric analysis (TGA) under controlled humidity. In TGA the mass of the sample is monitored along with the temperature. After drying the salt, the molar amount of anhydrate salt was determined. During hydration the mass increase in molar amount of H_2O was determined and the average hydration state of the salt at every point in time was calculated by dividing the molar amount of H_2O through the molar amount of salt. It is important to note that only preliminary results were obtained using the TGA measurements.

In the TGA measurements the mass of the sample is used to calculate the hydration state of the salt. In order to perform TGA under controlled humidity, in our measurements a TGA was adjusted to enable the inlet of an airflow of 20 mL/min with a controlled humidity. Before each measurement the humidity was checked.

The results of the TGA performed on calcium chloride at a water vapor pressure of 7.5 mbar are shown in Fig. 2. In Fig. 2 (a) the temperature and the calculated hydration state of the salt are plotted against the time. In Fig. 2 (b) the hydration state of the salt is plotted against the temperature. As calcium chloride is highly hygroscopic, the TGA measurement was started by drying the material at 150 °C for 2 hours to ensure that the material was completely dry in order to determine the molar amount of salt at the start of the experiment. After this drying period the temperature was lowered to 60 °C which induced hydration of the salt. The phase diagram of calcium chloride [14] suggests, however, that calcium chloride should be in the anhydrate state at 60 °C and 7.5 mbar. As the humidity was checked carefully before each TGA measurement, this might indicate that the phase diagram is not accurate.
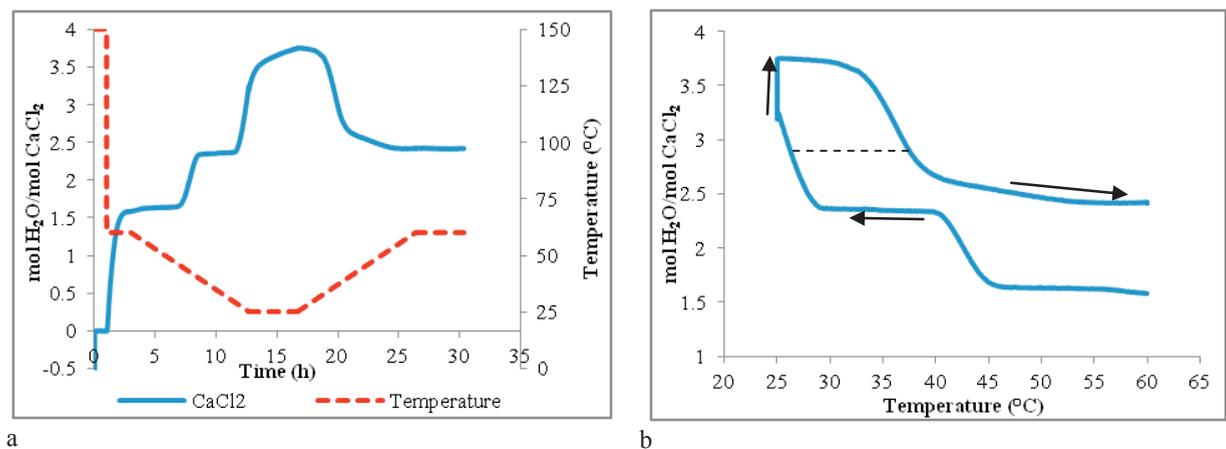

Fig. 2. Thermogravimetric analysis of calcium chloride under a water vapor pressure of 7.5 mbar.

During the ramp from 60 °C to 25 °C with 0.06 °C/min, the calcium chloride maintains a stable mass until the temperature is lowered to 40 °C after which the salt is hydrated and the mass remains stable again up to a temperature of 27 °C, after which the sample hydrates again. Calcium chloride seems to reach a hydration state of 3.5 mol H_2O/mol $CaCl_2$, whereas a hydration state of 6 mol H_2O/mol $CaCl_2$ would be expected under the conditions of 25 °C and 7.5 mbar. An explanation for the lower hydration state might be that the salt had not yet reached the equilibrium state during the 4 hours at 25 °C, as the mass of the calcium chloride still seems to be increasing. Another explanation may be that the dihydrate was reached at dehydration conditions, instead of the expected anhydrate; then the scale of the diagrams should be between the di- and hexahydrate.

In Fig. 2 (b) the dehydration process seems to require higher temperatures than the hydration process (hysteresis) and after hydration a different hydration state is reached at 60 °C, which indicates that the sample had not yet reached equilibrium, or that a higher temperature was required to dry the samples again. The arrows indicate the order in which the data were obtained: the materials were first hydrated and then dehydrated. The dashed line shows the processes that are related: the hydration step that is related with the dehydration step (in which the hydration is reversed).

The TGA measurements indicate that the phase diagram of calcium chloride might not be correct. However, as the salt hydrate did not seem to have reached equilibrium during the measurement, more inquiries have to be made in order to draw solid conclusions. The airflow might be too low to provide enough water to hydrate the salt in the given measurement time. Increasing the airflow, however, led to vibration of the sample holder. The TGA measurements might be improved by taking less steep temperature ramps and longer timeslots for the equilibration times. A large part of the water in the airflow will flow past the sample and cannot be used for hydration. At the TCM interface a surface layer of water vapor will be formed. When the salt initially takes up water the water vapor pressure at the salt interface will drop to lower value at which the remainder of the salt will reach a lower hydration state. This will inhibit the overall hydration. As the TGA measurement was performed at atmospheric pressure the hydration of the salt is limited by diffusion of water vapor through the air. By performing the TGA measurement under vacuum the diffusion processes will be accelerated to the speed of sound and equilibrium will be reached in shorter timeslots.

TGA measurements give important information about the hydration and dehydration of salt hydrates and will help to improve existing phase diagrams and to develop new phase diagrams. Phase diagrams of salt hydrates are necessary in order to determine suitable operating conditions for a thermochemical storage system.

4. Conclusions & Future developments

Based on the volumetric energy densities $MgCl_2$, Na_2S, $CaCl_2$ and $MgSO_4$ are the most promising candidates for thermochemical storage. More inquiries have to be made to gain information about other properties of the salt hydrates in order to make a solid choice for the material to use in thermochemical storage, depending on the operating conditions and other requirements. The Clausius-Clapeyron diagrams give important information about the operating conditions. With thermogravimetric analysis under controlled humidity insight can be gained in the phase diagrams of salt hydrates. It is important that the salt hydrate reaches equilibrium during the TGA measurements. By performing the TGA measurements under vacuum the equilibrium will be reached in a shorter timeslot. Problems with chemical and physical stability of salt hydrates might be solved by encapsulating the salt using water permeable polymers. In forthcoming papers we will elaborate on extensive TGA measurements under controlled humidity and stabilized materials for thermochemical storage applications, performed on the basis of results that were presented here.

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