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## Thermochemical heat storage – system design issues

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### Abstract

Thermochemical materials (TCMs) are a promising solution for seasonal heat storage, providing the possibility to store excess solar energy from the warm season for later use during the cold season, and with that all year long sustainable energy. With our fixed bed, vacuum reactors using zeolite as TCM, we recently demonstrated long-term heat storage with satisfactory output power. For domestic application, however, it will be necessary to considerably increase storage density and to reduce system costs. In this paper, we discuss issues on system, component and material levels for realizing a commercially attractive system. We first discuss a modular, fixed bed concept with a hot water storage. We show that with proper dimensioning of TCM modules and hot water storage, one can obtain a system where daily storage and on-demand heat delivery can be arranged by the hot water storage, while demands on output power, power control and material stability during operation are relaxed as much as possible. We also discuss atmospheric and central reactor concepts, which may provide lower-cost TCS systems. An important issue on component level is the implementation of a low temperature source providing evaporation heat in winter. We discuss several options, including the application of solar collectors in winter. Heat storage density can be increased by an order of magnitude by applying hydration reactions of hygroscopic salts, but this introduces physical and chemical stability issues during repeated cycles of hydration and dehydration. We discuss several of these stability issues as well as possible stabilization in a composite TCM, which should also provide sufficient vapor and heat transport.

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**Keywords:** thermochemical heat storage; energy storage; zeolite; sodium sulfide; thermochemical materials; hygroscopic salts

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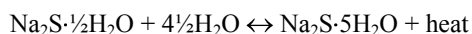
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## 1. Introduction

The yearly energy needs of the Netherlands could be satisfied by solar energy, as can be verified from the yearly average solar intensity of  $110\text{W/m}^2$  for the Netherlands (cf. [1]), and typical efficiencies of 10-15% for PV panels and about 30% for solar collectors. For instance, the yearly heat demand of 20GJ for a typical, well-insulated dwelling can be delivered by about  $20\text{m}^2$  of solar collectors. This is illustrated by Figure 1, showing the balance of heat demand and collector supply. As these do not overlap in time due to daily and seasonal fluctuations of solar irradiation, heat must be stored. Daily fluctuations during the warm season could be countered by a relatively modest hot water storage, e.g. at  $90^\circ\text{C}$ . But for seasonal fluctuations where about 10GJ must be stored, hot water storage would require a tank of at least  $50\text{m}^3$ , which is large compared to a typical dwelling. Besides, storage of  $90^\circ\text{C}$  water for the whole cold season would require exceptional insulation. An attractive alternative solution for seasonal heat storage is thermochemical heat storage (TCS), which is based on thermally reversible reactions such as:



This sorption or hydration reaction is an attractive example as it comes with a high energy density of about 2.7GJ per  $\text{m}^3$  of  $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$  [2], because it can be reversed by typical temperatures of solar collectors in summer and because it can produce heat at temperature levels of space heating (SH) and domestic hot water (DHW), as we will discuss later. Compared to hot water storage, TCS not only has the advantages of a higher heat storage density by about a factor 10-15, but also does not require thermal insulation. One only needs to keep chemical components separate, in the above case dried sodium sulfide and water, which is ideal for seasonal storage.

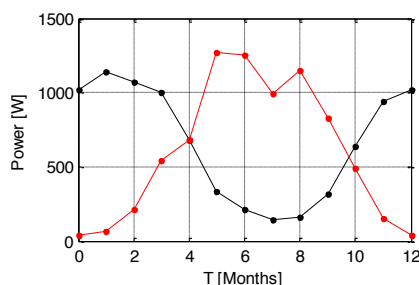


Fig. 1. Yearly heat balance for an insulated dwelling with heat needed (black) and available from solar collectors (red).

For this paper, seasonal storage of 10GJ for a typical dwelling serves as a business case and we discuss challenges for designing a TCS system which can operate for 20-30 years with minimum maintenance. Chapter 2 is on system operation and required system components, Chapter 3 is on components and Chapter 4 on material challenges. Our observations are summarized in Chapter 5. Throughout this paper, we refer to our activities in the EU FP7-projects E-hub and Einstein, where we work on reactor modeling and development, and realized an operational TCS system with a storage capacity of about 1kWh and up to 12kW of output power using 40kg of zeolite 5A as thermochemical material (TCM) [3]. In the EU FP7-project MERITS, we focus on a reactor with higher storage density TCM. Our work is also supported by internally funded research on composite TCM for improving physical and chemical stability [4]. With this paper, we hope to provide directions for designing and modeling future TCS systems.

## 2. System concepts

### 2.1. Modular TCM stock with hot water storage

In Figure 2, we sketched a system for seasonal storage of solar heat, showing the main components. During the warm season, solar energy is captured by solar collectors, heating up a hot water storage. The hot top, for instance at  $90^\circ\text{C}$ , can be fed to a heat exchanger (HX) through a TCM stock, which can provide sufficient heat for the cold

season. To handle an exceptionally cold season, one may use a conventional backup system or sufficiently enlarge the dimensions of the TCM stock. Desorbed water vapor is captured by the condenser, and condensation heat is stored in a large reservoir. Typical condenser temperatures are 20-30°C and typical reservoir temperatures are 10-20°C. During the cold season, heat is produced by vapor sorption of the TCM. Vapor is produced by the evaporator, which may physically be the same unit as the condenser. The reservoir provides heat for keeping the evaporator at 10-20°C. Thus, evaporation heat is stolen from the low temperature reservoir, and the system may be regarded as a heat pump, driven by solar energy. For water sorption, the amount of sorption heat is typically about 50-70kJ/mol H<sub>2</sub>O, while evaporation takes about 44kJ/mol. For TCS with vapor sorption it is critical that the liquid process water in the evaporator is thermally well-insulated from the reactor. Else a considerable part of the evaporation heat may be stolen from the reactor and we might as well hydrate with liquid water, providing a net heat to the reactor of only about 10-40% compared to vapor sorption. Our reactors developed for the E-hub and Einstein projects have a separate evaporator/condenser, as illustrated by Figure 2. For the MERITS project, we consider including liquid process water in each module, a compromise between good thermal insulation and minimizing the number of vacuum connections. Each module then needs a valve for separating dry TCM and process water.

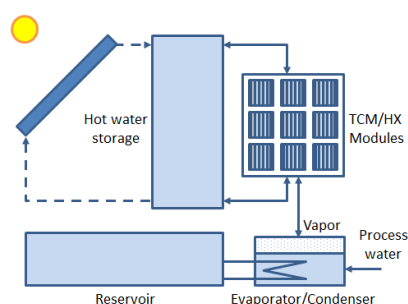


Fig. 2. Modular concept with separate hot water storage & evaporator/condenser.

On-demand sorption heat for SH or DHW requires rather high output powers of about 15kW, accurate vapor control for obtaining the right temperatures, and heating up the whole reactor at each request. This suggests division of the TCM stock in smaller and thermally insulated modules, each with its own HX, so that smaller thermal masses need to be heated up at each request. Modular TCM reactors have already been suggested for scalability and mass production (cf. [5]). Here we discuss the operational advantages, especially when we also have a hot water storage for heat delivery and short term storage. Instead of on-demand heat delivery by vapor control, one then periodically releases all heat from an entire TCM module into the hot water storage once the module is at operating temperature. SH and DHW delivery can then be arranged by the hot water storage using conventional technology, avoiding an advanced vapor control system. Summarizing, we have the following operation and dimensioning considerations:

- The hot water storage can store water at 40-60°C during the cold season and at 90°C during the warm season
- The hot water storage can store the sorption heat of an entire module
- The hot water storage suffices for countering daily fluctuations of solar irradiation
- The hot water storage takes care of the actual heat delivery to the dwelling
- When the hot water storage is emptied, the next complete TCM module is hydrated
- During the warm season, solar heat is initially stored in the boiler, and when the boiler is sufficiently full one starts dehydrating a TCM module
- Once dehydrating a module, one will try to completely dehydrate it, first with solar irradiation if still available, then from the hot water storage and then as quickly as possible during the next opportunity to save sensible heat

One can also think of saving sensible heat of freshly hydrated or dehydrated modules by sharing the heat with the next module in the row in a thermal wave. Alternatively, remaining sensible heat could be stored in the reservoir. The total amount of heat to be stored, the module dimensions and the required area of solar collectors follow from simulations with sufficiently small time steps. This is necessary to accurately follow solar fluctuations that strongly

affect collector efficiency. Figure 1 was obtained with time steps of 15 minutes during 1964-1965. To roughly estimate module dimensions for about one day of heat, one may assume that the totally required 10GJ is released in about 100 cold days, giving 100 modules of 100MJ. The main advantages of the above concept are:

- Only once heating up a TCM module to operating temperature for heat delivery or storage
- The TCM stock may gradually release 10GJ in about 100 days at a constant power of about 1200W, a much more relaxed constraint on output power than the typical value of 15kW for on-demand DHW delivery
- Heat can be delivered by known hot water storage technology instead of vapor control

Using TCM only for countering seasonal fluctuations means that TCM undergoes a cycle of hydration and dehydration only once a year, e.g. 20-30 times for 20-30 years of operation. This may also be an important advantage since physical and chemical stability of TCM under cycles of hydration and dehydration seems to be an important challenge, especially when using TCMs with higher storage density reactions, as we will discuss later.

## 2.2. Central reactor with TCM storage vessel

A disadvantage of a modular, fixed bed concept is that each module or heat battery requires its own HX and casing, requiring additional volume and material. This results in higher material costs and in a lower heat storage density than for pure TCM. The storage density of pure TCM can be approached by a central reactor concept (cf. [6]). Here, we discuss our version with a hot water storage for one day of heat, as illustrated by Figure 3.

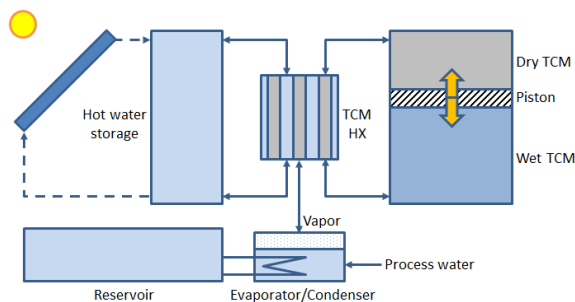


Fig. 3. Central reactor concept with a separate TCM storage.

Optimal system storage density is obtained with a single storage vessel for dry and wet TCM. The vessel may be divided in smaller compartment e.g. for one day of heat. Challenges of this concept are the required TCM transport from and to the reactor with low auxiliary power and without damaging the TCM, and to fill the reactor with sufficient compactness, and with sufficient vapor and heat transport. This particularly holds for solid TCM.

Instead of a single storage vessel with dry and wet TCM, one may also consider an open system where wet TCM is periodically removed from the system to be dried elsewhere. The storage vessel is then periodically refilled with dry TCM. If this is done several times a year, the TCM storage vessel can be smaller, leading to an even more compact system. The idea of mobile thermochemical storage has been demonstrated earlier for heating swimming pools with industrial heat (cf. [7]). In the absence of thermal losses, transport over very long distances such as to remote desert areas by oil tankers may even be feasible for drying TCM. For gasoline, transport amounts to roughly 0.10€ per liter. With 2GJ/m<sup>3</sup> for TCM, this amounts to 0.18€/kWh, of the same order as solar energy costs. Released fresh water from dehydration may be welcome in desert areas, but may not be commercially attractive.

## 2.3. Atmospheric or vacuum systems

Our research reactors and models concern vacuum systems, where water vapor is the only gas. Atmospheric systems are also considered (cf. [8]) and have their advantages. When no vacuum technology is required, construction and maintenance is simpler and cheaper. The main drawback is that water vapor transport requires

ventilation and that evaporation is difficult to realize at sufficient rate. In a vacuum system, water vapor is the only gas and transport is governed by total pressures and the speed of sound, which is typically about half of the molecular speed (cf. [9]). In an atmospheric system, one deals with partial water vapor pressures, and transport is governed by diffusion, a much slower transport process. Then, auxiliary ventilation power is required and a high power humidifier, breaking up liquid water mechanically rather than thermally. The required auxiliary power of atmospheric TCS systems is larger by an order of magnitude than for vacuum systems, which mainly require auxiliary power for circulation of HX fluids.

### 3. Component design

#### 3.1. Reactor/HX

The reactor contains the TCM stock and coolant tubes of the HX for providing desorption heat and carrying away sorption heat. Our reactors for the E-hub, Einstein and MERITS projects are based on standard air/water HXs, where the space between fins is filled up with TCM grains, as illustrated by Figure 4. The TCM bed is composed from sorted, spherical zeolite 5A grains, providing at least  $1-\pi/3\sqrt{2} \cong 26\%$  of open space for vapor transport. Each grain is in contact with a metal fin for effective heat transport towards the HX coolant tube. More details on these reactors can be found in one of our other papers [3]. Our E-hub reactor delivers its 1kWh of stored heat in about 5 minutes with an average power of up to 12kW, which is mainly limited by choked flow in the tubing. We earlier estimated that about 1200W is needed for a 100MJ module. It follows that vapor and heat transport are largely satisfactory for the given reactor/HX concept, even for on-demand DHW delivery if the E-hub reactor is scaled up to 100MJ.



Fig. 4. Unit cell of the E-hub reactor/HX.

The reactor has a rather complicated three-dimensional geometry for modeling. For rough HX dimensioning, we derived the following equation, assuming a uniform reactor temperature  $T_R$ :

$$T_L - T_0 = (T_R - T_0)[1 - \exp(-hSL / c_p \rho A v)] \quad (1)$$

Here,  $T_0$  and  $T_L$  are the temperatures of HX input and output,  $h$  [W/m<sup>2</sup>K] is the heat transfer coefficient,  $L$ ,  $S$  and  $A$  the length, circumference and cross section of the HX tube,  $v$  the flow speed and  $c_p$  [J/kgK] and  $\rho$  [kg/m<sup>3</sup>] the specific heat and the density of the HX coolant. We see that the HX saturates at length  $L = c_p \rho A v / hS$  or at coolant speed  $v = hSL / c_p \rho A$ . The delivered power reads:

$$P = c_p \rho A v (T_L - T_0) = c_p \rho A v (T_R - T_0)[1 - \exp(-hSL / c_p \rho A v)] \quad (2)$$

In particular, for a saturated HX, e.g. very long or with low coolant speed, the exponential function vanishes and we have  $P \cong c_p \rho A v (T_R - T_0)$  independent of the heat transfer coefficient  $h$ . On the other hand, for a very short HX or at very high coolant speed, Taylor expansion of the exponential yields  $P \cong hSL(T_R - T_0)$ , corresponding to a static heat contact. Equations (1-2) apply to sorption and desorption modes.

### 3.2. Evaporator and condenser

The amount of water that needs to be evaporated per second follows immediately from the required output power  $P$  [W], according to:

$$P = \frac{\Delta h}{M_w} \frac{dm}{dt} \quad (3)$$

Here,  $\Delta h$  [J/mol H<sub>2</sub>O] is the sorption enthalpy of TCM per mole water,  $M_w = 0.018$  kg/mol the molar mass of water and  $dm/dt$  [kg/s] the mass flow rate, which is in dynamic equilibrium equal to the evaporation rate. The evaporation rate is described by the Langmuir equation (cf. [10]):

$$\frac{dm}{dt} = A_w (p_{eq} - p) \sqrt{\frac{M_w}{2\pi RT}} \quad (4)$$

Here,  $A_w$  is the area of the water interface,  $p_{eq}$  is the equilibrium vapor pressure according to the vapor pressure line, and  $p$  is the actual pressure above the interface. For  $T$  we will substitute the evaporator or condenser temperature  $T_E$  or  $T_C$  depending on the mode of operation. Note that for water in vacuum, nucleate boiling can occur with a larger effective interface area. A similar equation describes sorption and desorption from the TCM stock. Combining the equations and taking the pressure drop in tubing and so on into account provides the operating pressure, from which we can determine mass flow and (de)sorption power using (3) and (4). For vacuum systems, the ratio of the pressures in the evaporator and the reactor may initially be large enough that choked flow will be rate limiting. This was also observed for the E-hub reactor.

### 3.3. Reservoir implementation

Implementation of a system based on (de)sorption of water vapor requires supply of evaporation heat from an external reservoir, which may be at a relatively low temperature of for instance 10-20°C. One may think of several implementations depending on the location of interest:

- Borehole to the soil, ground water or an aquifer
- Surface water such as a nearby channel, lake or the sea
- Ambient air or exit ventilation air
- Heat from solar collectors during the cold season

The storage density of a reservoir from which we for instance extract  $\Delta T = 10-5 = 5$  K is about 0.02 GJ/m<sup>3</sup>. The extracted heat must evaporate water for about 10 GJ of sorption heat. With 44 kJ/mol H<sub>2</sub>O for the evaporation of water and about 63 kJ/mol H<sub>2</sub>O of sorption heat for the Na<sub>2</sub>S reaction [2], this comes down to 7 GJ of evaporation heat and a reservoir of 350 m<sup>3</sup>. The total borehole length follows from a typical power of 10-50 W/m, e.g. 20 W per m borehole. If the 7 GJ of evaporation heat is consumed gradually in 100 days, we need about 800 W or about 40 m of borehole per dwelling in contact with the reservoir. Surface water will provide better heat conductivity and higher power, and may be cheaper to implement. If many neighbors access the same ground reservoir, stolen heat is bounded to one's own territory. But on the other hand, when many neighbors store heat in a larger volume, overall leakage of stored heat to the environment will be smaller.

Water reservoirs are large and costly and not always possible, so alternative ways to provide evaporator heat in winter would be welcome. Ambient air will often be too cold in winter to keep the process water in the evaporator at 10°C. Exit ventilation air from the dwelling will not contain enough heat, especially when an air-to-air HX is already used to recover heat from exit ventilation air. Another idea is using solar heat in winter, which may just suffice for keeping the evaporator at 10°C using a more modest reservoir, perhaps just the process water. And since the system already needs solar collectors in summer, we may as well use them in winter, when average solar intensity drops from 200 to about 20-70 W/m<sup>2</sup>, depending on the collector inclination (cf. [1]). The efficiency of the collectors is largely determined by periods of high solar intensity. Simulations within the MERITS project indicate

that for instance  $120\text{W/m}^2$  will produce water with  $\Delta T = 10\text{K}$  with an efficiency of about 50% in winter. This amounts to about  $0.50\text{GJ/m}^2$  in 100 days, so that a total collector area of about  $14\text{m}^2$  is needed for  $7\text{GJ}$ . The actually required area may be considerably larger, depending on the actual fluctuations of solar intensity during winter. Accurate estimation of the required area of solar collectors requires simulations with sufficiently small time steps. Note that this concept lacks a heat sink for the condenser in summer. This may particularly be an issue in warmer countries, but here it may help that at the same time more solar energy will be available for storage. On the other hand, in colder countries the condenser will heat up less and may sufficiently cool down during night.

## 4. Material challenges

### 4.1. Heat storage density and operation

The amount of heat that can be stored using a certain (thermo)chemical reaction is determined by the reaction enthalpy  $\Delta h_r$  [J/mol of reactions], which can be obtained from standard tables of formation enthalpies, taking the difference of the components on both sides of the reaction. The heat storage density  $Q/V$  [J/m<sup>3</sup>] is related to  $\Delta h_r$  by:

$$\frac{Q}{V} = \frac{\rho_h}{M_h} \Delta h_r = \frac{\rho_h}{M_h} \sum_j \Delta h_{rj} = \frac{\rho_h}{M_h} \sum_j x_j \Delta h_j \quad (5)$$

Here  $\rho_h$  [kg/m<sup>3</sup>] and  $M_h$  [kg/mol] are the density and molar mass of the hydrated state, which has the lowest density and thus determines system storage density. If the reaction takes place in several steps  $j$  with separate reaction enthalpies  $\Delta h_{rj}$  [J/mol of reactions] we can write  $Q/V$  as a summation over the reaction steps. For hydration reactions, it is practical to use the reaction enthalpy per step per mole water  $\Delta h_j$  [J/mol H<sub>2</sub>O]. We then include the number of water molecules  $x_j$  per hydration step. With (5) and standard tables of formation enthalpies, we can obtain a table of storage densities for different sorption reactions (cf. [2]).

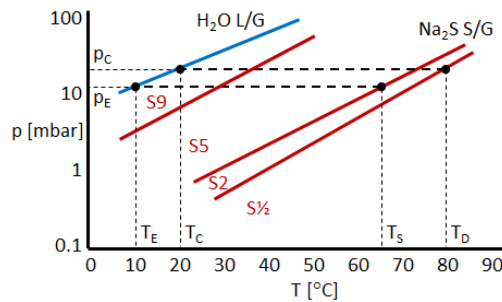


Fig. 5. Vapor pressure lines Na<sub>2</sub>S after [11].

But for application in an actual TCS system we also need the operating temperatures at which the (de)sorption reactions takes place. These depend on the operating pressures of (de)sorption, as illustrated by the vapor pressure diagrams of water and the relevant hydration states of Na<sub>2</sub>S in Figure 5. With the condenser at  $T_C = 20^\circ\text{C}$ , we have a vapor pressure of  $p_C = 23\text{mbar}$ , as we read from the vapor pressure line of water. Ignoring pressure losses, we find a minimum desorption temperature of  $T_D = 80^\circ\text{C}$  for Na<sub>2</sub>S·½H<sub>2</sub>O. On the other hand, with the evaporator at  $T_E = 10^\circ\text{C}$ , we have a vapor pressure of  $p_E = 12\text{mbar}$ . At this operating pressure, the maximum temperature of having Na<sub>2</sub>S·5H<sub>2</sub>O reads  $T_S = 65^\circ\text{C}$ , which is therefore the maximum sorption temperature. Vapor pressure diagrams are described by the Clausius-Clapeyron equation (cf. [12]):

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v} \cong \frac{p\Delta h}{RT^2} \quad (6)$$

Here  $\Delta h$  [J/mol H<sub>2</sub>O] and  $\Delta v$  [m<sup>3</sup>/mol H<sub>2</sub>O] are the molar enthalpy and molar volume differences between the phases of the sorbent, water in our case. The common approximation holds when discarding the volume of the liquid



or solid phase with respect to the volume of the gas phase and applying the ideal gas law for the gas phase. Integration of (6) with the assumption of locally constant  $\Delta h$  yields:

$$\ln\left(\frac{p}{p_0}\right) = \frac{\Delta h}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad (7)$$

This approximation holds around the reference point  $p_0, T_0$  for which  $\Delta h$  holds. We see that  $\Delta h/R$  is the slope of a vapor pressure line. This means that the slope of a vapor pressure line can be obtained from the reaction enthalpy, hence from tables of formation enthalpies. However, for system design we need the whole vapor pressure diagram, including the offset  $p_0$  at given  $T_0$ , which does not follow from formation enthalpy tables. The offset  $p_0$  at given  $T_0$  needs to be determined from an actual measurement of the vapor pressure diagram or perhaps from a very good theoretical model of the evaporation process. With (7), we can derive closed expressions for the (de)sorption temperatures  $T_D$  and  $T_S$  for given evaporator and condenser temperatures  $T_E$  and  $T_C$ :

$$T_D = \frac{\Delta h_D}{R} \left[ \frac{\Delta h_D}{RT_{D0}} + \frac{\Delta h_W}{R} \left( \frac{1}{T_C} - \frac{1}{T_{W0}} \right) + \ln\left(\frac{p_{D0}}{p_{W0}}\right) \right]^{-1}$$

$$T_S = \frac{\Delta h_S}{R} \left[ \frac{\Delta h_S}{RT_{S0}} + \frac{\Delta h_W}{R} \left( \frac{1}{T_E} - \frac{1}{T_{W0}} \right) + \ln\left(\frac{p_{S0}}{p_{W0}}\right) \right]^{-1} \quad (8)$$

Here,  $\Delta h_W$  is the evaporation enthalpy of water at offset  $(T_{W0}, p_{W0})$  and  $\Delta h_D$  and  $\Delta h_S$  are the (de)sorption enthalpies of the vapor pressure lines at offsets  $(T_{D0}, p_{D0})$  and  $(T_{S0}, p_{S0})$ . Table 1 contains a list of heat storage densities and (de)hydration temperatures based on available vapor pressure diagrams for sodium sulfide [11], strontium bromide [13], calcium chloride [14] and magnesium chloride [15]. In another paper [2], we give a longer list including other (de)hydration reactions, but without operational temperatures due to lacking vapor pressure diagrams.

Table 1. Storage densities and operating conditions for several reactions for  $T_E = 10^\circ\text{C}$ ,  $T_C = 20^\circ\text{C}$ .

Reaction	$Q/V$ [GJ/m <sup>3</sup> ]	$T_S$ [°C]	$T_D$ [°C]
$\text{Na}_2\text{S} \cdot \frac{1}{2}\text{H}_2\text{O} + 4\frac{1}{2}\text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$	2.7	65	80
$\text{SrBr}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O} \leftrightarrow \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	1.9	45	52
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O} \leftrightarrow \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.8	35	52
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.9	60	110

Instead of approximation (7), one may work with more sophisticated models of vapor pressure lines, such as from the quantum theory of evaporation (cf. [12]). Once vapor pressures lines are measured, one may use heuristic fits such as the Antoine equation for water or the Toth equation for zeolite and silica gel (cf. [16]). We note that the Toth equation can be inversed, yielding the following formula for the vapor pressure:

$$p = \frac{n}{[a^t - (bn)^t]^{1/t}} \quad (9)$$

Here,  $n$  [mol H<sub>2</sub>O/kg zeolite] is the water loading,  $a = a_0 \exp(E/T)$ ,  $b = b_0 \exp(E/T)$  and  $t = t_0 + c/T$ , where  $a_0$ ,  $b_0$ ,  $c$ ,  $E$  and  $t_0$  are constants. We use this equation for modeling our zeolite reactors, together with the following expression for the sorption enthalpy, which can be derived from (9):

$$\Delta h = Rc \left\{ -\frac{\ln[a^t - (bn)^t]}{t^2} + \frac{1}{t} \frac{1}{[a^t - (bn)^t]} \left[ a^t \left( \ln a + \frac{tE}{c} \right) - (bn)^t \left( \ln(bn) + \frac{tE}{c} \right) \right] \right\} \quad (10)$$

It is interesting to compare the cycles of seasonal storage with sorption chillers or sorption heat pumps. For the latter, solar heat is immediately used for cooling to  $T_E$  or for heating at  $T_S = T_C = T_M$ , hence with sorption and



condensation at the same temperature as illustrated by Figure 6a. This allows addition of sorption and condenser heat, leading to coefficients of performance up to for instance 2-3 in theory, or about 1.6-1.7 in practice (cf. [17]).

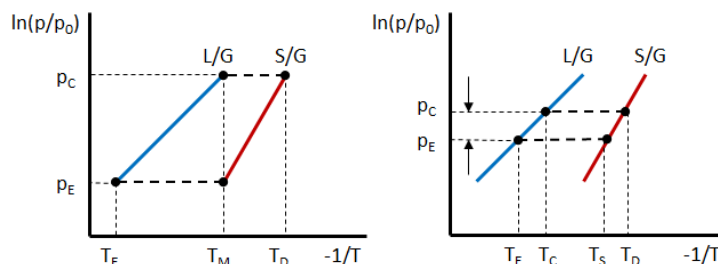


Fig. 6. (a) Sorption chiller/heat pump; (b) Seasonal storage.

For seasonal storage, sorption occurs during the cold season and condensation during the warm season, so it is impossible to add sorption and condensation heat. Instead, one will store condenser heat at  $T_C$  in a reservoir for later use in winter. If the reservoir is large and in winter kept at  $T_E$  near  $T_C$ , and if only a single vapor pressure line is involved, the sorption temperature  $T_S$  can be near  $T_D$ . We then approach the ideal case of reversible seasonal storage, where stored solar heat is recovered at nearly the same temperature, as illustrated by Figure 6b.

#### 4.2. Stability under operation

The reactor should be physically and chemically stable during lifetime, e.g. for 20-30 years and a similar number of cycles of hydration and dehydration. Examples of physical stability problems are coagulation and pulverization of TCM. Coagulation can be induced by undesired contact with liquid water or by melting at locally peaking temperatures. System design therefore requires the phase diagrams of the candidate TCMs. In Figure 7, we sketched the phase diagram of sodium sulfide and water. Here V, L, S refer to vapor, liquid and solid phases, where the numbers indicate the numbers of water molecules in the hydrated state. According to the phase diagram, melting occurs at 83°C for the 0, 2 and 5 hydrates and at 50°C for the 9 hydrate. This means that application of the  $\frac{1}{2} \leftrightarrow 5$  reaction requires  $T_D < 83^\circ\text{C}$ , which is challenging for dehydration at  $T_D = 80^\circ\text{C}$  at  $T_C = 20^\circ\text{C}$ .

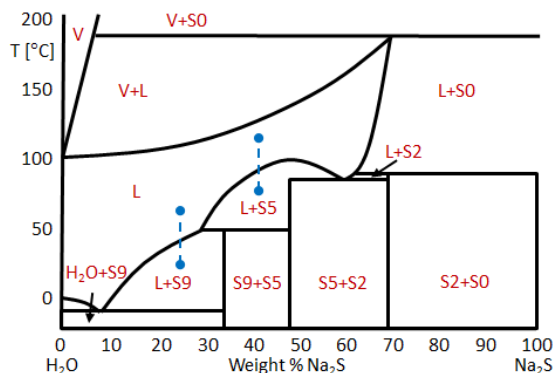


Fig. 7. Phase diagram of Na<sub>2</sub>S and water after [11].

Pulverization may occur due to different molar densities of the different hydration states. For instance, the molar volumes of the 0 and 5 hydrates of Na<sub>2</sub>S are 42 and 106 cm<sup>3</sup>/mol respectively and hence differ by a factor of about 2.5. When crystal structures actually change during cycles of hydration and dehydration, resulting mechanical stress may lead to pulverization and detachment from the HX. It should be studied whether these structural changes really occur, or whether perhaps the crystal structure of the highest hydration state remains. If not, stabilization by incorporation of the TCM in a suitable matrix material may help. Note that then, the vapor pressure and phase diagrams may both be different and must be determined again. We note that the phase diagram is also useful for the

production of TCM in the desired state for reactor construction. For instance,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  hydrate can be precipitated on the HX starting at a solution with about 25 weight % of  $\text{Na}_2\text{S}$  at  $60^\circ\text{C}$  and cooling down to  $20^\circ\text{C}$ . This is indicated by the left dotted blue line in Figure 7. The right dotted blue line produces  $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ .

Chemical stability during operation amounts to control or prevention of side reactions of TCM, which may lead to toxic or corrosive byproducts or to considerable depletion of the TCM stock. For sodium sulfide, we deal with the formation of  $\text{H}_2\text{S}$  vapor by the reaction of  $\text{Na}_2\text{S}$  with water. This may occur by undesired contact with liquid water, but perhaps also at lower pace in contact with water vapor.  $\text{H}_2\text{S}$  vapor can spread through the system including the evaporator, dissolve in (microscopic) water layers and cause corrosion of metal components with the formation of  $\text{H}_2$ . Coatings,  $\text{H}_2\text{S}$  and  $\text{H}_2$  getters or the addition of  $\text{OH}^-$  may help. But even if the chemistry can be controlled, buildup of non-condensable gases such as  $\text{H}_2\text{S}$  and  $\text{H}_2$  may block the condenser and considerably slow down vapor transport if the partial pressures become of the same order as the water vapor pressure.

Likely, the ultimately used TCM will be a composite with a stabilizing matrix providing physical and chemical stability, sufficient heat and vapor transport, maximum storage density and minimum production costs. An attractive option may be a bulk TCM structure containing heat conducting fibers towards HX channels and vapor channels for vapor transport towards the periphery of the whole TCM volume, which may thus contain a branched structure of conducting fibers and vapor channels. Graphite may be an attractive material for the conducting fibers, as it is inert and has a rather good heat conductivity of  $160\text{W/mK}$ . Vapor channels may be empty channels, empty channels with porous walls or porous fibers, if this is easier realized. For large volume production, it may be attractive to build up the reactor from prefabricated building blocks of composite TCM, perhaps including the HX channel as well.

In order to make advances on reactor/HX and evaporator/condenser design, we selected zeolite 5A for our E-hub and Einstein reactors. This TCM has a storage density of only about  $0.1\text{GJ/m}^3$  at operating conditions, but is robust and inert. For MERITS, our first choice is  $\text{Na}_2\text{S}$  because of its high storage density, because it is inexpensive, does not melt, and because vapor pressure and phase diagrams are known from literature. We will try to solve the known corrosion issues by coatings and the physical stability issues by a composite TCM of  $\text{Na}_2\text{S}$  and a matrix material. As a backup, we will also study the relevant properties of several other hygroscopic salts.

## 5. Conclusions

A system with a hot water storage for daily fluctuations of solar power combined with a TCM storage for seasonal fluctuations is an attractive option for providing all year long sustainable heating by solar energy. In particular, when the TCM modules and the hot water storage are dimensioned on the amount of heat of for instance about 1 day, one can fully hydrate and dehydrate modules once they are at operating temperature. The actual heat delivery can then be arranged by well-known hot water storage technology, so that the constraints on output power and vapor control can be ultimately relaxed. In addition, TCM modules then only need to be hydrated and dehydrated once a year, minimizing the demands on material stability during operation.

For the actual implementation, one can choose between vacuum or atmospheric systems and between fixed bed or central reactor concepts. Atmospheric systems could be cheaper for e.g. tubing, connections and maintenance. On the other hand, atmospheric systems require considerable amounts of auxiliary power for vapor transport and low temperature evaporation, in contrast with vacuum systems, which are ideal for vapor transport and evaporation. A central reactor with a separate TCM storage vessel would optimize system storage density and may therefore also be realized at lower costs, provided that TCM transport from and to the reactor can be implemented effectively.

Our E-hub reactor delivers its  $1\text{kWh}$  of stored heat in about 5 minutes with an average power of up to  $12\text{kW}$ , which is mainly limited by choked flow in the tubing. It follows that the applied vacuum technology with a fixed  $2\text{mm}$  zeolite 5A bed and a pool evaporator largely satisfies for vapor and heat transport, even for on-demand DHW delivery when the modules are scaled up to for instance  $100\text{MW}$ .

The necessary low temperature reservoir may be implemented by groundwater or surface water such as a nearby channel or lake, depending on the location. Else, one may consider to keep a reservoir of more modest dimensions and use collector heat in winter to keep the reservoir at the desired evaporation temperature.

The TCM storage density is determined by the reaction that can be reversed at given operating temperatures. Hydration and dehydration of sodium sulfide between the  $\frac{1}{2}$  and 5 hydrates is an attractive reaction as it occurs at operation temperatures favorable for solar collectors and SH/DHW delivery. However, for application in TCS

systems, sodium sulfide must be stabilized physically and chemically, e.g. by incorporation in a composite TCM. There may be more suited reactions for TCS systems, perhaps hydration reactions of other salts, but for several promising alternatives we encountered, additional research on the physics and chemistry at operation conditions would be required for a proper system evaluation.

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The project is carried out by four research institutes (TNO, VITO, Tecnalia, Fraunhofer ISE), two universities (Ulster University, University of Lleida), two SME's (De Beijer RTB, Zonne-Energie Nederland BV), and two industries (Mostostal, Glen Dimplex). The team will work with novel high energy density thermochemical materials that can supply required heating, cooling and domestic hot water for a dwelling with up to 100% renewable energy sources (e.g. the sun) throughout the year. The key development issues are:

- The delivery of heat on different dedicated temperature levels for heating, cooling and domestic hot water
- The tailoring to the requirements of individual dwellings
- The design and development of a dedicated solar collector
- The integrated design for the components and enhanced thermo-chemical materials, including the control system

Furthermore the project includes the development of business models and market strategies to foster market take-up before 2020. More information on MERITS is available on our public website “[www.MERITS.eu](http://www.MERITS.eu)”.

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