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# Recent progress in thermochemical heat storage: materials and applications

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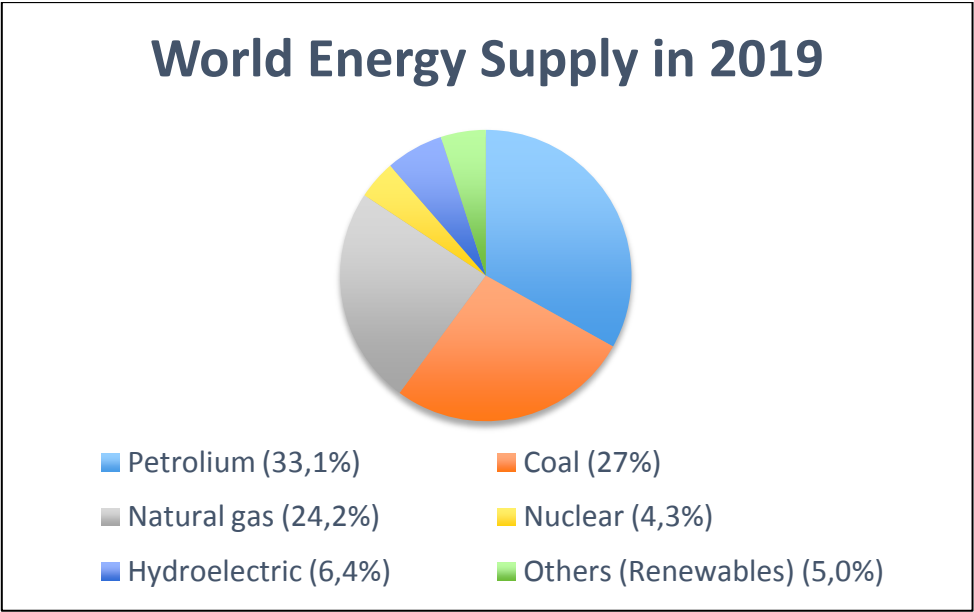
## Abstract

Thermochemical heat storage (TES) is among the most promising options to increase the use of renewable energy by by-passing the issue of the intermittence of the related sources. In this review, at first, articles based on hydroxide-based systems (working at high temperature, up to 500°C) have been considered. Then, sorption systems, in particularly systems constituted of salt hydrates-containing composites have been reviewed. These systems can be regenerated (charged) at temperature around 150°C and they are then adapted for building applications. Issues on technical solutions as well as on the storage material choice still present and need to be solved for reaching a higher technology readiness level. The aim of this review is to provide a general view of recent progress in term of materials for thermochemical heat storage systems.

**Key words:** Sorption, Salt hydrates, Calcium Hydroxide, Domestic heating, Concentrated solar power, Thermochemical heat storage

**Abbreviations:** GHG, greenhouse gas emissions; TESS, thermal energy storage system; SHS, sensible heat storage; LHS, latent heat storage; TCHS, thermochemical heat storage; PCM, phase change material; TC, thermal conductivity; ESD, energy storage density; CSP, concentrated solar power; TCM, thermochemical material; HBN, hexagonal boron nitride; CTAB, cetyl trimethyl ammonium bromide; EG, expanded graphite; CaL, calcium looping; SG, silica gel; MPC, mesoporous carbon; CNT, carbon nanotube; ENG, expanded natural graphite; RH, relative humidity; AC, activated carbon; DRH, deliquescence relative humidity; XRD, X-ray diffraction; SEM, Scanning Electron Microscope;

**1. Introduction**



*Figure 1. Illustration of the world energy supply sources in 2019*

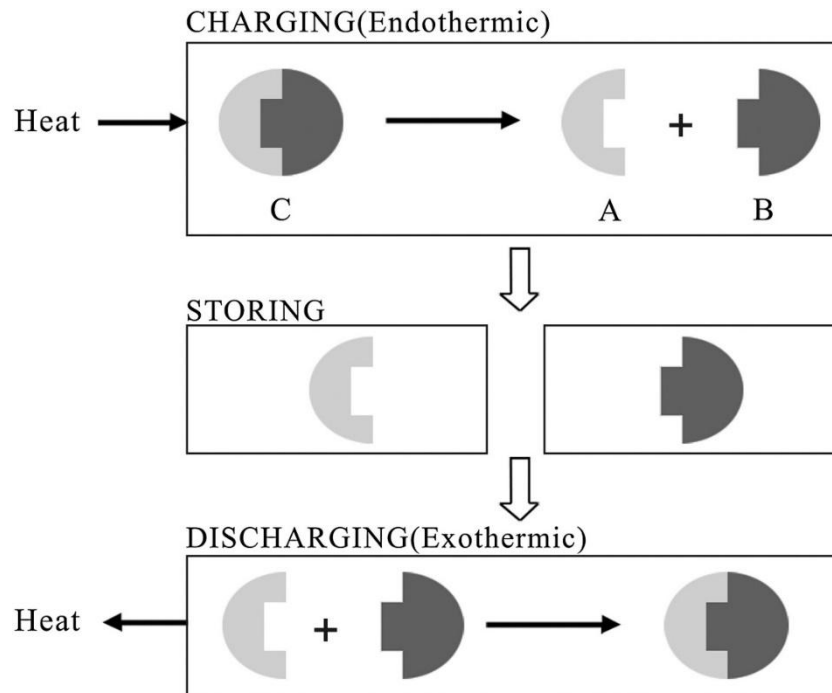
Over the past few decades, we face the uncontrolled increasing of the energy consumption worldwide. As the world population has reached 7.8 billion people and continue to grow with an estimation of over 9 billion in 2050 [1], providing energy for the long-term needs of future generations represent a colossal problem of the 21<sup>st</sup> century. *Figure 1* shows the world energy sources used in 2019 (data collected from [2]). Primary fossil energy sources (petroleum, coal, and natural gas) represent 84% of the global energy consumption. This acceleration of fossil fuels utilization led to serious and negative impact on the environment (global warming and pollution), and consequently on human health. The acceptance of the Paris Agreement imposes to each signatory to take action to reduce the greenhouse gas emissions (GHG) and to enhance the use of renewable energy [3]. Renewable energies can be produced from: biomass, wind, water, earth (geothermic), and sun. Among the others, solar irradiation appears to be the most adapted thermal energy source, due to its vast availability and relative easy collection. However, in many places in the world, due to the intermittent and location-dependent nature of the sun, important mismatch between supply and demand of energy affects implemented solar technologies both at short and long-term. As a consequence, integrating an adequate thermal energy storage system (TESS) could be the promising solution to tackle this seasonal energy difference [4-7]. A TESS works as a collector and a storage of the excess solar energy

during the hours of sunshine. The stored energy can be then released for usage when needed (for buildings heating as an example). Sensible heat storage (SHS), latent heat storage (LHS) and thermochemical heat storage (TCHS) are 3 types of TESS that have been investigated and widely discussed in literature up to now [7-12]. The SHS system stores energy by exchanging the temperature within the storage medium. A variation of 50°C can generate an energy storage density (ESD) of 200MJ/m<sup>3</sup> [13]. The advantages of this system are its simplicity and the low-price implementation since the maturity of this technology is already at industrial scale. Major drawbacks of SHS systems are the low energy density, the large volume of installation, and the heat perditions (that lead to a significant and relatively fast loss of the stored energy) [14]. LHS systems operate in a small temperature range and the storage materials are phase change materials (PCM). These systems present a higher energy density than SHS with an ESD up to 500MJ/m<sup>3</sup> [13]. Nevertheless, PCMs suffer of low thermal stability which leads to the uncertainty behavior at long-term [14].

TCHSs are based on reversible exo-/endothermic reactions. The thermal energy is stored as chemical potential by separating the reactants through endothermic reaction (charging process). Reversely, the discharge process happens during exothermic reaction when the reactants are put in contact (*Figure 2*). The TCHS system offers a much higher storage density than the other two systems, resulting in a smaller volume of the storage material. Another clear advantage of this system is the very low heat loss during the time when the charged material is kept isolated from the environment. As the other technologies, TCHS systems also present some limitations such as: the installation complexity and the heat and mass transfer limitations due to the low thermal conductivity (TC) of the storage materials [4,15,16]. Recent researches are focus on solving these drawbacks and extend the application panel to the industrial scale. On this point, Farulla *et al.* [10] discussed the recent advancements in power-to-heat technologies, and Liu *et al.* [12] reviewed the potential of storage materials for electricity production in concentrated solar power (CSP) plants using high temperature storage material system. The storage capacity of the TCHS system depends on the involved reversible reaction: a high reaction enthalpy corresponds to a high heat storage capacity. Thermochemical materials (TCM) are also selected by their intrinsic properties and by matching the process conditions [4,7]:

- High reaction enthalpy and high ESD under operating working conditions
- Appropriate TC to increase mass and heat transfer
- Completely reversible reaction and no secondary reactions

- Low cost and abundance
- Non-toxic and non-corrosive materials
- Regeneration temperature compatible with the specific application (for example a charging temperature below 150°C for applications in the building sector and up to 1000°C for the application in electricity production in power plants).



**Figure 2.** Principle steps in a TCHS cycle: charging, storing and discharging (from Abedin *et al.* [6])

Based on above selection criteria, potential TCMs, such as metal hydride [17-22], redox system [23-27], methane reforming [28-30] have been drawing attentions of various research groups. Among them, most of studies privileged the development and application of hydroxide-based materials and sorption material systems because of their properties answering to the requirement just listed above. André *et al.* [31] pointed out that the  $\text{Ca(OH)}_2/\text{CaO}$  couple shows a great potential as storage system due to the high enthalpy of reaction, the low cost, and the easy implementation in the industrial applications. Among the others, Kyaw *et al.* [32] studied the  $\text{CaO}/\text{CO}_2$  working pair at high temperature to store thermal energy. Frazzica and Freni [33] concluded in their study that employing ammonia as a working fluid can exploit lower evaporator temperatures, even if the performance is still limited. Donkers *et al.* [34] reported that salt hydrates are very promising storage materials for domestic seasonal heat storage, but not realistic for a large-scale implementation.

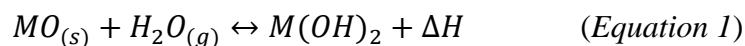
Due to the wideness of the heat storage domain, in this review only the latest research (since 2018) focused on hydroxide for CSP technologies and sorption materials for residential space heating applications, focusing of three main fluids (CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O). Challenges and future perspectives in the research of new materials will be also given.

## 2. Solid-Gas TCHS reaction systems

TCHS reactions are categorized into solid-gas reactions, liquid-gas reactions, and gas-gas reactions [8,35,36]. This review is mainly focused on solid-gas reactions: hydroxide-based systems (Ca(OH)<sub>2</sub>/CaO or Mg(OH)<sub>2</sub>/MgO) and sorption systems with different working fluids (NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>O). Their storage properties will be as well discussed in this section.

### 2.1. Hydroxide-based reactions

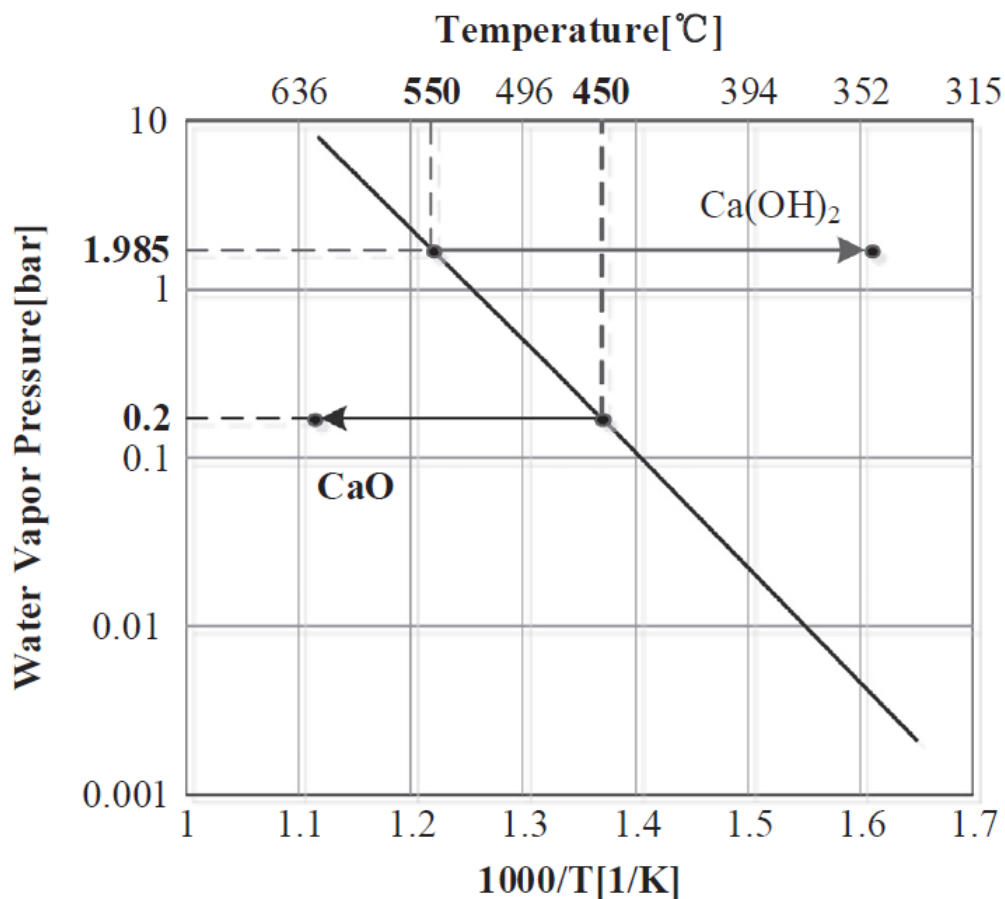
Reversible hydration/dehydration reactions of metal oxides (*Equation 1*, where M represents the metal) have been of key interest in recent years. Original articles can be traced back to the 80s [35,37]. Ca(OH)<sub>2</sub>/CaO and Mg(OH)<sub>2</sub>/MgO are the most studied hydroxides and considered potential candidates for thermal energy storage systems at medium and high temperature (up to about 500°C). Their potential is also due to their abundance, their high ESD (up to 800kJ/kg<sub>composite</sub>) and their high reaction enthalpy ( $\Delta H = 104\text{kJ/mol}_{\text{H}_2\text{O}}$  for Ca(OH)<sub>2</sub> and  $\Delta H = 81\text{kJ/mol}_{\text{H}_2\text{O}}$  for Mg(OH)<sub>2</sub>, respectively) [38].



#### 2.1.1 Ca(OH)<sub>2</sub>/CaO systems

The dehydration reaction of Ca(OH)<sub>2</sub> occurs between 400 and 508°C, so the Ca(OH)<sub>2</sub>/CaO system can be used for high temperature thermal energy storage. Samms and Evans [39], Schmidt *et al.* [40] concluded that the optimal operating conditions of the system (*Figure 3*) corresponded to a temperature of 510°C and a water vapor pressure of 1bar. This system has attracted enormous attention especially in CSP [41]. In this study, Takham and Tippayawong developed a small TCHS unit using charged in Ca(OH)<sub>2</sub> powder as reactants and analyzed the hydration behavior of the material. The hydration rate revealed to be high; a rapid increase of the temperature was observed. The energy efficiency was relatively high, in the 60-83% range. The agglomeration of the powder after hydration was also observed, causing mass

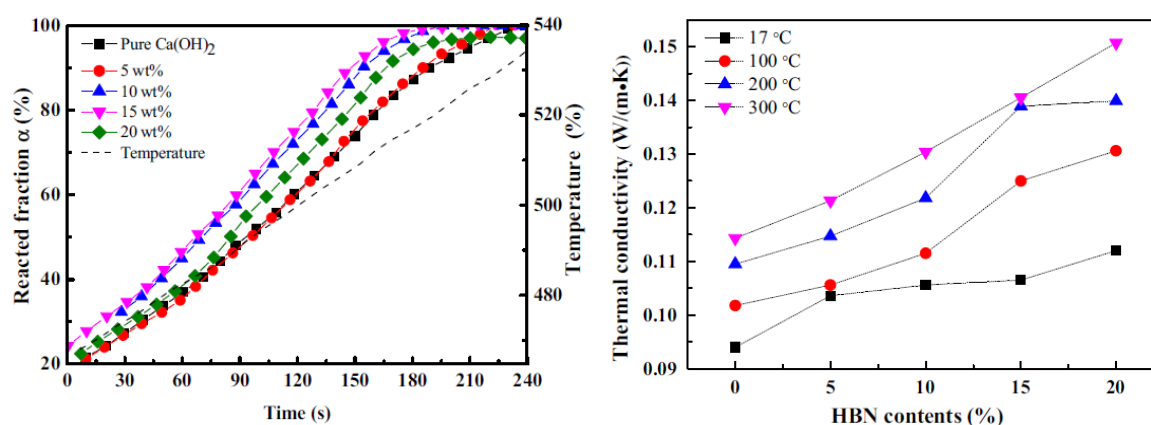
transfer issues due to the non-uniform diffusion of water in the bed. At 510°C and 1 bar, another TCHS setup was built by Dai *et al.* [42] to monitor the thermal cycling stability of the system. Their results suggested that there was no performance decreasing of the material after 20 cycles, but technical problems, as the powder agglomeration and the poor TC, had been still to be overcome. Yan *et al.* [43] investigated the influence of the dehydration temperature on the performance of the  $\text{Ca(OH)}_2/\text{CaO}$  system. They have verified that by choosing a higher dehydration temperature and a thinner sample layer, the overall kinetics, as well as the energy efficiency, could be improved. Xia *et al.* [44] ameliorated the mass transfer through the CaO bed by integrating a fractal porous media. Effective gas diffusion coefficients of 0.228 and 0.188 $\text{cm}^2/\text{s}$  were respectively measured for CaO and  $\text{Ca(OH)}_2$ . For comparison, these values are higher than that of oxygen diffusion in air at 25°C (0.176 $\text{cm}^2/\text{s}$ ).



**Figure 3.** Equilibrium line for the  $\text{Ca(OH)}_2/\text{CaO}$  reaction system  
(from Schmidt *et al.* [40])

Recently, Xia *et al.* [25] presented a novel composite made from CaO, sodium carboxymethyl cellulose and vermiculite to overcome the problems related to the pure CaO powders (mass transfer issues and low TC). The composite was structurally stable during

several cycles of dehydration/hydration and a significant improvement of the heat storage rate was observed, when compared to the natural product. Always in 2020, another group in Japan, Funayama *et al.* [45], also developed a new composite material prepared depositing  $\text{Ca}(\text{OH})_2$  on a Si-SiC ceramic honeycomb support with the aim to enhance the heat transfer through the reaction bed. A heat output rate of 1.6kW/L-bed was recorder, being two times higher than that of the pure  $\text{Ca}(\text{OH})_2$  pellet bed. It should be noted that the Si-SiC ceramic honeycomb is an inert support and that no side-products were formed during the cycling experiment.



**Figure 4.**  $\text{Ca}(\text{OH})_2$  conversion (dehydration) a), and thermal conductivity b) as a function of HBN content (from Huang *et al.* [46])

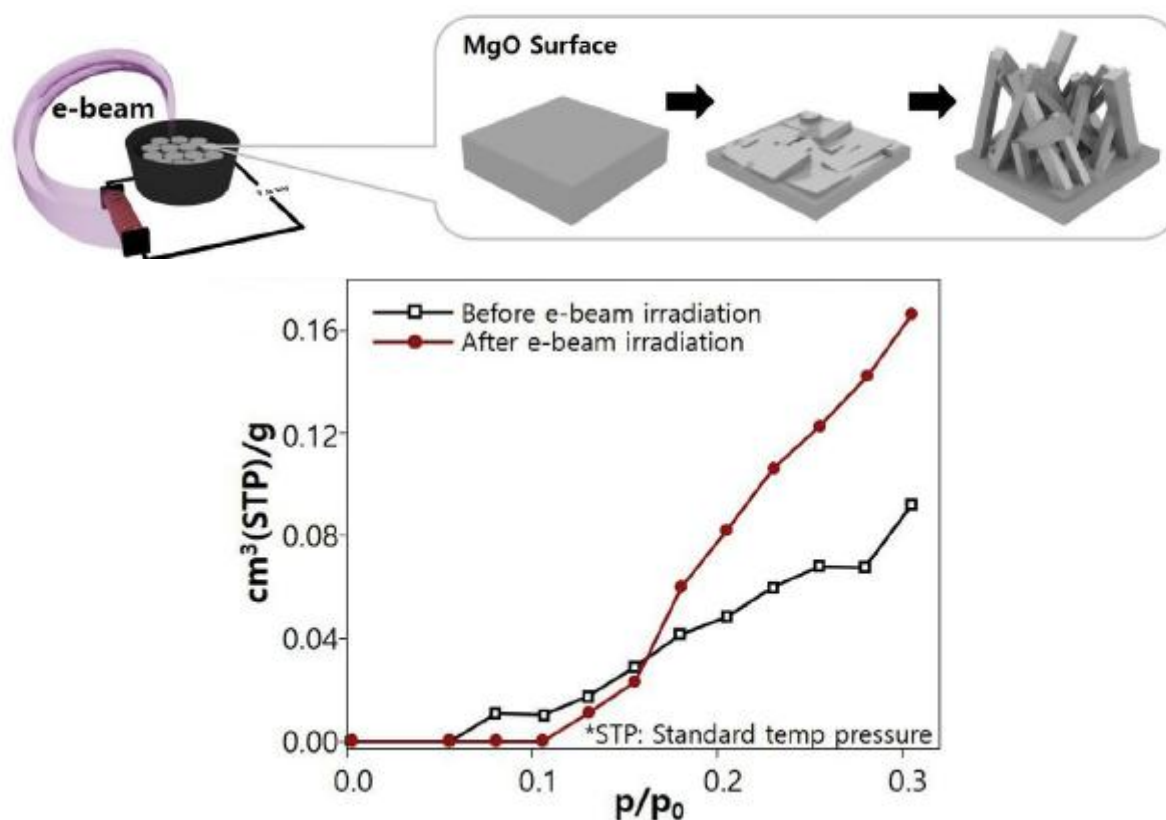
Huang *et al.* [46] investigated the dehydration of the hexagonal boron nitride (HBN) doped  $\text{Ca}(\text{OH})_2$ . The composites revealed to be more performing than the pure calcium hydroxide. First, the dehydration rate of the 15%wt. HBN-doped composite was much higher than that of the pure  $\text{Ca}(\text{OH})_2$  (Figure 4a). Figure 4b illustrates the enhancement of the TC (improvement of 13.2% at 17°C and nearly of 23% at 300°C) of the material after being doped with different content of HBN. The same research group [47] synthesized a spindle-shaped  $\text{Ca}(\text{OH})_2$  nanomaterial and evaluated its performances. The study proved that the spindle-shaped material increased the specific surface area of the storage bed, resulting in a better heat storage capacity (up to 1300kJ/kg<sub>composite</sub>). The newly synthesized material also provided a faster reaction kinetic and a higher cycling stability than the “normal-shaped” commercial calcium hydroxide. This indicated that morphology of the material selected could play a crucial role in the development of TCHS.



### 2.1.2 $Mg(OH)_2/MgO$ systems

Even though presenting a lower ESD than the  $Ca(OH)_2/CaO$  systems, the  $Mg(OH)_2/MgO$  systems are still largely studied. Piperopoulos *et al.* and Yan *et al.* [48,49] synthesized magnesium hydroxide in presence of a cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), to diminish the material's natural tendency to aggregate. At specific operating conditions (150°C for 6h at pH 11) and at the identified optimal concentration of 2mM of CTAB, the resulting  $Mg(OH)_2$  particles aggregate less easily. The composite exhibits a better volumetric heat capacity, almost double than that of the material without CTAB and presented a very good stability after 13 cycles of dehydration/hydration.

Kim *et al.* [50] irradiated MgO pellets with an electron beam (*Figure 5a*) and used the obtained micro-beamed MgO in the  $Mg(OH)_2/MgO$  TCHS working pair. The electron beam irradiation seems to have an impact on the specific surface area that doubled after treatment (*Figure 5b*). The  $Mg(OH)_2$  flakes synthesized from these micro-beamed MgO dehydrated much faster than the common MgO based materials.

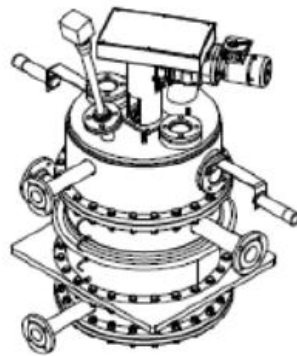


**Figure 5.** Illustration of the irradiation of the electron beam on a MgO pellet a), and pore volume evolution before and after the beam irradiation b)

(from Kim *et al.* [50])

### 2.1.3 Application

Both  $\text{Ca(OH)}_2/\text{CaO}$  and  $\text{Mg(OH)}_2/\text{MgO}$  systems operate at high temperature (up to  $500^\circ\text{C}$ ), so they are applied at large scale, in particularly in CSP. In a recent review, Prasad *et al.* [8] reported on the inertia of  $\text{MgO}$  towards hydration in highly super-heated steam. For this reason, the  $\text{Mg(OH)}_2/\text{MgO}$  system is considered less attractive than  $\text{Ca(OH)}_2/\text{CaO}$ . Laboratory and pilot scale systems have been tested to explore their potential in electricity production. Angerer *et al.* [51] have done a research work on the design of an MW-scale  $\text{Ca(OH)}_2/\text{CaO}$  TCHS reactor including a bubbling fluidized bed. A reactor volume of  $100\text{m}^3$  was estimated capable to generate 15MW of heat power. In 2016, Schmidt *et al.* [52] mixed the reaction material with nano-additives for facilitating the fluidization and to ameliorate the low TC of  $\text{Ca(OH)}_2$ . The final material was then used in an innovative moving-bed reactor (Figure 6). Lately, Ugo *et al.* [53] modeled and simulated a TCHS system integrated in a CSP plant using  $\text{Ca(OH)}_2$  and coupled to a Rankine power cycle. An overall energy efficiency increase higher than 10% was measured for the using such TCHS integration. Moreover, an efficiency slightly higher than 30% could be stably maintained over one year by using the turbine integration concept.



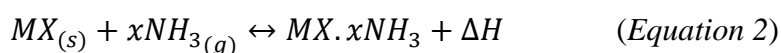
**Figure 6.** Moving bed reactor used in pilot plant using  $\text{Ca(OH)}_2/\text{CaO}$  modified with nano additives

(from Schmidt *et al.* [52])

## 2.2 Sorption systems

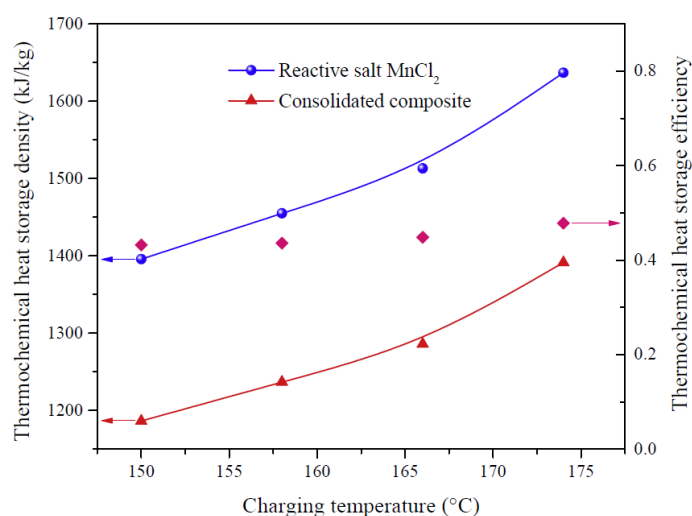
### 2.2.1 Ammonia sorption/desorption

Metal halide ammines have been reported to have an exceptionally good cycling stability and high ESD [54], thus they are viable material options for TCHS applications. Equation 2 represents the reversible sorption reaction of metal halide salts (MX) with ammonia gas as a working fluid. The reaction is endothermic so heat needs to be supplied to separate ammonia and the halide salt. The ammonia gas can then be condensed as a liquid in a storage tank. As a result, this system works mainly as a heat storage, but can also indirectly store ammonia.



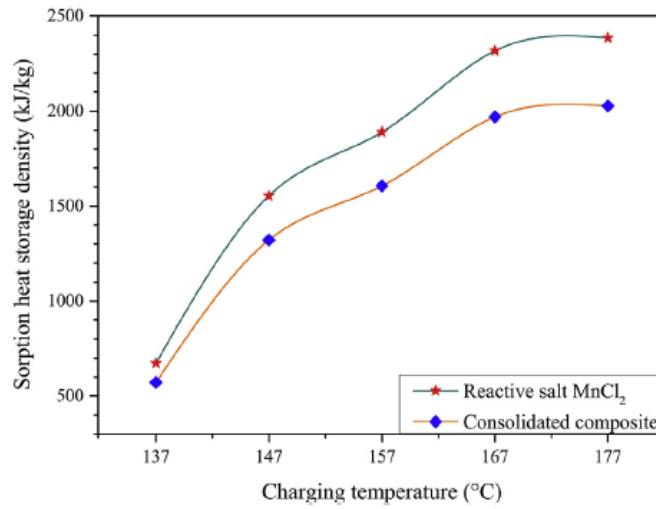
Recently, Berdiyeva *et al.* [55] analyzed spatio-temporal development of  $SrCl_2 \cdot 8NH_3$  powder within a reactor using *in-situ* neutron imaging. This method allows them “to study simultaneously  $NH_3$  spatial distribution and the structural changes”. They stated that the stainless-steel honeycomb used to embed the powder did not ameliorate the heat transfer during the desorption process as expected. A volume expansion of 10% was also observed during  $NH_3$  absorption. The study provides crucial information for improving safety and efficiency of TCHS reactors.

An intensive experimental research has been conducted by Yan *et al.* [56], at laboratory scale, to study the  $MnCl_2/NH_3$  storage system. With the presence of EG, the heat and mass transfer properties of the composite material were significantly enhanced with an energy efficiency of 48%. Figure 7 shows a surprisingly high ESD of  $1391 \text{ kJ/kg}_{\text{composite}}$ , recorded at a very low charging temperature  $150\text{-}180^\circ\text{C}$ . This range of temperature is compatible with solar collectors in summer and for industrial applications for the reducing of the waste heat in factories.



**Figure 7.** Evolution of ESD with the charging temperatures of pure salt  $MnCl_2$  and composite  $MnCl_2/NH_3$  (from T. Yan et al. [56])

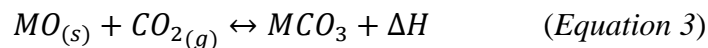
More recently, instead of working on a single salt/ammonia composite, Yan et al. [54] decided to develop a composite containing a mixture of salts.  $MnCl_2$  and  $SrCl_2$  were used for the reversible sorption reaction with ammonia. The double salts/ammonia composite material generated 45% more of ESD ( $2MJ/kg_{composite}$ ) than the single salt/ammonia composite (Figure 8). The latest research article [57] from the same authors refers to another double salts/ammonia composite. This time, they investigated  $NiCl_2-SrCl_2/NH_3$  storage system. They obtained a significant heat efficiency of 0.978 with a relatively high ESD of  $2.1MJ/kg_{composite}$ .



**Figure 8.** Evolution of ESD with the charging temperature of pure salt  $MnCl_2$  and  $MnCl_2-SrCl_2/NH_3$  composite (from Yan et al. [54])

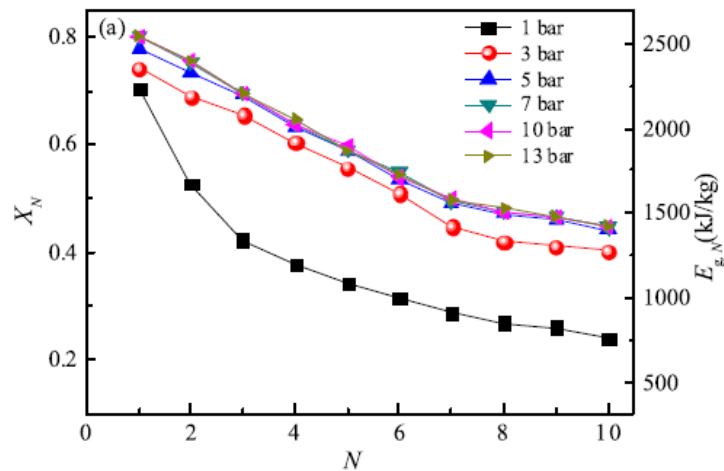
### 2.2.2 $CO_2$ sorption/desorption

Baker suggested in 1970s [58] an energy storage system based on the reversible carbonation/decomposition reaction (Equation 3). One of the most common and studied system is the  $CaCO_3/CaO$  couple integrated in CSP technologies, and also called “Calcium Looping (CaL) process”. In this system,  $CO_2$  and  $CaO$  are stored separately and the stored energy is released when needed by combining the two products following the exothermic reaction reported in Equation 3. The CaL process presents advantages in term of low cost, availability of the used products, and zero risk towards the environment because of the use of natural compounds ( $CaO$  and  $CO_2$ ) [59].



The  $\text{CaCO}_3/\text{CaO}$  system works at a very high temperature, at least  $700^\circ\text{C}$ . Addition of doping agent has been investigated to decrease the working temperature. This permits to enlarge the working temperature domain, and avoid certain drawbacks, as the sintering of  $\text{CaO}$ , that slow down the reaction kinetics. In order to avoid sintering, the carbonation of  $\text{CaCO}_3$  needs to be carried out at temperatures below  $925^\circ\text{C}$ . Khosa et Zhao [60] analyzed the heat storage/release performance of the system before and after doping with  $\text{SiO}_2$ . After being doped, the decarbonation temperature was reduced to  $800^\circ\text{C}$  and the reaction rate improved thanks to the easier diffusion of  $\text{CO}_2$  in the smaller  $\text{CaO}$  particles. The addition of  $\text{SiO}_2$  helps improve the cyclic stability of the  $\text{CaCO}_3$  by 13%.

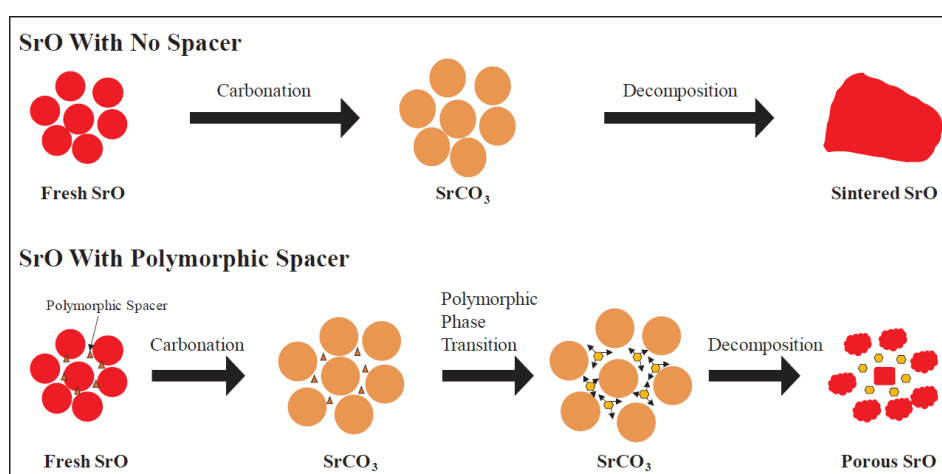
As alternative to the calcined limestone (natural  $\text{CaO}$ ), Li *et al.* [61] used  $\text{CaO}$  pellets under high pressure carbonation (up to 13bar). When the pressure of the carbonation reaction is increased to 5bar (*Figure 9*), the heat storage density is reported to increase up to  $1400\text{kJ/kg}_{\text{composite}}$  after 10 cycles and increasing the pressure over 5bar does not seem to increase the energy stored. The addition of biomass (5%wt. bagasse or 5%wt. pine) in the  $\text{CaO}$  pellets was also investigated with the aim to inhibit the decreasing in heat storage capacity after multiple cycling.



**Figure 9.** Effect of carbonation pressure on heat storage density of  $\text{CaO}$  pellets at  $800^\circ\text{C}$  (from Li *et al.* [61])

In a more recent article about  $\text{CaL}$  system materials, Teng *et al.* [62] succeed in enhancing the solar absorbance of  $\text{CaCO}_3$  in the conventional  $\text{CaL}$ -CSP system. They applied particle doping and ion doping by using  $\text{Mn-Fe}$  ( $\text{MnFe}_2\text{O}_4$ ) oxide composite. At a molar ratio of 100:6:12 ( $\text{Ca}:\text{Mn}:\text{Fe}$ ), the solar absorbance of  $\text{CaCO}_3$  increased significantly from 11% to 90%. The energy efficiency was also find to be stable at 93% ( $1438\text{kJ/kg}_{\text{composite}}$ ) over 60 cycles, compared to 20% for the commercial  $\text{CaCO}_3$ .

A similar energy storage system to  $\text{CaCO}_3/\text{CaO}$  is  $\text{SrCO}_3/\text{SrO}$ . This system operates at extremely high temperature, up to  $1200^\circ\text{C}$  at atmospheric pressure. The same sintering problem detected for  $\text{CaO}$  was also observed for  $\text{SrO}$ . So, to overcome this issue, Bagherisereshki *et al.* [63] used a polymorphic spacer to produce sintering resistant sorbents.  $\text{CaSO}_4$  and  $\text{Sr}_3(\text{PO}_4)_2$  are two potential sintering inhibitors and were added to the parent material to maintain the particle size when reaching high temperatures (*Figure 10*). Compared to calcium sulfate (only  $350\text{kJ}/\text{kg}_{\text{composite}}$  after 10 cycles), strontium phosphate appears to be more promising since seemed to maintain a higher energy density ( $500\text{kJ}/\text{kg}_{\text{composite}}$ ) after 10 cycles. The addition of 25%wt of  $\text{Sr}_3(\text{PO}_4)_2$  seems to be the best compromise to obtain the highest performances.

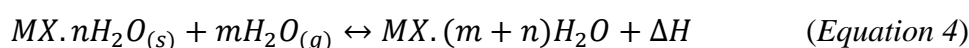


**Figure 10.** Illustration of the effect of the polymorphic spacer added to pre-carbonated  $\text{SrO}$  (from Bagherisereshki *et al.* [63])

Gigantino *et al.* [64] investigated another aspect of the system. They want to maintain (or even improve) the cycling stability by mixing strontium acetate hemihydrate and porous  $\text{MgO}$  to the  $\text{SrO}$ -based materials. They concluded that the composite containing 40%wt. of  $\text{SrO}$  maintains the same carbonation-decomposition performance during over 100 consecutive cycles with an ESD of  $810\text{kJ}/\text{kg}_{\text{composite}}$ . A year later, Ammendola *et al.* [65] studied oxide another as additive for the  $\text{SrCO}_3/\text{SrO}$  system. Investigations of different  $\text{Al}_2\text{O}_3/\text{SrO}$  composite compositions were carried out to understand the effect on sintering limitation and energy storage capacity. The optimum content of the aluminum oxide to achieve the best compromise between the lowering of sintering and the maintaining of a high heat storage performance was identified to be around 34%wt. A higher content will not increase the reactivity, but only reduce the overall energy density due to the lack of the reactive phase  $\text{SrO}$ . On the other hand, a lower amount would not avoid the sintering and agglomeration of the  $\text{SrO}$  particles.

### 2.2.3 H<sub>2</sub>O sorption/desorption

Wu *et al.* [9] presented in their work different properties of some selected working fluids (H<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, ...) especially concerning the safety issues. Methanol, ethanol and ammonia are flammable in air. Ammonia vapors can be extremely toxic if inhaled or if contacted with eye and skin. Carbon dioxide (higher than 10% concentration in air) presents long-term toxicity, which is harmful to the cardiovascular system. Water is the best candidate because of its high accessibility and non-toxicity to humans and environment. Consequently, water is the most adapted and investigated working fluids for TCHS. The freed water does not need to be stored, which reduces the complexity of the system, thus reducing the cost of the overall ESD. Reversible hydration/dehydration (*Equation 4*) reaction systems with various sorbents (especially hydrate salts and composites) are the subject of numerous research works.



Padamurthy *et al.* [66] explored the characteristics of sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) for TCHS. The temperature to reach the total dehydration is around 130°C, which is appropriate for solar collector applications. In a single cycle test, the hydration process was performed at 30°C during 2 hours for reaching the complete dehydration, and the corresponding reaction enthalpy was 1012J/g<sub>material</sub>, corresponding to an ESD of 1.81GJ/m<sup>3</sup>. Erlund and Zevenhoven [67] evaluated the thermal behavior of an inorganic carbonate. They set up a lab-scale reactor design using MgCO<sub>3</sub>/silica gel (SG) as reactive material and matrices support, respectively. At 50% wt. salt content, the hydration enthalpy resulted to be of 410J/g<sub>composite</sub>. A slight decrease of the storage capacity was observed by increasing the MgCO<sub>3</sub> content of 10%. This behavior can be explained by mass transfer limitations.

Another inorganic carbonate salt hydrate received a lot of attention in recent years: potassium carbonate. A detailed research was performed by Gaeini *et al.* [68] on K<sub>2</sub>CO<sub>3</sub> in terms of cyclability, kinetics and energy density. It is reported that the kinetics becomes faster cycle after cycle because of the expansion of the material upon hydration. The authors also measured the ESD presenting a value of 0.75GJ/m<sup>3</sup>. Shkatulov *et al.* [69] also investigated K<sub>2</sub>CO<sub>3</sub>, but mixed with expanded vermiculite. In this study, compact K<sub>2</sub>CO<sub>3</sub> was used instead of granular material; the kinetics seemed ameliorated (about 2-5 times better). A composite



containing 69% wt. of  $K_2CO_3$  can release up to  $0.9GJ/m^3$  energy, 20% higher than for pure  $K_2CO_3$  [68]. Moreover, the conversion was surprisingly stabilized at least for 47 cycles.

Due to the high ESD of  $1440kJ/kg_{composite}$  and the low charging temperature ( $\sim 100^\circ C$ ) [70,71],  $LiOH.H_2O$  is one of the most promising thermochemical materials for storage applications. Different  $LiOH$ -based composites were prepared and analyzed (Table 1). Kubota *et al.* [70] improved the hydration kinetic of  $LiOH$  by over 5 times by depositing  $LiOH$  (10%wt.) on mesoporous carbon (MPC). Li *et al.* [72] modified  $LiOH$  with Ni-carbon nanotubes (Ni-CNT) and found improvements in the released energy and the TC. These two parameters could be also enhanced when  $LiOH$  was modified with graphene oxide [71] or multiwalled CNT [73]. EG was also used as a matrix support by Li *et al.* [74] to improve the heat and mass transfer of  $LiOH.H_2O$ . Even if the heat storage capacity was 22% lower than that of the pure  $LiOH.H_2O$  salt, the composite containing EG presented a TC 6.5 times higher than the pure salt and an improved cycling stability. Another  $LiOH$ -based composite was synthesized and analyzed. Li *et al.* [75] using 13X zeolite as hygroscopic support with an ESD 35% higher than that of the pure hydrate salt.

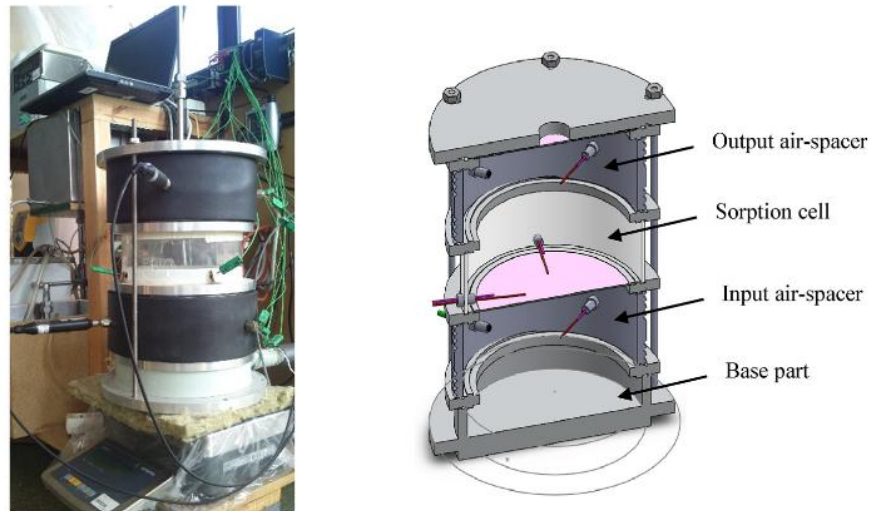
**Table 1.** Comparison of different  $LiOH$ -based composite with pure  $LiOH$ .

Composite	ESD ( $kJ/kg_{composite}$ )	Thermal conductivity ( $W/mK$ )	Reference
$LiOH$	1440		[70,71]
$LiOH$ (14%)/Ni-CNT	4000	3.78	[72]
$LiOH/graphite\ oxide$	1980	1.8	[71]
$LiOH/MWCNT$	1804	1.75	[73]
$LiOH/EG(8\%)$	1120	6.52	[74]
$LiOH/13X$	1949		[75]

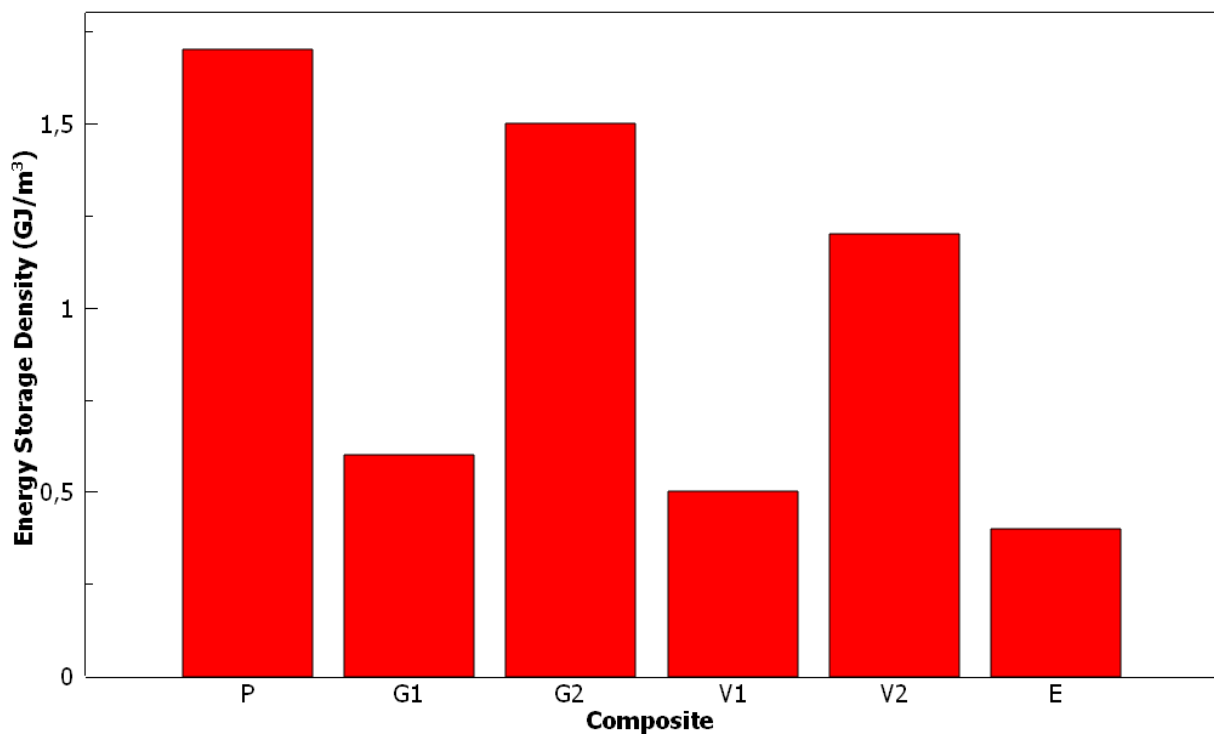
Besides  $LiOH.H_2O$  and carbonate salts, hygroscopic chloride salts are also investigated as potential candidates for TCHS.  $CaCl_2$  is one of the chosen materials due to its properties.  $CaCl_2$  is cheap, easily available [76], and presents a high water absorption capacity of  $0.9g/g$  at temperature and pressure ambient [77]. For these reasons  $CaCl_2$  is one of the most used and studied hydrates salt in industry and building sector. Shi *et al.* [78] tried to employ MOFs based on MIL-101(Cr) as porous matrices support and they did not measure any significant loss in the heat storage capacity during 17 consecutive cycles ( $1274kJ/kg_{composite}$  for MIL-101(Cr)- $SO_3H/CaCl_2$ ).



Different SG-based composite materials were also synthesized for long-term heat storage potential. Pierre D'ans *et al.* [79] encapsulated 43%wt.  $\text{CaCl}_2$  in mesoporous SG and measured TC in the 0.129-0.155W/mK range. Skrylnyk *et al.* [80] evaluated the storage capacity of the same composite and reported ESD up to 145kWh/m<sup>3</sup> in a laboratory-scale prototype reactor (*Figure 11*).



*Figure 11. Laboratory-scale prototype reactor used for cycling test of  $\text{CaCl}_2/\text{SG}$  (from Skrylnyk *et al.* [80])*



**Figure 12.** ESD of  $\text{CaCl}_2$  based composite materials on different supports, where  $P$  is the pure  $\text{CaCl}_2$ ;  $G1$ ,  $G2$ ,  $V1$ ,  $V2$  are respectively the Graphite and Vermiculite modified samples, and  $E$  the encapsulated sample (data collected from [81])

Gaeini *et al.* [81] investigated 3 distinct porous supports: expanded natural graphite (ENG), vermiculite, and ethyl cellulose (used for microencapsulation). They were used as matrices for  $\text{CaCl}_2$ -based composite materials. Figure 12 shows the results reported of ESDs of these composite materials. Over-hydration was observed in samples containing vermiculite and graphite, leading to agglomeration. Consequently, the storage performances are low compared to those of the pure  $\text{CaCl}_2$ . A second deposition was effectuated on the impregnated composites to verify a possible improvement in the heat storage capacity. As expected, the twice impregnated samples revealed higher performances:  $1.5\text{GJ/m}^3$  compared to  $0.6\text{GJ/m}^3$  in case of graphite and  $1.2\text{GJ/m}^3$  compared to  $0.5\text{GJ/m}^3$  in case of vermiculite. To avoid aggregation,  $\text{CaCl}_2$  was encapsulated with ethyl cellulose. This sample showed good cycling stability, but unfortunately a lower ESD ( $0.4\text{GJ/m}^3$ ). This poor ESD of the  $\text{CaCl}_2$ /vermiculite/composite was also confirmed by Nejhad and Aydin [82] and Yilmaz *et al.* [83].

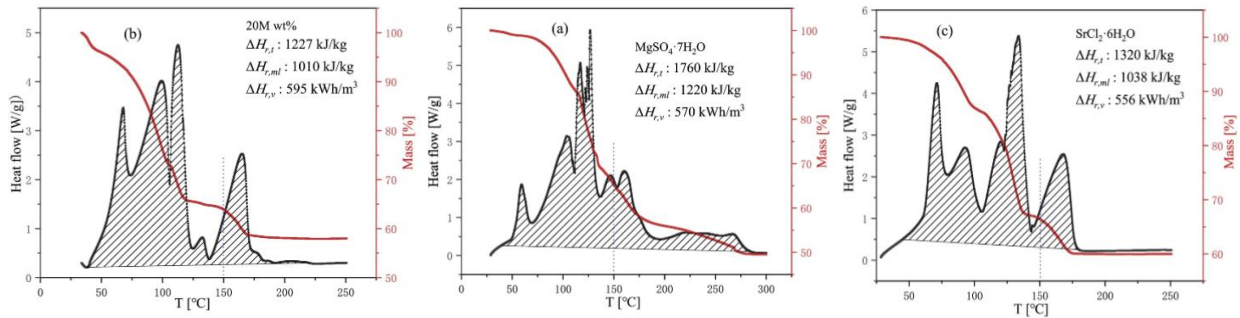
Hygroscopic chlorides are claimed to coagulate even at low relative humidity (RH) during the discharge phase [84-86]. Efforts have been done on  $\text{CaCl}_2$  - modified by graphite or vermiculite to overcome the problem, but the expectations were too high. Mehrabadi and Farid [87] tried to use expanded clay and pumice as host matrices for  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  for low-grade thermal energy storage applications. Despite having low dehydration temperature ( $<150^\circ\text{C}$ ) and a high theoretical ESD ( $2.4\text{GJ/m}^3$ ), the synthesized composite materials presented a dramatically low ESD of  $26.3\text{MJ/m}^3$  (pumice- $\text{SrCl}_2$  with 14% wt.) and  $100\text{MJ/m}^3$  (expanded clay- $\text{SrCl}_2$  with 40% wt.). Besides the low composite salt content, the salt leaching and agglomeration was found to be the main cause of the low power generation. Until 2017, the composite with the highest salt content reported in the literature was 70% wt. of  $\text{CaCl}_2$  deposited on activated carbons (ACs) [88]. Unfortunately, its thermal storage performance was not investigated. Later, Kallenberger *et al.* [89] successfully synthesized alginate-based matrices composites allowing the macroscopic structuring of the composite as beads. The shaping had the advantage to decrease the pressure loss in packed beds. Table 2 shows the results, from calorimetric investigation, of the hydration carried out at  $30^\circ\text{C}$  on different composite materials with 86% wt. salt content. High volumetric storage densities up to

1.5GJ/m<sup>3</sup> (CaCl<sub>2</sub> composite sample) combined with relatively high water uptake were reported, proving the potentials of these composite materials for heat storage applications.

**Table 2.** Thermal storage performance (storage density and water uptake) of different alginate-based composite materials at different RH.

Composite	Relative humidity at 30°C (%)	Storage density (GJ/m <sup>3</sup> )	Water uptake (g/g)
MgSO <sub>4</sub> /alginate	84	1.32	0.65
MgCl <sub>2</sub> /alginate	30	1.27	0.93
	20	0.59	0.38
CaCl <sub>2</sub> /alginate	30	1.50	0.88
	20	1.10	0.64
SrCl <sub>2</sub> /alginate	60	1.05	0.55

In their studies, Posern and Osburg [90] concluded that crystalline salts or salts pellets of SrCl<sub>2</sub> (at 30°C and 60%RH) and MgSO<sub>4</sub> (at 30°C and 84%RH) generate similar amounts of heat of sorption, 2.04 and 1.70kJ/g<sub>material</sub>, respectively. Additionally, an evaluation of the temperature increasing (for experiments carried-out in the same conditions) was also done on composites made of SrCl<sub>2</sub> (35 and 49% wt.) and AC. The results revealed that the hydration kinetics was improved thanks to the well dispersion of the salt in the porous support AC. Consequently, the temperature increasing was higher in the composite than in the pure salt. Instead of working with pure SrCl<sub>2</sub> or MgSO<sub>4</sub>, Li *et al.* [13] decided to mix them in different proportions varying from 10% to 50%wt. of MgSO<sub>4</sub>. Hydration experiments were carried out at 30°C and 55%RH (value lower than the deliquescence relative humidity (DRH) of the highest hydrates form of each of the two salts) [90,91]. The composite containing 20%wt. of MgSO<sub>4</sub> showed impressive ESD (595kWh/m<sup>3</sup>) and a better dehydration (at 150°C) than both pure salts (*Figure 13*). A higher cyclic stability was also observed for this composite that, after 20 cycles, still presented a heat storage capacity equal to 75% of the initial. For the pure salt, this value was of 64% wt. for SrCl<sub>2</sub>.6H<sub>2</sub>O and 51% wt. for MgSO<sub>4</sub>.7H<sub>2</sub>O.



**Figure 13.** Comparison of the storage performance of the 20%wt.  $\text{MgSO}_4$  composite and two pure salts (adapted from Li *et al.* [13])

Hygroscopic sulfates salts are thermally stable and they have a relative high DRH. So,  $\text{MgSO}_4$  was recently investigated as a high potential material for TCHS [92,93]. The heptahydrated salt presents a very high theoretical ESD ( $2.8\text{GJ/m}^3$ ), but this value could not be achieved due to the only partial reversibility of the hydration reaction [94,95]. To solve this issue, the integration of host materials in the composite formulation seems to be a promising solution.  $\text{MgSO}_4$  was among the most investigated salts in the last decade. More recently, it was impregnated on zeolite 13X by Hongois *et al.* [96]. The benefic effect of the presence of zeolite was proved. After hydration and dehydration at  $150^\circ\text{C}$ , the 15% wt.  $\text{MgSO}_4$ /zeolite 13X composite, could still store 80% of the original energy density (for experiments carried-on 10mg of sample). When increasing the quantity of storage material (200g) the heat storage density strongly decreased and represented only 45% of the original value after 3 cycles. Wang *et al.* [97] prepared a 15% wt.  $\text{MgSO}_4$ /zeolite 13X composite material by impregnation. At 80% RH and  $25^\circ\text{C}$ , hydration was not homogeneous, as observed by X-ray Diffraction (XRD). Different hydrate forms were detected, but the  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ , the highest hydrated phase, was not detected, even at such a high relative humidity. However, the composite shows a relatively good hydration energy of  $632\text{J/g}_{\text{composite}}$ . The deposition of  $\text{MgSO}_4$  onto the zeolite 13X enhanced the stability to hydration/dehydration cycling. After simulation of years' application, the materials resulted more resistant also towards the pollutants present in the air [98].

Another porous structure material was proposed by Brancato *et al.* [99], who made use of silicone foams. According to the authors, two water vapor permeable silicones were chosen: poly(methylhydrosiloxane) (PDMS) and a silanol terminated poly-dimethylsiloxane (PMHS) to form a polymeric foam porous matrix. The composites containing  $\text{MgSO}_4$  were observed by Scanning Electron Microscope (SEM). The salt was well dispersed into the porous structure. It is worth to note that the optimal salt content that the polymeric foam can host was

around 60% wt. of  $\text{MgSO}_4$ . A year later, Calabrese *et al.* [100] performed mechanical tests on this novel material. Due to the hydrophobic nature of the silicone materials, only 87% of the salt left after 50 of hydration cycles. In the early '20, Piperopoulos *et al.* [101] carried-on experiments to evaluate the morphology and the dehydration/hydration cycling process of the same composite. With the composite containing the optimum salt content (60% wt. of  $\text{MgSO}_4$ ), they found an ESD of  $821\text{J/g}_{\text{composite}}$  (after a charging step, dehydration, performed by heating up the sample from  $30^\circ\text{C}$  up to  $180^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ ). No degradation of the silicone matrices was observed upon cycling, which suggests an improvement in term of the material durability. AC is another common TCHS porous support that show some advantages when compared to zeolites. One of the reasons is the very high specific surface area of AC, which can offer a better water vapor sorption rate. Akcaoglu *et al.* [102] prepared pellets of  $\text{MgSO}_4$  and AC. Expanded natural graphite was also added to enhance the thermal conductivity. The  $\text{MgSO}_4/\text{ENG} + \text{AC}$  (1:1) composite was hydrated at  $20^\circ\text{C}$  during a week and the hydration heat released was equal to  $1395\text{J/g}_{\text{composite}}$ . The presence of ENG improved the heat transfer of the composite by 86%. Recently, another sulfate hydrates salt,  $\text{ZnSO}_4$ , received more attention from the researchers. In Ref. [103], Rehman *et al.* compared the hydration behavior at  $100^\circ\text{C}$  of three hydrated sulfate salts:  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ , and  $\text{ZnSO}_4$ . They found that zinc sulfate is an interesting material for heating in buildings because it exhibits a relatively high ESD ( $1.26\text{GJ}/\text{m}^3$ ), when compared to  $\text{MgSO}_4$  ( $0.52\text{GJ}/\text{m}^3$ ) and  $\text{FeSO}_4$  ( $0.84\text{GJ}/\text{m}^3$ ). In Ref. [104], the authors highlighted the effect of the RH on the water sorption ability. At 75%RH, the value of water sorption was of  $0.148\text{g}/\text{g}$  for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , but at 85%RH, this value decrease to  $0.114\text{g}/\text{g}$  after 10 hours of hydration and eventually go down to  $0.001\text{g}/\text{g}$ . The observed phenomena were related to the deliquescence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  when RH exceeds 75%.

A screening method was applied by Richter *et al.* [105] to 308 different inorganic salts to find the most suitable candidate for the industrial waste heat recycle ( $150\text{-}300^\circ\text{C}$ ) applications. It was concluded that  $\text{SrBr}_2$  is the most promising material with some remarkable properties as follows: harmless for human, no decomposition up to  $300^\circ\text{C}$ , reversible hydration/dehydration reaction, and stability for at least 10 charging/discharging cycles. Furthermore, with a theoretical ESD of  $628\text{kWh}/\text{m}^3$  [106] and a low dehydration temperature ( $100^\circ\text{C}$  is sufficient to lose 5 water molecules going from hexahydrated to monohydrated),  $\text{SrBr}_2$  is also considered a good candidate for applications in heating of building. One of the main drawbacks of  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  is the corrosion of the materials

constituting the reactor. Pierre D'ans *et al.* [107] studied the corrosion rate caused by  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  in low carbon steel and copper at  $80^\circ\text{C}$  at different relative humidity (RH 35% and 24%). In this condition, a severe corrosion of over 1mm/year (estimated) was observed. This behavior was explained by the presence of  $\text{SrCO}_3$ , identified as co-product of the reaction bringing to the formation of  $\text{HBr}$ , extremely corrosive. A similar study was carried on  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  by Fernandez *et al.* [108], but this time the experiments were ran under vacuum at the pressure of 123 mbar and  $78^\circ\text{C}$ . Corrosion was largely suppressed, and the carbon steel material showed a corrosion rate of only 0.038mm/year. However, the materials presenting the higher resistance to corrosion were identified to be aluminum and stainless steel, with a corrosion rate of only 0.002mm/year. Other solutions were also suggested to inhibit the corrosion problem, such as incorporate the salt in an inert matrix in contact with metallic surface (*Table 3*).

**Table 3.** Performance of  $\text{SrBr}_2$  after being incorporated into inert matrices.

Composite	ESD	Other properties	Reference
63% $\text{SrBr}_2/\text{MIL-101}(\text{Cr})$	233kWh/m <sup>3</sup> at 30°C	Water sorption capacity 0.4 g/g	[109]
$\text{SrBr}_2/40\%-\text{ENG}$	500kJ/kg <sub>composite</sub> ( $T_{\text{charge}}=80^\circ\text{C}$ ) 600kJ/kg <sub>composite</sub> ( $T_{\text{charge}}=150^\circ\text{C}$ )	- Cp increased from 0.6kJ/kg.K to 1.3kJ/kg.K - TC increased 5 times from 0.5 to 2.5W/mK	[110]
$\text{SrBr}_2/20\%-\text{ENG} + 0.5\% \text{wt.}$ $\text{NH}_4^+$ polyelectrolyte	550kJ/kg <sub>composite</sub>	Hydration rate is increased 3 times at $23^\circ\text{C}$ , 50%RH	[111]

### 3. Conclusion and Perspectives

Promising sorption materials for thermochemical heat storage needs to present certain properties, such as: environmental non-toxic, relatively cheap, appropriate affinity between sorbents and sorbates, and high heat storage density. Sorption materials can be adapted to wide temperature range for targeted applications, in particular for low-temperature building heating. Various drawbacks are currently stopping the implementation of these materials in commercial system, and intensive research has been carried to understand the mechanisms involved and find solutions. For example, in the high temperature range,  $\text{SiO}_2$  was added to  $\text{CaO}$  to reduce the sintering temperature and thus increase its durability, while white  $\text{CaCO}_3$  was “blackened” to be able to absorb more efficiently the solar irradiance. Other candidates, as

metal halide amines, suffer from low heat transfer capacity, but by coupling them with graphite-based materials, the final composites could reach high ESD (as for example  $\text{MnCl}_2/\text{NH}_3$  with about  $1400\text{J}/\text{g}_{\text{composite}}$ ).

Among others, salts hydrates and water are considered the most suitable couple for TCHS, especially for residential building heating applications, in relation to their high ESD. Additionally, water does not need to be stored, thus reducing the complexity of the system. Unfortunately, also salts hydrates system present numerous drawbacks, including 1) deliquescence of the salts above a certain humidity (DRH), bringing to leaking into the surrounding materials, and/or agglomeration during recrystallization 2) low TC and porosity, connected to poor heat transfer, and low mass transfer, respectively and affecting the overall kinetics. The integration of the salts into a porous matrix seems to be the most efficient way to answer to these issues. The low-cost and the high water absorption capacity are the two main reasons because of which  $\text{CaCl}_2$  is widely studied, alone or in the presence of various types of host materials. SG, vermiculite and graphite, are employed as supports, but their corresponding composites did not improve much their performances, and, in certain cases, even reduced the heat capacity. Embedding  $\text{CaCl}_2$  in ethyl cellulose significantly reduced agglomeration and improved cycling stability, but a too low heat capacity was reported. Having the highest theoretical ESD and high DRH,  $\text{MgSO}_4$  appears to be the most adapted salt for heat storage systems. Zeolites are the most widely studied support, often coupled to  $\text{MgSO}_4$  to produce composites. A composite containing 15%wt. of  $\text{MgSO}_4$  deposited on zeolite 13X could release over  $630\text{J}/\text{g}_{\text{composite}}$  with a good cyclability. ENG is recently investigated to enhance the poor TC of salt hydrates; this parameter needs to be optimized for the implementation of storage systems.

To carry on future research in the building sector, the following points need be considered:

- To search for new composites to improve the heat storage capacity of the system.
- To ameliorate the heat and mass transfer of hydrated salts composites (that are the most promising candidates)
- To perform more consistent durability and cyclability tests
- At the pilot scale, to take into consideration the type of reactor material since corrosion in presence of salt(hydrates) can impact the lifetime of the installation. Moreover, to perform for adapted up-scaling simulation as disproportional results when increasing sample mass can false the final project.



- Lastly, to take into consideration the material cost, energy price and installation energy efficiency to facilitate the implementation of the technology at industrial level.

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