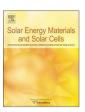
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A review on the use of SrBr₂·6H₂O as a potential material for low temperature energy storage systems and building applications



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ABSTRACT

The combination of its sorption capacity, reaction enthalpy, melting temperatures around available industrial waste heat and solar source and high thermal efficiency (compared to others salt hydrates) makes strontium bromide and its two respective hydrates a potential material for low temperature energy storage and building applications. It is considered among suitable materials for low thermochemical and sorption energy storage application (NTsoukpoe et al. [7]) due to its high-energy storage density and end-user temperature. Strontium bromide is simultaneously considered as a phase change and a thermochemical material. A short analysis of the general physical and chemical properties such as thermodynamics, melting temperature, density, sorption kinetics, exergy, thermal conductivity, specific heat capacity and permeability highlights the advantageous properties. The review on the use of strontium bromide in pure or modified form is further extended to applications such as building structure, composite design for thermal storage, and heating and cooling. The usefulness and disadvantages of its use in closed/open processes are discussed. Possible solutions to issues are further presented or proposed.

1. Introduction

Inorganic salt hydrates have proven to be reliable in developing thermal energy storage systems for building applications [1–4] and heat recovery [5], under pure or composite forms. However, SrBr₂·6H₂O recently draw attention to low temperature application [6,7]. It is therefore important to gather reliable data on thermo-physical and chemical properties together with knowledge of maintaining these properties during the system's lifetime for future heating or cooling storage systems based on the present salt hydrate. Salt hydrates are widely used for latent [2] and thermochemical [7] heat storage systems in the temperature range between 10 °C and 200 °C. Though well known as thermochemical storage material, SrBr₂·6H₂O is not well studied as a latent heat storage material. SrBr₂·6H₂O can be considered as an inorganic phase change material [8] and thermochemical material (TCM) due to its isostructural stability [9] that allows sorption and/or hydration reaction without destroying the structure.

It is considered as a phase change material (PCM) since its phase change transition is regarded as dehydration or hydration of the salt, though similar to melting or freezing. Actually, the phase change occurs in the range of 76–88 °C. During the phase transition, liquid water

within the salt hydrate is released and dissolves the non-hydrated salt molecules [4]. The idea of phase change is supported by the definition of a "phase", as two distinct phases in a system have distinct physical or chemical characteristics and are separated from each other by definite phase boundaries. Meaning this salt melts to either salt hydrate with fewer moles of water or to its anhydrous form. As a PCM, SrBr₂·6H₂O could present incongruent melting due to the insufficient release of water (uncompleted melting or charging) to dissolve the remaining salt crystals. Many solutions such as the use of excess water, addition of thickening agents and encapsulation exist to overcome this issue, as mentioned in Ref. [4]. It is considered as TCM since a thermal source is used for dehydration and another to provide water vapour for hydration. The major difference with PCM is that, melting is generally avoided during this reversible chemical process. Actually, material can melt if heated above melting temperature in a thermochemical process, but it is not reflected on the process. However, it is technically contained to rapidly recrystallize as previously demonstrated in [5].

For heating and cooling purposes, the hexahydrate is decomposed to the monohydrate, not to the anhydrous due to stability feature. In fact, Dyke and Sass [10] proved it in comparison to the stable barium halide crystal lattices, by showing that the greater stability of SrBr₂.

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Nomenclature

 d_b bulk density (kg m⁻³) ΔH_r^0 reaction enthalpy (J mol⁻¹ K⁻¹) $\Delta H_{l/g}$ enthalpy of the evaporation (J mol⁻¹ K⁻¹) k permeability (m²) m_s sample mass of the salt hydrate (kg)

 V_0 volume occupied by the sample in the cylinder (m³)

Greek symbols

 λ_s thermal conductivity of the salt bed (W m⁻¹ K⁻¹)

H₂O over SrBr₂ is primarily due to the increase in coordination number of the strontium ion by the water molecule. As the present salt just draws attention to heating and cooling storage application, its actual price is seen as a major inconvenient. Depending on the purity of the hydrate salt, anhydrous (SrBr₂) costs between 210 and 320 €/kg for 95-99% of purity, respectively (Alfa Aesar GmbH[©]) and the hydrate, 24 €/kg [11] or 17.6 €/kg [12]. However, N'Tsoukpoe et al. showed that, when an external heat source is used for the evapouration and that heat is considered as free and not considered in the evaluation of either the heat storage density and the thermal efficiency, the SrBr₂· 6H₂O remained the best among over 125 screened materials from a thermodynamic point of view [7]. This salt hydrate has a white colour in the solid state and may change colour when reacted with other metals such as aluminium. In fact, this salt can turn pale yellow (Fig. 1 [13]) in the presence of Al ions under the action of heat. Compared to other salt hydrates, it is non-toxic and does not present any risk of explosion or combustion. However, eyes and skin irritation can occur when exposed to this product. The present review aims to gather and determine the thermo-physical properties of the reactive pair water/ strontium bromide along with some paragraphs on ammonia/strontium bromide. The paper reviews the use of strontium bromide in different forms, pure or composite material, in thermal and building applications. Emphasis is put on theoretical and experimental investigations in order to point out interesting aspects of the material processing, physical and chemical properties, proven uses, remaining challenges and ideas for future researches.

2. Sorption characteristics and properties

The reactive couple $SrBr_2/H_2O$ has already been theoretically and experimentally investigated with success in previous works [5,6,14–17]. Its ideal energy storage density is very high: 628 kW h m⁻³ (referring to the density of 2390 kg m⁻³ and the molar mass of non-porous salt hydrate of 0.3555 kg mol⁻¹) but decreases when accounting for additional components at prototype level. For example, it was found to be 400 kW h m⁻³ in an open system [16] and 531 kW h m⁻³ in a closed system [18]. A temperature range of 80–90 °C is sufficient to

Subscripts

 $\begin{array}{cc} g & \quad \text{gas phase} \\ l & \quad \text{liquid phase} \end{array}$

s1 salt in hydrated form s0 salt in dehydrated form

insure the dehydration from the hexahydrate to the monohydrate without incongruent dissolution of water vapour in the solid phase, as the solubility curve shows in Fig. 2a. The solubility line informs about the approximate limit of saturated solution of the $\rm SrBr_2\cdot 6H_2O$. An evapourator pressure above 12 mbar (~10 °C) is required to reach above 50 °C output in the reactor, which can be used directly for a desired application. Note that in those conditions, the energy required to afford 10 °C at the evapourator can be done with geothermal source energy. In an open-air system, the exothermic reaction of hydration induces simultaneously water vapour consumption (i.e. decrease of absolute water content) and temperature increase (Fig. 2b). If the inlet air conditions is in A, the outlet air conditions will be somewhere around B. In a similar way, for the endothermic dehydration, with inlet air conditions in C, the outlet air conditions would be somewhere around D [6].

The retained solid-gas thermochemical reaction in the system is related to the two following monovariant equilibriums:

$$SrBr_2 \bullet 6H_2O_{(s1)} + 5\Delta H_r^0 \leftrightarrows SrBr_2 \bullet 1H_2O_{(s2)} + 5H_2O_{(g)}$$
 (1)

$$H_2O_{(l)} + \Delta H_{l/g} \quad \leftrightarrows \quad H_2O_{(g)} \tag{2}$$

with $\Delta H_{l/g}$ =2519 kJ kg⁻¹ H₂O (at 10 °C) the enthalpy of evapouration and ΔH_r^0 =3744 kJ kg⁻¹ H₂O, the reaction enthalpy. Further tests on a TGA-DSC show energy yield of 798 kJ kg⁻¹ SrBr₂·1H₂O at 100 °C and of 834 kJ kg⁻¹ SrBr₂·1H₂O at 200 °C.

The solid/gas equilibrium temperature for the dehydration phase and the hydration, which already indicates minimum expected output temperatures, are given on the basis of the diagram in Fig. 2. Under closed system, meaning operating under pure water vapour, the Clausius-Clapeyron stands for the solid/gas equilibrium temperature determination. However, the operating cycle for an open system is not easily represented in Clausius-Clapeyron diagram, because the process does not happen under equilibrium condition. For the present salt hydrate, in closed system, solid/gas equilibrium temperature for the dehydration phase and the hydration was found similar as 43 °C in Ref. [15]. Fopah-Lele et al., however found 58 °C for the dehydration phase and 45 °C for the hydration phase [5]. The difference lies in the evapo-

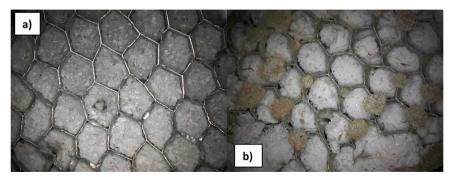


Fig. 1. Strontium bromide in the (a) hydrate form and the (b) dehydrated form in the honeycomb structure heat exchanger [13].

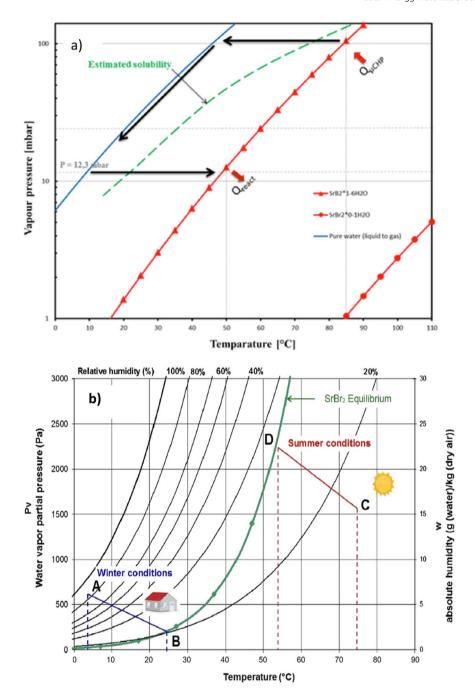


Fig. 2. Equilibrium curve and thermodynamics of the SrBr₂·6H₂O as TCM for direct heating supply application, (a) in closed system [5] and (b) psychometric chart in the case of open system [6]. Q_{HCHP} represents an external source such as from heat loss of a micro combined heat and power device or solar. Q_{react} is the heat of the exothermic reaction.

condenser design and the needed temperature to charge the system. For example, Mauran et al. worked with a charging heat at 80 °C whereas Fopah-Lele et al. worked at 89–90 °C [15]. In an open system, dehydration can be performed at 60 °C [6] or 80 °C [16] according to the humidity and air flow condition, whereas hydration outputs 19 °C [19] or 34 °C [16]. Besides, the performances of the present salt to the other TCMs are discussed in terms of theoretical and prototype efficiency in Ref. [7]. From thermodynamic point of view, it is considered as the most promising among the three top salt hydrates to be used in low-temperature application but exhibits a lower thermal efficiency (less than 40%) without considering condensation heat recovery.

As a PCM, strontium bromide works very well with the addition of a metal halide. For instance, the obtained PCM composite exhibits different phase change temperatures according to the amount of metal halide in the composite (see Fig. 3 with the example of ${\rm MgBr_2\text{-}6H_2O}).$

In the range (76–89 $^{\circ}$ C), there are also several inorganic PCMs that could compete with strontium bromide. Table 1 presents different PCMs along with their interested thermophysical properties (melting temperature and heat of fusion).

One should notice that PCM based strontium bromide exhibits higher heat of fusion leading to greater latent heat. However, there are not much developed PCM heat storage systems based on strontium bromide, though having good latent potential. Reason to that might be the high price of the salt (24 €/kg) compared to other PCMs such as Naphthalene (about 2 €/kg). The previously mentioned prices were obtained from a chemical company supplier (Alfa Aesar GmbH $^{\tiny (\!C\!)}$) by online request. They are provided just for rough indications as they may vary from a provider to provider.

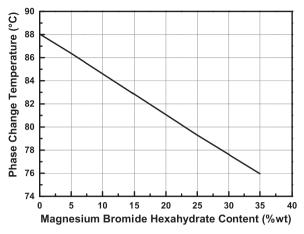


Fig. 3. Phase change temperature of PCM composite ($SrBr_2 \cdot H_2O + xMgBr_2 \cdot H_2O$), where x represents the wt% of $MgBr_2 \cdot H_2O$ in the composite [8].

2.1. Melting temperature

The melting temperature of 88 °C for SrBr₂·6H₂O to SrBr₂·H₂O was presented by Lide [24] but originally had been obtained by the International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST) as for most chemical compounds. Strontium bromide hexahydrate is considered to be a perspective material for applications in the low-temperature range, which can be supplied by solar source or industrial waste heat. The hexahydrate (SrBr2·6H2O) loses all six water molecules upon heating at 180 °C and loses five waters at 89 °C to form SrBr₂·1H₂O [25], but needs 345 °C to change from SrBr₂·1H₂O to anhydrous SrBr₂ [26]. Its melting temperature for losing only five waters was determined to be 88.62 °C using sufficiently accurate methods and of 65 °C on a differential thermogravimetry (DTG) [27]. Later, the value of 88.6 °C was confirmed in the investigations conducted by Lahmidi et al., with a deployment of a high accuracy technique (DTG and DSC from SETARAM) [14]. The melting temperature with the value of 88.3 °C was obtained with own measurement on simultaneous TGA-DSC from Mettler Toledo [18].

These different values of melting temperature are due to the fact that a pure substance generally has a melting range (the difference between the temperature where the sample starts to melt and the temperature where melting is complete) of one or two degrees. Another reason to Buzágh-Gere et al. results [27] might be a high heating rate, meaning the salt may have melt before the thermometer had a chance to register the actual temperature. A summary is presented in Table 2.

Table 1
Comparison of strontium bromide and others PCM with similar temperature conditions.

	Compound	Melting temperature (°C)	Heat (latent) of fusion, in $(kJ/kg)/(GJ/m^3)$	Refs.
Salt hydrates	SrBr ₂ ·H ₂ O	88.6	814/1.93	[11]
	65 wt% $SrBr_2 \cdot H_2O + 32$ wt% $MgBr_2 \cdot H_2O + 3$ wt%	77	< 814/n.a	[20]
	Water			
	Ba(OH) ₂ ·8H ₂ O	78	301/0.65	[21]
	$Mg(NO_3)_2 \cdot 6H_2O$	89	162.8/0.23	[22]
Inorganic and organic PCMs	Acetamide	81	241/0.27	[21]
	Tri-MethylolEthane (TME) or Pentaglycerine	81.1	192-240/0.23-0.29	[21,23]
	$(C_5H_{12}O_3)$			
	Naphthalene	80	147.71/0.16	[22]
	Propionamide	79	168.22/0.18	[22]
	26.4 wt% LiNO ₃ +58.7 wt% NH ₄ NO ₃ +14.9 wt%	81.5	116/n.a.	[4]
	KNO_3			
	27 wt% LiNO ₃ +68 wt% NH ₄ NO ₃ +5 wt% KNO ₃	81.6	108.07/n.a.	[4]

n.a: not available compound density data.

 Table 2

 Summary of melting temperatures for possible thermochemical reactions.

Reversible chemical reaction	Melting temperature (°C)	Refs.
SrBr ₂ ·6H ₂ O <-> SrBr ₂ ·1H ₂ O	88.62	[27]
$SrBr_2 \cdot 6H_2O < -> SrBr_2 \cdot 2H_2O$	89	[25]
$SrBr_2 \cdot 6H_2O < -> SrBr_2$	180	[25]
$SrBr_2 \cdot 1H_2O < -> SrBr_2$	345	[26]

2.2. Density

From the literature search conducted by authors of the current work, there have been no experimental investigations conducted on determination of the temperature dependence of the density of $SrBr_2 \cdot 6H_2O$ or $SrBr_2 \cdot 1H_2O$ in the solid or molten states. However, a static bulk measurement based on the following formula was performed:

$$d_b = \frac{m_s}{V_o} \tag{3}$$

where V_o is the volume occupied by the sample in the cylinder, m_s the sample mass, and d_b the bulk density of the sample. From Ref. [28], bulk density of SrBr₂·6H₂O could be range from 976 and 1606 kg m⁻³ and of SrBr₂·1H₂O, from 842 to 1509 kg m⁻³. The grain density of SrBr₂·6H₂O however ranges from 2386 to 2406 kg m⁻³, with this last value calculated from structural data [26]. The grain density of SrBr₂·1H₂O is up-to-date not determined and is only estimated based on the knowledge of anhydrous SrBr₂ value which is ranged from 3400 to 4549 kg m⁻³. However, 4216 kg m⁻³ was found to be the accurate one [26]. Bulk and grain densities are presented in a broad range due to the fact that, bulk always differs from its composition, voids or occupied volume within a defined recipient and grain shape is not homogeneous at all.

2.3. Kinetic, sorption and heat storage capacity

Half-century ago, strontium bromide was found to have four hydrates namely hepta-, hexa-, di-, and monohydrates. However, the heptahydrate was unstable and the di- and monohydrates were very similar in structure and transition as shown by Pascal et al. [26]. Previous work on salt hydrates enforced to focus only on hexa- to monohydrate. To support the previous statement, Hull et al. found out that the tetragonal phase of $\rm SrBr_2$ undergoes a first-order transition to a cubic fluorite phase at a very high temperature (647 °C), which showed the presence of extensive disorder within the anion sub-lattice [29]. Thermochemical phenomena are observed for dehydration and hydration. Kinetics can be then discussed and analysed from those observations. One important question to answer is to know how many

dehydration or hydration steps occur at corresponding temperature and pressure conditions. The enthalpy of the reversible reaction from hexa- to monohydrate is about 213 kJ mol⁻¹, representing the actual energy storage potential of this salt [7], meaning the real energy storage at the end-use. This thermal energy storage potential value decreases when considering the volume to store the condensed water.

2.3.1. Dehydration as TCM or melting as PCM

Dehydration or charging of this salt also corresponds to its decomposition. Several authors have been performing decomposition of this salt hydrate at different heating rates and temperatures, using simultaneous thermogravimetry and differential scanning calorimetry (TGA-DSC) device, as well as in hydration. Dehydration above the melting temperature was performed. Melting was avoided by programming an isotherm and ramp steps before reaching the higher temperature. The assumption is that, after these two steps, SrBr₂·6H₂O is no more at the hexahydrate state. But in reality, and sometimes, the reaction is accompanied by liquid phase formation and the solid salt undergoes incongruent melting during water crystallization [27]. According to the literature, at different rates (1, 2, 4, 5, 10 °C min⁻¹) and temperatures (60, 70, 90, 95 °C) under atmospheric pressure, the dehydration of SrBr₂·6H₂O to SrBr₂·1H₂O is monotonous (seen as onestep chemical process) with a maximum desorbed/dehydrated water of 26% [7,17-19] on the 30.4% of available water content [30] of this salt hydrate. Hexahydrate looses 5 molecules of water directly without any transition. As a matter of fact, it is one of the salt hydrates that allows high-energy storage potential below 105 °C [7].

Reaction advancement on the present salt generally depends on the kinetic factor and should be around 10⁴ as recommended from simulation results [5]. In addition, in an open system, kinetics also depends on the permeability of the salt [31]. Consequently, particle size plays an important role in heat storage systems, as demonstrated in Ref. [32]. Fig. 4 shows that the sample with higher permeability (sample 3) reacts faster than the one with low permeability (sample 2) [33].

Strontium bromide is categorized as solid-solid phase PCM [34], since during the melting it does not completely turn into liquid or gas. Solid-solid phase change materials change their crystalline structure from one lattice configuration to another at a fixed and well-defined temperature, and the transformation can involve latent heats comparable to the most effective solid/liquid PCMs. Such materials are useful because, unlike solid/liquid PCMs, they do not require nucleation to prevent supercooling. Additionally, because it is a solid-solid phase change, there is no visible change in the appearance of the PCM (other than a slight expansion/contraction), and there are no problems associated with handling liquids, i.e. containment, potential leakage, etc. Fig. 1 clearly shows the two solid states after phase transition. According to Pillai et al., this type of PCM presents the advantage of having less rigorous container requirements and greater design flexibility [21]. Relatively few solid-solid PCMs with suitable heats of fusion and transition temperatures for building applications have been identified. One of the most promising is pentaglycerine (melting temperature 81.1 °C, latent heat of fusion 0.26 GJ m⁻³) [23] which is not much different from strontium bromide (melting temperature 88.6 °C, latent heat of fusion 1.50¹ GJ m⁻³).

The activation energy, one of the kinetic parameters, of this salt hydrate, that defines the chemical bond strengths was determined to be 117 kJ mol⁻¹ [27] and is above 276 kJ mol⁻¹ if incongruent melting is avoided. Looking at the DTG curve of SrBr₂·6H₂O obtained by Buzágh-Gere et al. [27], it is understandable why so low value of activated energy was found in the first place. In terms of energy efficiency and exergy for the charging phase of the present salt hydrate, some studies

provided approximated values. Theoretical thermal efficiency of this salt was found to be 34% (this efficiency discussion is based on a system without condensation heat recovery) [7]. Two years before, Abedin and Rosen showed that, for 15 kg of SrBr₂·6H₂O and ensuring a temperature difference between heat transfer fluids (HTF) of 20 K; the charging energy efficiency could reach 86% [35]. Concerning the exergy, the physical exergy change of the components was assumed negligible relative to the chemical exergy changes. So, from standard chemical exergy of selected components of the salt hydrate in Table 3, it was found a charging exergy efficiency of 21% [35]. Here, the exergy indicates here how much the components chemically contribute to the overall thermal energy efficiency. It can be an indicator, among others, to compare thermochemical materials potential.

2.3.2. Hydration as TCM or recrystallization as PCM

Hydration or discharging of the salt (SrBr₂·1H₂O) also corresponds to its synthesis along with exothermic reaction, which induces simultaneously water vapournhgga consumption and temperature increase. As the reaction from SrBr₂·6H₂O to SrBr₂·1H₂O is reversible, a monotonous water sorption with hydrated water of 26% is also observed. Higher hydrated water such as of 36% could be observed if the hexahydrate was first heated above 180 °C [7]. The present salt hydrate normally rehydrates in the presence of water vapour at 20 mbar and 25 °C after being subjected to a heating rate of 1 °C min⁻¹ and preferably of 10 $^{\rm o}{\rm C}~{\rm min}^{\rm -1}$ [7]. Even though a water vapour pressure above 40 mbar (corresponding to water saturation temperature at 29 °C) is required to reach 60 °C in a chemical reactor [7]. However, no hydration is observed at water saturation temperature above 60 °C. Attention must be paid to avoid overhydration. Deliquescence (when the relative humidity/pressure is so high that the product of the hydration is a saturated salt solution, rather than a salt hydrate), which is not very pronounced on this salt should also be kept in mind and avoided. In the other hand, deliquescence phenomenon favors some issues such as chemical instability. The forming of a liquid film on the surface of salt crystal will not only prevent hydration reaction from occurring, but also cause corrosion problems due to the solution dripping on other metal components [18]. Just like in the charging process, discharging energy efficiency could reach 58% along with an exergy efficiency of 42%. In others words, chemically speaking, the exothermic reaction is more efficient than the endothermic one. This justifies the fact that several authors focused only on the hydration part of a thermochemical heat storage system to investigate its performance

Most salt hydrates undergo an incongruent transition. The water released not being sufficient to dissolve all the solid phase present. Thus, at the transition point, two solid phases may be present, along with a saturated solution of the lower hydrate. Complete recrystallization of the present incongruently melting salt can be promoted, either by mechanical means (stirring, vibration, etc.) or by the use of small quantities of thickening/nucleating agents, which prevent the settling of the lower hydrate. That is why Bissel et al. invented a PCM-based strontium bromide where the addition of agents, such as acetamine. glycerol and trimethylolethane will depress the melting point and allow recrystallization [8]. Another way of ensuring reversibility for such solid-solid phase change, is to set consecutive reactions to eliminate reversibility problems and therefore improving the overall efficiency as promoted by Cabeza et al. [38]. The challenge will be to find corresponding inert and associated components to operate the expected products and reactants.

3. Thermal properties

As a thermal energy storage material, thermal properties of $SrBr_2$ · $6H_2O$ should be known in order to define the operating conditions of the storage system in application or to adapt to the building environment. In such storage systems, prevalent phenomena are heat and

 $^{^{1}}$ Calculated based on the theoretical enthalpy of fusion (1031.4kJmol $^{1})$ in NBS Table [20].

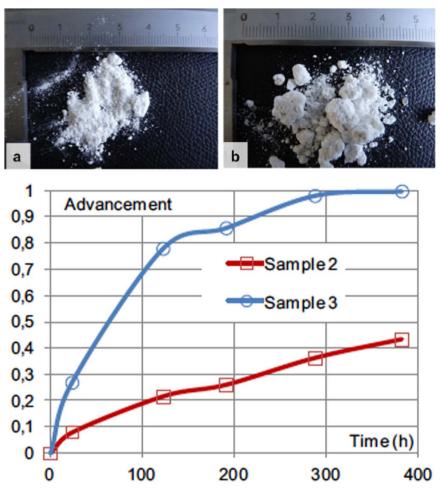


Fig. 4. Advancement vs. time for the hydration of SrBr2-sample 2 (a) and sample 3 (b) [31].

 Table 3

 Standard chemical exergy of selected components [35].

Component	Molecular weight (g mol ⁻¹)	Gibbs energy of formation (kJ mol ⁻¹)	Standard chemical exergy (kJ mol ⁻¹)
SrBr ₂ ·6H ₂ O	355.49	-2121.02	158.43
SrBr ₂ ·1H ₂ O	265.44	-934.42	154.65
SrBr ₂	247.42	-697.10	153.90
H ₂ O (gas)	18.02	-228.75	9.33
H ₂ O (liquid)	18.02	-237.32	0.76

mass transfers, which are physically characterised through properties such as thermal conductivity, specific heat capacity and permeability.

3.1. Thermal conductivity

In order to determine this property, two devices operating on

steady and transient state were used [28]. Hydrates measured here are the hexahydrate (SrBr $_2$ ·6H $_2$ O) and anhydrous is the heated hexahydrate to 200 °C during 4 h in a vacuum oven. Average results of 0.67 and 0.50 W m $^{-1}$ K $^{-1}$ were respectively obtained for the hexahydrate and anhydrous form. A temperature dependency of the thermal conductivity in the range 20–70 °C was also given as follows [28]:

For
$$SrBr_2 \cdot 6H_2O$$
: $\lambda_s = -0.0016 \cdot T^2 + 0.15 \cdot T - 2.73$ (4)

For anhydrous SrBr₂·1H₂O:
$$\lambda_s = -0.0039 \cdot T^2 - 0.32 \cdot T + 6.67$$
 (5)

For thermal energy storage application, these values are too low and as recommended in Ref. [18], thermal conductivity of the salt bed should be around $10 \text{ W m}^{-1} \text{ K}^{-1}$. An improvement is to design composites based on this salt such as expanded natural graphite and $SrBr_2 \cdot 6H_2O$ as performed by Mauran et al. [15].

Table 4
Specific heat capacity of different materials based on the two applied methods: displacement method and area method at the isothermal steps (60 and 90 °C) [18].

	Specific heat capacity (J $kg^{-1} K^{-1}$) at isothermal steps Methods		Specific heat capacity (J kg ⁻¹ K ⁻¹) at isothermal steps			Literatur	Literature ^a [39,40]	
Materials	Area method (60 °C)	Displacement method (60 °C)	Standard deviation	Area method (90 °C)	Displacement method (90 °C)	Standard deviation	60 °C	90 °C
SrBr ₂ ·6H ₂ O SrBr ₂ ·1H ₂ O	986 457	979 434	0.69% 5.35%	890 498	935 506	4.80% 1.60%	967 456	970 456

^a The literature results are obtained using theoretical calculation and displacement method based on critical compilations.

3.2. Specific heat capacity

For the heat capacity (C_p) determination, two isothermal steps were imposed at 60 and 90 °C. With a slow heating rate (2 °C min⁻¹) and an adequate isothermal step (5 min), equilibrium condition was reached. Heat capacity was then calculated by two methods, either from the displacement or from the area generated during isothermal step [18]. Specific heat capacities from the two methods are listed in Table 4. Good accuracy was achieved for most of the sample materials. No significant difference was found between the two methods, which supports the accuracy of the measurements. Calculating the area under the curve based on the displacement (mW) was similar to the area from the peak analysed based on the tangent lines from the DSC-TA software, as listed in Table 5. This indicates that any of the methods can be used to determine the values of specific heat capacity of any materials. In spite of that, averaging the two values is recommended to reduce associated errors.

Standard deviation between literature and experimental values are up to 6%. Literature values were experimentally determined at 25 °C and interpolated through the C_p equation function of temperature and coefficients (fitted from experiments). So, literature values of C_p at 60 and 90 °C are interpolated while actual values are obtained subjecting to the exact temperature. Compared then to literature, average C_p of ${\rm SrBr_2\cdot 6H_2O}$ is low and for ${\rm SrBr_2\cdot 1H_2O}$ it is high.

3.3. Permeability

Works on the determination of thermochemical material's permeability is still under study and few researchers have been performing it in different conditions. That is why relevant literature about it is very limited. The nitrogen-based results show a bigger difference than the ones with helium and are closer to the formal results [33] under air flow in an open system containing the strontium bromide. However, the results have an uncertainty of around 25% due to the pressure loss in air (the ambient) caused by the thermal mass flow meter. The pressure compensation with calibration was difficult to reach due to the low differential pressure. However, results are satisfactory for the closed system. Table 6 exhibits the results of the Helium and Nitrogen permeability and highlights the overestimation made when using the helium as gas flow. The reason might be that helium is lighter than nitrogen and therefore passes easily through the voids of the bed. Concerning standard deviation, SrBr₂·6H₂O presents about 45% between the two-gas utilisation. However, the N2 permeability gives realistic and reliable results, especially in the case of strontium bromide. Theoretical evaluation of this property shows a higher underestimation and might lead to a biased result during practical design or simulations. This conclusion is based on particle size determination using a sieve, which is normally not the appropriate device. Further, better knowledge on particle size distribution may alter this conclusion drawn.

4. Field of application

SrBr₂·6H₂O has been already well investigated at laboratory and prototype level for a long time for various applications either for solar cooling and heat storage in a closed process [14,15,18], or for seasonal storage of solar energy in an open process [6,16,19,41]. In short, it can be considered as storage and thermal comfort material. Either for long-term or short-term storage, the present salt is worth using. Nagel et al. reviewed the features and applications concerning the water/strontium bromide system [42]. In this paper, additional applications, especially for building structure and composites design are added to complete at our best knowledge the field application of SrBr₂·6H₂O. The present salt can also be integrated into roof, ceiling and floor as intensively performed with phase change material in Ref. [43].

4.1. Building application

Three decades ago, the idea of integrating storage materials into building structure of modern houses was initiated in order to store/ release the thermal energy coming from solar or internal sources [44]. Main studies focused on phase change materials. The idea of integrating thermochemical materials is instead presented. SrBr₂·6H₂O can be considered as building structure material. Nevertheless, several parameters and operating conditions should be first investigated such as "what parameters should be regarded as structure performance in terms of building comfort"? The life cycle and degradation of the material are very important issues for the present application that should be carefully considered. Encapsulation could not work with this salt hydrate since dehydration and hydration should be done under atmospheric conditions. At least, if a perforated piping is inserted within the thermochemical material (concrete-SrBr₂·6H₂O-concrete), so that dehydration and hydration are performed similarly to what Uribe et al. [45] did. A similar illustration is presented in Fig. 5. Instead, coating techniques might be appropriate. For example, coating external and internal building walls with SrBr₂·6H₂O, and observing dynamic behaviour according to climate conditions to insure thermal comfort performances. From an ecological point of view, the present application is environmentally free. As comparison, SrBr2·6H2O is, according to the NFPA 704 standard, categorised at level 2 (moderate skin irritation) and cement for building construction at level 1 (slight skin irritation and moderate skin corrosion). In addition, economical considerations due the material cost should highly be taken into account.

The main inconvenient of the present application to building wall is the life cycle and degradation of the material although its solid-solid state is an advantage for the building structure. Most of the researches involving $SrBr_2\cdot 6H_2O$ were dedicated application in building, except that only the material or the reactor part was presented. However, Lahmidi et al. presented a complete process (Fig. 6) to heat a building from the floor by using solar energy [14]. The system featured a heating capacity of 60 kW h.

SrBr $_2$ -6H $_2$ O was recently considered in a cascade concept of providing heating and domestic hot water (DWH) to buildings [12]. From a detailed comparison of the performance and thermophysical properties with other materials according to defined constraints for heating purpose, the authors came out with suitable materials to work together in order to enhance the energy and exergy efficiency of the system (Fig. 7). It is shown in Fig. 7 that SrBr $_2$ -6H $_2$ O can be coupled in a cascade way to Na $_2$ S·5H $_2$ O in order to ensure heating at 40 °C and DWH at 60 °C for the building. With useful exergy efficiency of 27% and the exergy conversion efficiency of 28%, the energy storage density of the cascade system is about 599 kW h m $^{-3}$, not very different from the system with only SrBr $_2$ -6H $_2$ O of 531 kW h m $^{-3}$ [18]. Considering the material price of SrBr $_2$ -6H $_2$ O, the corrosiveness and the toxicity of Na $_2$ S·5H $_2$ O, the cascade system might not be competitive in terms of energy storage density and output temperature.

4.2. Composite design

SrBr₂·6H₂O can be a suitable salt for entrapment to several host

Table 5Comparison between the area at the isotherm from DSC scan and the calculated one from the displacement value [18].

	Based on area at isotherm		Calculating the area under the curve= (displacement (mW)×(60 min/2 °C)×10)		
Material	J/g 60 °C	J/g 90 °C	J/g 60 °C	J/g 90 °C	
SrBr ₂ ·6H ₂ O	5.935	5.29	5.76	5.43	
SrBr ₂ ·1H ₂ O	4.81	5.273	4.59	5.34	

Table 6Experimental permeability results and comparison [18].

Materials	Void fraction (%)	He permeability (m ²)	N_2 permeability (m ²)	Theoretical permeability (m ²)	Literature
SrBr ₂ ·6H ₂ O	24	5.6×10^{-11}	$\begin{array}{c} 3.1 \times 10^{-11} \\ 0.7 \times 10^{-10} \end{array}$	0.04×10^{-10}	$0.86 \times 10^{-11} \text{ m}^2 [33]^a, 3.2 \times 10^{-11} [19]^b$
SrBr ₂ ·1H ₂ O	11	0.15×10^{-10}		0.32×10^{-10}	$0.3 \times 10^{-10} \text{ m}^2 [33], 1.6 \times 10^{-11} [19]$

^a This is the result for the first hydration of the bed using air as gas flow, obtained with an uncertainty of 0.32×10^{-11} m². At the seventh hydration an average of 6.5×10^{-12} m² is obtained as the air-permeability of the bed.

b Results obtained with an uncertainty of 11%. Void fraction of SrBr₂·1H₂O is 17% and of SrBr₂·6H₂O is 25%.

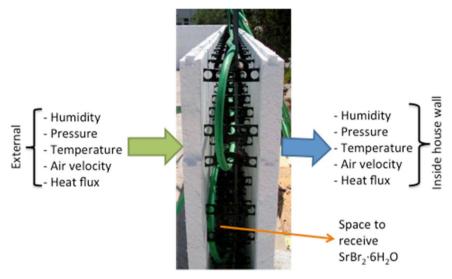


Fig. 5. Illustration of building wall integrated storage material for thermal comfort (adapted from [44]).

materials, such as expanded natural graphite (ENG), exfoliated vermiculite (EV), silica gel (SG), and metal halides. Combining salt hydrates with host matrices is utilized to overcome the heat and mass transfers issue encountered in sorption and solid-gas thermochemical processes, such as agglomeration, deliquescence, and side chemical reaction. Lahmidi et al. [14,15] intensively studied the present salt and designed a composite with the expanded natural graphite (SrBr₂·6H₂O+ENG) by physical mixing in order to increase the heat capacity and the storage density, hence the specific power (W m⁻³) of the material. The composite featured suitable characteristics. In fact, by increasing the composite bed thickness, bed thermal conductivity was increased from 1 to 1.6 W m⁻¹ K⁻¹ and bed permeability from 0.7 to 2.77·10⁻¹² m². Their experimental tests on the composite demonstrated that power levels in the range of 40 kW m⁻³ could be reached with reactive

composites having heating storage capacities higher than 250 kW h m $^{-3}$. The aim was to solve the agglomeration or deliquescence issue that could occur when using only pure $SrBr_2 \cdot 6H_2O$. Also by physical mixing, Michel et al. [33] designed a composite material with exfoliated vermiculite (EV), to solve the mass transfer issue of the open system. Composition ratio was not provided. Tests performed with the composite ($SrBr_2 \cdot 6H_2O + EV$) exhibited lower energy density and slower hydration kinetics so that at the end, mass transfer and kinetics were not better than using pure salt. From the previous works, it is recommended using the chemical impregnation methods (vacuum, immersion and filtration) to design composite based $SrBr_2 \cdot 6H_2O$ as the chemical bonds exhibit high potential energy. Thus, Zhang et al. recently designed a composite ($SrBr_2 \cdot 6H_2O + EV$) by chemical impregnation, named as "novel $EVM/SrBr_2$ " [46]. They experimentally found

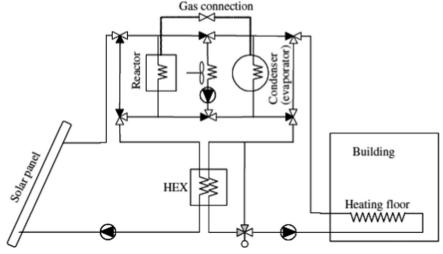


Fig. 6. Building-heating system based on SrBr₂·6H₂O using solar energy [14]. HEX: Heat Exchanger.

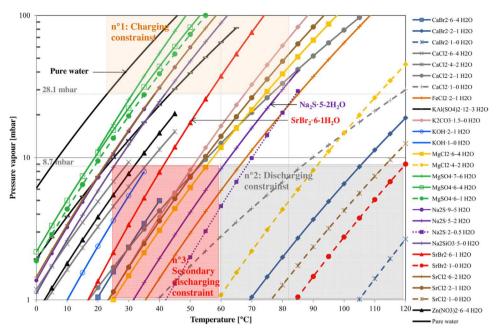


Fig. 7. Equilibrium curves for various thermochemical materials and thermodynamic constraints. In order to satisfy both charging and discharging constraints (n°1 and n°2), the equilibrium curve of the salt must cross both charging and discharging constraints areas [12].

a water uptake of $0.53\,\mathrm{g\,g^{-1}}$, mass energy storage density of $0.46\,\mathrm{kW}\,\mathrm{h\,kg^{-1}}$ and volume energy storage density of $105.36\,\mathrm{kW}\,\mathrm{h\,m^{-3}}$ for the composite. Authors mentioned that the novel EVM/SrBr₂ presents excellent potential than bulk SrBr₂·6H₂O, ignoring the fact that they obtained energy storage density at material scale, which considerably decreases at reactor/prototype scale. As comparison, SrBr₂·6H₂O presents a volume energy storage density of 213 kW h m⁻³ at material scale and 133 kW h m⁻³ at prototype scale [7]. By mixing, the addition of expanded natural graphite treated with sulfuric acid (ENG-TSA) to SrBr₂·6H₂O led to a composite with the aim to improve the heat transfer performance [47]. Bissell et al. [8] used the impregnation method to develop a phase change composite based mixture (SrBr₂·H₂O+MgBr₂·H₂O) for optimal heat-storing at about 76–88 °C temperature range, as it was difficult to find such a phase-change

material with a melting temperature in this range. It has to be mentioned that solid-solid PCMs are obtained by dispersing considered PCM into higher melting point materials acting as supporting materials, so that, as long as the temperature is below the melting point of the supporting materials, the compound materials can keep their solid shape, even if PCM changes from solid to liquid [34]. This combination aims at solving the incongruent melting at this PCM temperature range, knowing that melting temperature of MgBr₂·6H₂O is about 174 °C [48]. The designed phase change composite comprised 32 wt% MgBr₂·H₂O, 65 wt% SrBr₂·H₂O and 3 wt% water which has a phase change of about 77 °C. Courbon et al. used the impregnation method to design a SG+ SrBr₂·6H₂O composite that exhibits a water uptake of 0.22 g g⁻¹, corresponding to an energy storage density of 203 kWh·m⁻³ of packed bed composite [49]. The SG+ SrBr₂·6H₂O composite showed

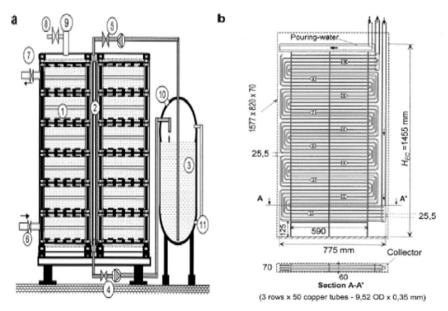


Fig. 8. SOLUX prototype of the closed heat/cold storage system based on SrBr₂·6H₂0 [15]. (a) The reactor and its auxiliaries: a module (1), the Evaporator/Condenser (2) between the two stacks of modules, the reactive water stored in the water tank (3), the collection of the pouring-water at the EC bottom and its reintroduction at the top by means of two pumps (4, 5), the inlet and outlet collector (6, 7) of the coolant of the exchanger plates, a vacuum valve (8), the pressure (9, 10) and liquid level (11) measures. (b) Some details of the EC unit constituted by three staggered rows of five parallel tubes, which are uniformly wetted with the reactive water by a shower at the top.

a good stability after 14 cycles. From the literature search, there is not yet an invention (patent) about a composite thermal storage material based on strontium bromide and ENG, EV or SG. Laboratory tests should be performed as feasibility study.

4.3. Heat and cold storage

The solid-gas reactive pair water/strontium bromide was first used for direct floor heating and cooling by Mauran et al. [14,15], then for seasonal solar heat storage for residential heating [16,41,50] and for production of heat and domestic hot water by Marias et al. [6,19]. Recently, the same chemical pair was used to recover waste heat from micro combined heat and power device for households purpose [13] and to store heat [47]. From these references, several laboratory scale device and prototypes were developed. For closed process, prototype (SOLUX [15]) and laboratory scale (LEUPHANA [13]) devices capable of storing 60 kW h and 65 kW h for heating function were demonstrated, respectively (Figs. 8 and 9). A recent development of closed system (Fig. 10) exhibits a heat-storing capacity of 67.5 kWh despite the mass transfer resistance [47]. Cold storage with a capacity of 40 kW h was also experimented with the SOLUX project. Both closed systems were design to produce at least 80 kW h. But the constraints (tightness, leakage) due to the vacuum state were not practically well handled. Both systems faced the poor heat transfer coefficient (less than 200 W m⁻¹ K⁻¹) between the involved media. For open process, laboratory scale devices with specific power of 2.9 W kg⁻¹ of SrBr₂·6H₂0 (ESSI [16]) followed by another one with storage powers between 0.6 and 1.4 kW were developed in a similar way as the SOLUX one (Fig. 11). Tanguy et al. [50] also developed a seasonal open heat storage system for building purposes (Fig. 12). From these projects, only few gave the corresponding thermal efficiency and heating capacity of the system. LEUPHANA project exhibited a thermal efficiency of 78% [13] whereas open seasonal storage system from Tanguy et al. exhibited 75% [50]. These previous results might appear as good, but process limitations can be optimized to obtain greater performances. For instance, a reactor shape optimization, material configuration into the reactor and dynamic simulations with auxiliary devices such as evapo-condenser and heat exchangers should be performed in a first place.

Cooling storage systems can be operated with strontium bromide, because under normal conditions (ambient temperature and atmospheric pressure), it forms with ammoniac the $SrBr_2 \cdot 8NH_3$. From a decomposition isotherm study, two stables, namely $SrBr_2 \cdot 2NH_3$ and $SrBr_2 \cdot 1NH_3$ were found [26]. The SOLUX prototype, capable of storing 40 kW h for cooling function, was demonstrated many years ago, however with water as a refrigerant [15]. The present authors believe that more efficient results can be achieved by using ammoniac as refrigerant instead since heat of condensation is not required.

5. Conclusion

The use of strontium bromide in thermal and building applications is reviewed. From the thermodynamics analysis to the physic-chemical properties determination, this paper gathers the information related to applying strontium bromide in thermal and civil engineering. Such thermophysical properties as heat of fusion, density, specific heat, permeability and thermal conductivity of SrBr₂·(1-6)H₂O are not sufficiently studied in the literature. At this moment in time, no standards have been fixed to define the minimally acceptable set of thermophysical properties and the temperature range for which these thermophysical properties should be determined. In the framework of the international energy agency/energy conservation through energy storage (IEA/ECES) programme, some round-tests are ongoing [51], but not yet on the present salt hydrates. These round-tests can be considered as a potential standardized benchmark for thermochemical material, especially for SrBr₂·(1-6)H₂O. Gathering this information about strontium bromide will prevent the scientific community from work with parameters obtained from general correlations and that do not fit to simulation-experimental data. The main drawback of the use of strontium bromide in heating and cooling systems is the material cost per kilogram.

The present working pair has already showed some cycling-stability. In fact, 13–14 cycles during a closed process [18,49] and 25 during an open process were successfully performed [19], making it suitable for seasonal thermochemical heat storage. On discussion on the efficiency and exergy analysis, Abedin and Rosen showed that 50% of thermal efficiency could be obtained for thermal energy storage system based on the present salt hydrate [35]. In addition, Istria et al. performed some calculations and measurement with a conclusion that similar thermal systems involving only one salt could reach at least a thermal performance of 50% [52]. Somehow, the use of this salt for thermal energy applications is beneficial. Besides, a techno-economical

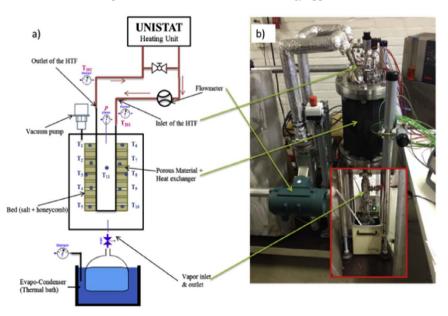


Fig. 9. LEUPHANA prototype of the closed heat storage system based on $SrBr_2 \cdot 6H_20$ [13]. (a) The corresponding 2D schematic system with honeycomb heat exchanger and (b) the experimental lab-scale thermochemical energy storage system.

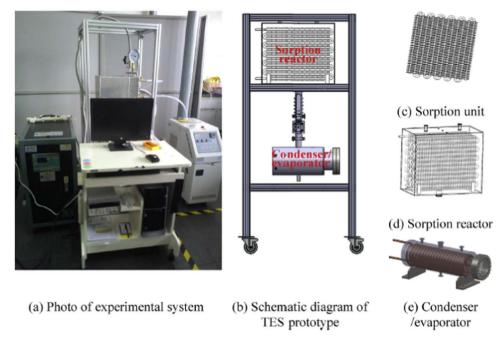


Fig. 10. Design and configuration of the experimental closed thermal energy storage [47].

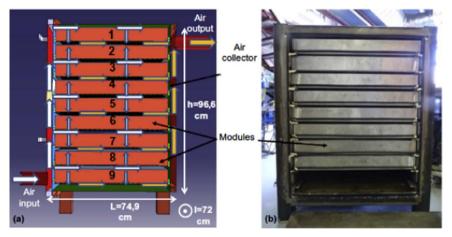
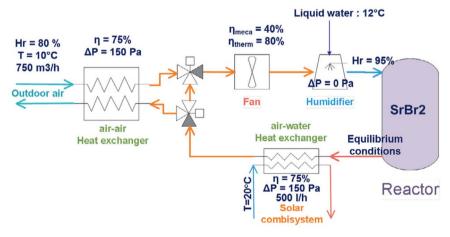


Fig. 11. ESSI prototype of the open heat storage system based on SrBr₂·6H₂0 [16]. (a) Vertical section, including the airflow paths. (b) Photography of the prototype before closing it.



 $\textbf{Fig. 12.} \ \ \text{Seasonal thermochemical heat storage for building application based on } SrBr_2 \cdot 6H_2O\ [47].$

study should be undertaken. Concerning the salt hydrate permeability, the correlations used caused the theoretical underestimation. Here, the Carman-Kozeny correlation was used. However, this correlation was

established for porous media that do not melt or do not change their state as salt hydrates. So, recommendation on further works permeability correlation for salt hydrates should be undertaken. Although different designs and characteristics of experiments, comparison of the use of $\rm SrBr_2\text{-}6H_2O$ in closed or open system is difficult. For example, in closed system, the specific power is completely dependent on the amount of heat exchangers, while the power of open systems can be adjusted by tuning up the flow rate. So it is not possible to compare the powers for these two different modes. In addition, the specific power is usually reported in Watts per kilogram of the material, not the volume of the system. So the volume of the implemented heat exchangers in the closed system is not taken into account.

The use of strontium bromide hexahydrate as phase change composite material allows simple stabilization application around 77 °C without machinery, and as thermochemical, pure and composite material above 50 °C. High considerations are put on strontium bromide, reasoned by controllable power, higher energy density and cycling-stability. Despite significant advances on thermochemical heat storage concept, the technology, especially that based on $SrBr_2 \cdot 6H_2O$ is still not fully developed. Therefore, the present work brings a plus to further advancement and development activities before the introduction of the technology to the market.

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