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A review of available technologies for seasonal thermal energy storage

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Abstract

Solar energy storage has been an active research area among the various solar energy applications over the past few decades. As an important technology for solving the time-discrepancy problem of solar energy utilisation, seasonal/long-term storage is a challenging key technology for space heating and can significantly increase the solar fraction. It widens the use of solar collectors and results in better solar coverage of the space heating demand. This paper reviews all three available technologies for seasonal heat storage: sensible heat storage, latent heat storage and chemical storage. Sensible heat storage is a comparatively mature technology that has been implemented and evaluated in many large-scale demonstration plants. Water, rock-sort material and ground/soil are frequently used as storage materials. Latent heat and chemical storage have much higher energy storage densities than sensible storage, which means that they can remarkably reduce the storage volume, and they seldom suffer from heat loss problems. However, the latter two technologies are currently still in the stages of material investigations and lab-scale experiments. The characteristics of each concept have been presented in detail in this review. The latest studies and related projects are reviewed. The paper is structured as follows: fundamental investigation on storage materials, existing plants or projects and future outlook.

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1. Introduction

Rapid worldwide population growth has put a heavy burden on conventional energy resources, such as fuel, coal and oil, which are estimated to run out in several decades. These conventional resources are also blamed for CO₂ and other harmful gas emissions that lead to climatic change problems, for example, global warming and the deterioration of the ozone layer. All of these severe consequences cause people to begin to reconsider what acceptable and sustainable development patterns are.

In recent years, considerable progress in renewable energy development has made new energy resources quite competitive with conventional energy in terms of both efficiency and reliability. Solar energy, as a pollution-free,

inexhaustible and affordable energy resource, has received extensive study and numerous applications throughout the world. However, one of the longstanding barriers to solar energy technology lies in the noticeable misalignment between energy supply and consumption. Therefore, the energy storage concept is proposed as an essential way to address the mismatch.

The idea of thermal energy storage (TES) was first mentioned and investigated to address the energy shortage crisis in the 1970s. By means of energy storage, intermittent solar energy is able to not only meet the demands of space heating and domestic water supply but also to offer a high grade heat source all year round regardless of timing or seasonal constraints.

Energy storage can be classified into short-term storage and long-term storage according to different storage durations. Using excess heat collected in the summer to compensate for the heat supply insufficiency during the wintertime is

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the concept of seasonal thermal energy storage (STES), also called long-term heat storage.

Fisch et al. (1998) summarised thirteen existing and fourteen planned large-scale solar heating systems in Europe with different storage applications of short-term (diurnal) and long-term (seasonal) storage and compared the cost-benefit-ratios of them. The results showed that the pattern of seasonal storage could satisfy 50–70% of the annual heat demand, whereas the diurnal pattern could only meet 10–20%. The investigation indicated that seasonal storage was more capable of conserving energy and reducing fossil fuel consumption for the environment's sake.

Although seasonal storage has greater potential in practical applications, it is more technologically challenging than short-term storage. It requires large storage volumes and has greater risks of heat losses, and the material chosen for implementation must be economical, reliable and ecological.

There are three different mechanisms for energy storage: sensible heat storage, latent heat storage and chemical reaction/thermo-chemical heat storage. Over recent decades, related studies addressing diverse applications and storage mechanisms have been carried out throughout the world (Dincer and Rosen, 2002). The concept of seasonal energy storage is not only realised in district heating (Schmidt et al., 2003) but also in greenhouses for space heating (Alkilani et al., 2011; Sethi and Sharma, 2008) because heating for the plants during winter nights consumes a large portion of heat input in agricultural greenhouses (Bricault, 1982; Kavin and Kurtan, 1987; Santamouris et al., 1994). Many international collaborative efforts have been performed on this interesting topic, and some of them have yielded remarkable achievements. For instance, IEA-SHC Task 32 (The Solar Heating and Cooling Programme of the International Energy Agency) and Solarthermie 2000 are two such programs that focus on the topic of advanced storage concepts. In the framework of Task 32, chemical and sorption, phase change materials and water tank storage technologies were studied and discussed. The cooperative research efforts of IEA–ECES (International Energy Agency: Energy Conservation through Energy Storage) developed the storage concept of underground thermal energy storage (UTES) and investigated phase change materials for energy storage. For UTES, previous study results have already been successfully transformed into large-scale applications through the international collaborative efforts of IEA–ECES. Solarthermie 2000 is a German program in which pilot and demonstration projects of seasonal heat storage for district heating have been realised. All the large-scale plants in Solarthermie 2000 adopted the concept of sensible heat storage.

Sensible heat storage comprises water tank storage (Novo et al., 2010) and UTES (Bakema et al., 1995; Givoni, 1977; Reuss et al., 1997). The major methods employed for UTES include aquifer storage and underground soil storage, which will be elaborated in detail in Section 2. Latent heat storage stores heat nearly isothermally in phase

change materials and can provide higher energy density than the sensible storage. Chemical heat storage is a newly studied technology that permits more compact storage through greater energy storage densities without heat losses, and it is mainly classified as sorption and chemical reaction storage.

Distinct from previous reviews on a particular technology or material comparison (Alkilani et al., 2011; Farid et al., 2004; Hasnain, 1998; Jegadheeswaran et al., 2010; Kenisarin and Mahkamov, 2007; Khalifa and Abbas, 2009; Novo et al., 2010; N'Tsoukpoe et al., 2009; Pinel et al., 2011; Shukla et al., 2009; Zhou et al., 2012), this article focuses on thermal energy storage on a seasonal scale and covers all three seasonal storage technologies. The aim of this paper is to provide a state-of-the-art review based on the theoretical and experimental research. The latest studies and projects are presented and analysed.

2. Sensible heat storage

The sensible heat storage method converts collected solar energy into sensible heat in selected materials and retrieves it when heat is required. The stored heat amount is determined by the specific heat of the material and its temperature increase. Sensible heat storage is considered to be a simple, low-cost and relatively mature technology for seasonal energy storage compared to the other alternatives. Due to its feature of inexpensive and reliable, it has been implemented in a significant number of projects.

2.1. Materials and fundamental studies on sensible heat storage

Fernandez et al. (2010) used a methodology that combines multiple objectives and restrictions of use to find potential materials for sensible thermal energy storage. They studied materials whose application temperature range was 150–200 °C by considering their physical properties and energy densities and evaluating them from an environmental point of view. In Fig. 1, the specific heat capacity values c_p of the hundred most commonly used engineering materials are presented, among which natural and polymeric materials, such as natural rubber or the thermoplastic copolymer ABS, have the highest c_p values of approximately 2 kJ/kg K. Specific heat capacity and density are regarded as two critical indices by which one of the major storage evaluation criteria, energy density ($c_p\rho$, heat capacity unit volume), is determined. The author also plotted a comparison of the thermal conductivities of those materials with the intention of providing a good selection method for finding materials that meet different application demands. Aside from good thermal performance, low cost of the material is another key criterion for screening potential materials, especially for long-term storage.

Recently, seasonal storage technology has mainly been applied in space heating and domestic hot water (DHW) supply for which the required temperature ranges from



Fig. 1. Bar chart of specific heat capacity for a hundred of the most used materials, obtained with CES Selector. (Fernandez et al., 2010).

40 to 80 °C. As a result, water, rock-sort materials (such as gravel, pebbles, and bricks) and ground/soil become popular candidates for storage media and have been widely selected in large-scale demonstration projects.

Table 1 (Schmidt et al., 2003) lists a comparison of several commonly used sensible heat storage methods. To choose a suitable storage concept for a plant, the relevant boundary conditions, such as local geological conditions, available site size, temperature levels of the store, legal issues about drilling, and investment costs, need to be considered. Among the storage concepts listed in **Table 1**, duct and aquifer (Seibt and Kabus, 2006) heat stores demands most on the geological characteristics. Hydraulic conduc-

tivity and natural groundwater flow can severely affect system performance, so geological investigations must be performed prior to system design, and each geological requirement should be strictly met.

2.2. Past sensible heat storage projects

Compared with the other options, sensible heat storage is the most mature and reliable technology for seasonal storage purposes. Sweden pioneered research on large-scale seasonal solar thermal energy storage during the 1980s, and through an extensive international collaboration via the International Energy Agency (IEA), this concept has been

Table 1
Comparison of sensible storage concepts (Schmidt et al., 2003).

Hot-water	Gravel-water	Duct	Aquifer
<i>Storage medium</i>			
Water	Gravel-water	Ground material (soil/rock)	Ground material (sand/gravel...-water)
<i>Heat capacity (kWh/m³)</i>			
60–80	30–50	15–30	30–40
<i>Storage volume for 1 m³ water equivalent</i>			
1 m ³	1.3–2 m ³	3–5 m ³	2–3 m ³
<i>Geological requirements</i>			
• Stable ground conditions	• Stable ground conditions	• Drillable ground	• Natural aquifer layer with high hydraulic conductivity ($k_f > 1.10 \text{ m/s}$)
• Preferably no groundwater	• Preferably no groundwater	• Groundwater favourable	• Confining layers on top and below
• 5–15 m deep	• 5–15 m deep	• High heat capacity	• No or low natural ground flow
		• High thermal conductivity	• Suitable water chemistry at high temperatures
		• Low hydraulic conductivity ($k_f < 1.10 \text{ m/s}$)	• Aquifer thickness 20–50 m
		• Natural ground-water flow <1 m/a	
		• 30–100 m deep	

Table 2
Realised seasonal sensible heat storage projects.

Project	Heated living area (m ²)	Demand by district heating (GJ/a)	Solar collector area (m ²)	Storage volume (m ³)	Solar fraction (%)	References
<i>Hot water</i>						
Hamburg, DE	14,800	5796	3000	4500	49 ^a	(Schmidt et al., 2004b)
Friedrichshafen, DE	39,500	14,782	5600	12,000	47 ^a	(Schmidt et al., 2004b)
Hannover, DE	7365	2498	1350	2750	39 ^a	(Schmidt et al., 2004b)
Munich, DE	24,800	8280	2900	5700	47 ^a	(Dalenbäck, 2012)
Eggenstein, DE (Pit)	12,000		1600	4500	37	(Schmidt and Mangold, 2006)
Rise, DK	115 buildings		3575	5000		(Dalenbäck, 2012; SOLARGE)
Marstal, DK	1300 houses	104400	26,000	70,000	29	(Fisch et al., 1998)
Herlev, DK		4520	1025	3000	35	(Heller, 2000)
Ottrupgard, DK		1630	560	1500	16	(Heller, 2000)
Hoerby, DK				500		(Dalenbäck, 2012)
Ingelstad, SE	50 houses		1320	5000		(Dalenbäck, 2012)
Lambohov, SE	50 houses		2700	10,000		(Dalenbäck, 2012)
Lyckebo, SE			4320	100000		(Dalenbäck, 2012)
Neuchatel, CH	Office		1120	1000		(Dalenbäck, 2012)
Calabria, IT	1750	111	91.2	500	28.2	(Oliveti et al., 1998)
Lisse, NL	Agriculture		1200	1000		(Bokhoven et al., 2001)
Charlestown, US	Historic park		5700			(Breger and Michaels, 1984)
<i>Aquifer</i>						
Rostock, DE	7000	1789	1000	20,000	62 ^a	(Schmidt et al., 2004b)
Berlin, DE		57,600 (heat)	^b		77 (heat) 93	(Schmidt et al., 2003; Seibt and Kabus, 2006)
		18,000 (cold and heat)			(cold and heat)	
Rastatt, DE		18,345	6780	23,000	41	(Fisch et al., 1998)
Neubrandenburg, DE					46	(Kabus and Wolfgramm, 2009)
2 MW, NL			2900			(Dalenbäck, 2012)
Westway Beacons, UK	130 apartments					(Dalenbäck, 2012)
Richard Stockton, US	College with 7000(cold) students					(Dalenbäck, 2012)
Balcali, TR	Hospital	50,400				(Paksoy et al., 2000)
Cukurova, TR	360m ² greenhouse		Use greenhouse as solar collector			(Turgut et al., 2006)
Antwerp, BE	Hospital				81	(Vanhoudt et al., 2011)
<i>Gravel</i>						
Chemnitz, DE	4680	4450	2000	8000	42 ^a	(Schmidt et al., 2004b)
Steinfurt, DE	3800	1170	510	1500	34 ^a	(Schmidt et al., 2004b)
Stuttgart, DE		360	211	1050	62	(Hahne, 2000)
Augsburg, DE				6500		(Schmidt et al., 2003)
<i>Duct</i>						
Neckarsulm, DE	20,000	5987	2700	20,000	50 ^a	(Schmidt et al., 2004b)
Attenkirchen, DE	30 homes	1386	836	500 + 10,500 (hot-water + duct)		(Reuss et al., 2006)
Crailsheim, DE	School and gymnasium	14,760	7300	37,500	50 ^a	(Dalenbäck, 2012)
Anneberg, SE	50 residential units	1980	2400	60,000	70 ^a	(Lundh and Dalenbäck, 2008)
Lidköping, SE		3528	2500	15,000	70	(Fisch et al., 1998)
Groningen, NL			2400			(Dalenbäck, 2012)
DLCS, CA	52 homes		2313	33,657	80	(Drake Landing Solar Community, 2012)
Kerava, FI			1100			(Dalenbäck, 2012)

DE = Germany, DK = Denmark, SE = Sweden, CH = Switzerland, IT = Italy, NL = Netherlands, US = United States of America, UK = United Kingdom, TR = Turkey, BE = Belgium, CA = Canada, FI = Finland.

^a Calculated values for long-time operation.

^b Combined heat and power plant (waste heat and ambient cold).

popularised throughout the world. Currently, numerous facilities are in operation in Sweden, the Netherlands, Germany and some other European countries, as well as in Canada and the United States. Existing large-scale seasonal storage projects involving water-based storage, rock (mostly using gravel) storage and ground/soil storage are listed in Table 2. In the following subsection, a detailed description of each type will be given.

2.2.1. Water-based storage

Water is considered to be a favourable material for energy storage due to its high specific heat (compared with other sensible heat storage media) and high capacity rate while being charged and discharged. Water-based storage systems literally employ water as the storage medium or heat carrier fluid for storing/transferring heat. They can be further classified into water tank and aquifer storage systems. Water tank/pit storage systems store water in an artificial structure, whereas aquifer storage uses natural water directly from the underground layer.

2.2.1.1. Water tank systems. Water tanks are artificial structures that are made of stainless steel or reinforced concrete surrounded by thick insulation. They are usually buried underground (also called water pits) or placed on the roof or outside of a building (Bauer et al., 2010). Water storage tanks operate in a stratified manner with water at the top of the tank being hotter than that in the bottom due to thermal buoyancy, and the subsequent mixing effect caused by the temperature difference may degrade the heat source level and negatively impact the system efficiency. To minimise such a phenomenon, many studies have investigated methods for maintaining the inside water in a stable thermal stratification status. A horizontally partitioned water tank with thermal stratification in a large-scale solar powered system developed at SJTU is shown in Fig. 2 (Han et al., 2009).

The experimental results showed that the temperature gap between each chamber remained at 15–20 K with an inlet and outlet temperature difference of 70 K. It was demonstrated that the horizontally partitioned water tank could achieve good thermal stratification performance and was efficient as a heat storage application.

In addition to the studies on the optimisation of stratification status, another popular research area in water tank storage lies in the reduction of heat losses during the heat storage process. Efforts have been made in tank design and selection of insulation materials. Glass wool and polyurethane are widely used insulation materials. As shown in Fig. 3, stainless steel or high-density polyethylene layers placed on the roof and the vertical inside part of the tanks are used as liners to reduce heat losses resulted from vapour diffusion through the concrete wall. In a project in Hannover (Lottner et al., 2000), a granulated foam glass filled into textile bags was employed between the soil and the high-density concrete (HDC) wall of an artificial tank. At the Technique University of Ilmenau, researchers developed a wall material made of glass fibre reinforced plastics (GFPs) with an integrated heat insulation layer. All the aforementioned methods were studied and introduced into water tank construction to guarantee water tightness and avoid leakage problems.

A large number of demonstration projects have been realised using the water tank type storage. In a seasonal hot water heat store system in Friedrichshafen, Germany (Raab et al., 2004), a 12,000-m³ store with an additional inner stainless-steel liner for heat loss reduction was built, and 3513-m² integrated roof collectors were constructed on top of a multi-family building to provide energy for the water tank. This storage unit was connected to a district heating system (Fig. 4 shows the schematic layout) and was put into operation in 1996. From 1997 to 2003, the solar fraction achieved varied between 21% and 30%, which was lower than the designed value, and the heat

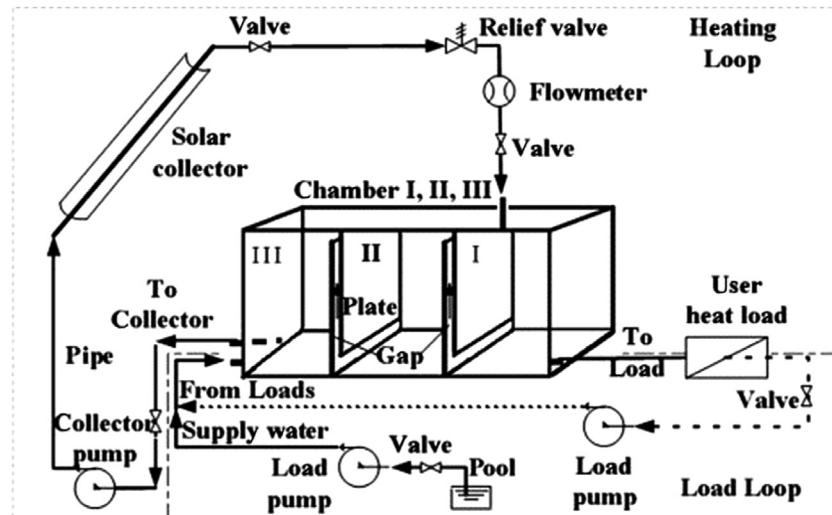


Fig. 2. Horizontally partitioned water tank for a large-scale solar powered system at SJTU (Han et al., 2009).

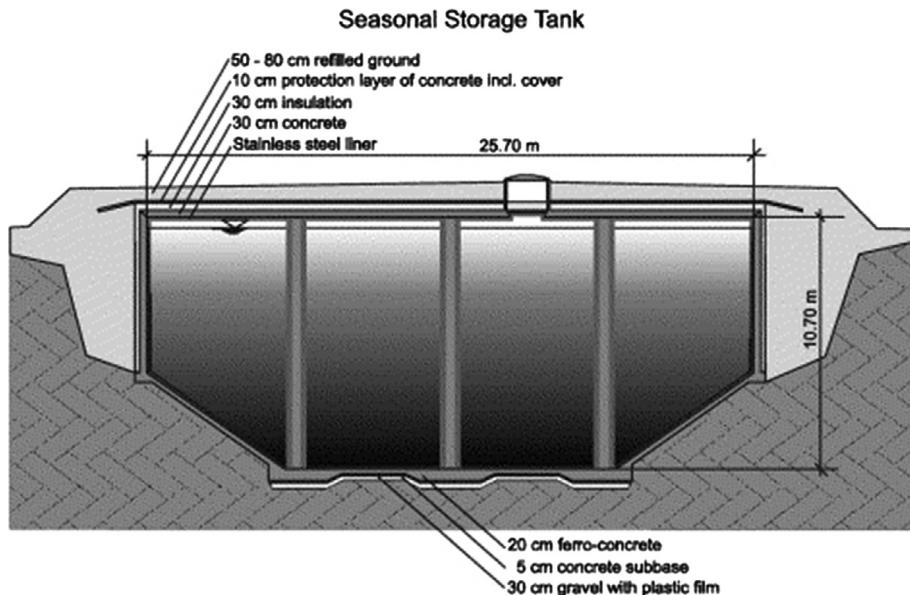


Fig. 3. 4500-m³ hot water storage tank in Hamburg-Bramfeld. (Lottner et al., 2000).

losses from the seasonal heat store were in the range of 322 to 360 MW h per year, which was 40% higher than calculated. It was mentioned that the high net return temperature was the main cause of the high heat losses, and admixing the return flow to the supply flow might be a possible solution. Another system in Hamburg (4500 m² storage volume) has a similar scheme, as reported by Schmidt et al. (2004).

Table 2 provides a summary of past and present projects that use water tanks as a seasonal storage unit. The solar fractions of these systems vary from 16% to 49%, differing due to the diverse configurations.

In some seasonal storage plants, water tanks also play the role of buffer storage in connection between solar collector thermal systems and other storage units.

2.2.1.2. Aquifer systems. According to Lottner et al.'s report (2000), aquifer storage is referred to as a “promising cost-effective option” for seasonal storage. The idea of aquifer thermal energy storage (ATES) was first launched in 1976 and has frequently been used in practice. A large number of preliminary theoretical studies (Dickinson et al., 2009) and practical applications have been carried out and documented on an industrial scale (Seibt and Kabus, 2006; Snijders, 2000).

In an ATES for seasonal heat storage, a suitable aquifer into which at least two thermal wells (one is called the hot well and the other the cold well) should be drilled is required. The aquifer geologic formation is used as the storage medium, whereas groundwater is employed as the heat carrier fluid. Because of the features of the porous

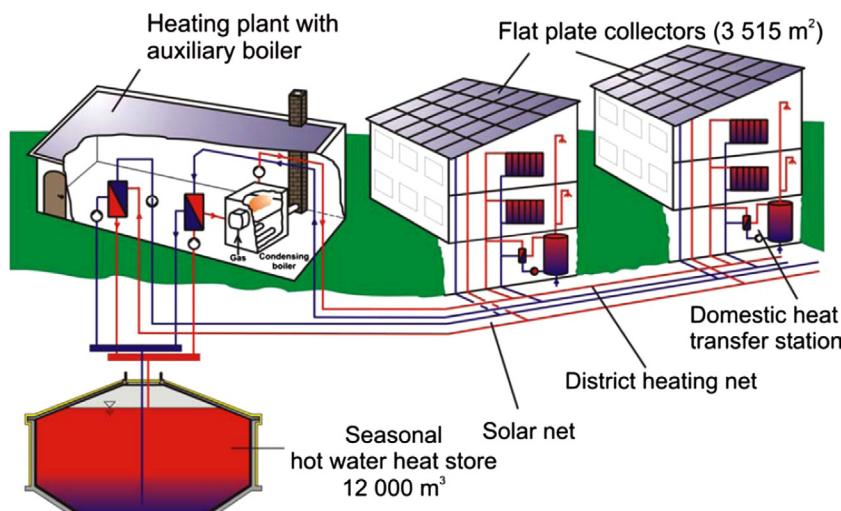


Fig. 4. Schematic layout of the district heating system (Raab et al., 2004).

media and the high specific heat capacity of water, an aquifer is a capable medium where heat can be stored and retrieved. During the charging process, ground water is produced from the cold well, heated by solar energy and then injected into the warm well. During the discharging phase, the flow reverses. As mentioned in Section 2.1, geological conditions at the site are the decisive factors for aquifer thermal energy stores. Relevant ordinances and regulations from the local water authorities should be complied with.

Table 3 summarises the most critical hydro geological parameters of the aquifer applications in Germany (Seibt and Kabus, 2006). Industrial-scale applications of aquifer storage began in Germany in the 1990s, and a number of sites were constructed and examined. The achievements indicated the energy-saving and economical potential of aquifers.

Schmidt and Müller-Steinhagen (2004), Schmidt et al. (2004), introduced an ATES system (in Rostock, as shown

in Fig. 5) coupled with 1000-m² solar collectors on the roof of the building that supplied domestic hot water and space heating for 108 apartments with a heated area of 7000-m². It was the first central solar heating plant with a seasonal aquifer thermal energy storage system in Germany, and the shallow 30-m deep aquifer was operated in a temperature range between 10 and 50 °C. For heat distribution, a low temperature heating system (maximum supply temperature of 45 °C) with radiators was employed to solve the problem of the high return temperature, which was unfavourable for the heat capacity of the heat store. The storage of solar energy in the summertime compensated for the energy shortage during the winter, and the solar fraction calculated for this long-term operation reached 62%.

An aquifer thermal energy storage has been in regular operation in Neubrandenburg since 2005 (Kabus and Wolfgramm, 2009). The ATES was installed at a depth of approximately 1200 m and was charged with 14,300 MW h and

Table 3
Hydrogeological parameters of the aquifer thermal energy stores in Germany (Seibt and Kabus, 2006).

Site	Dresden (field test)	Rostock-brinckmanshohe	Buildings of the German parliament in Berlin	Neubrandenburg
Geological formation	Quaternary	Quaternary	Hettangian	Quaternary
Depth	7–10 m	13–27 m	285–315 m	30–60 m
Porosity	~25%	~20%	30%	~30%
Permeability	>2 μm ²	8 μm ²	2.8–4.2 μm ²	>1 μm ²
Mineralisation	Freshwater	Freshwater	29 g/L	Freshwater
Store temperature (initial)	8 °C	10 °C	19 °C	10 °C

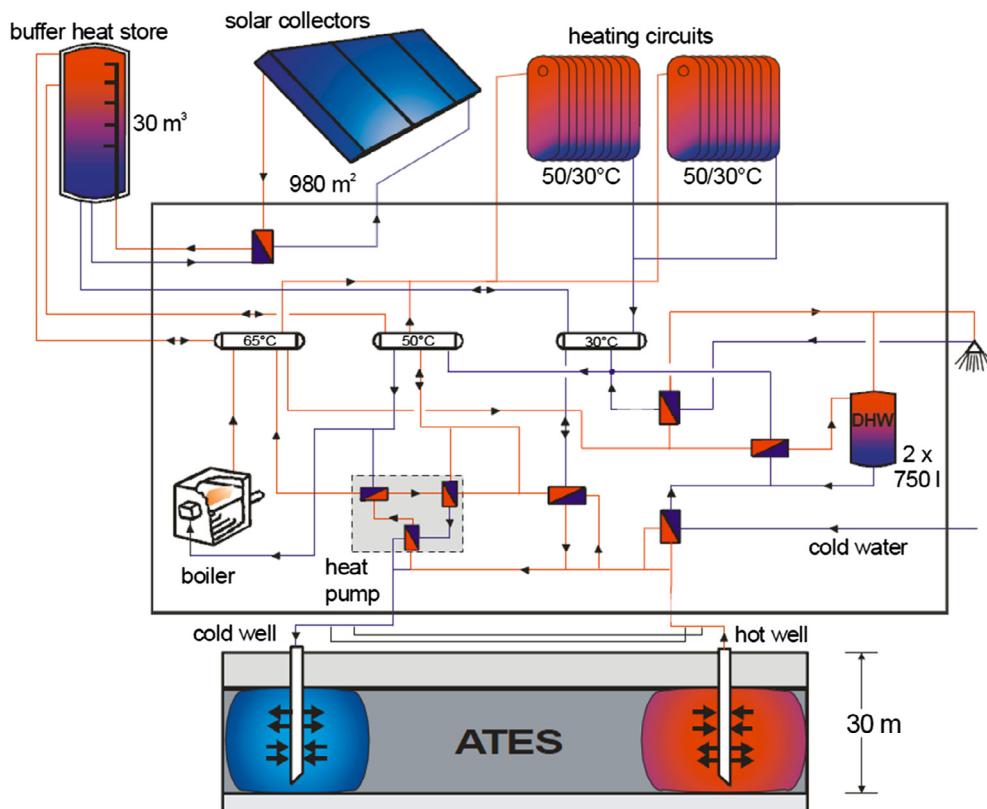


Fig. 5. Scheme of a heat supply system (DHW, domestic hot water) (Schmidt and Müller-Steinhagen, 2004a).

12,800 MW h and discharged with 6500 MW h and 5900 MW h in 2005/06 and 2007/08, respectively. The achieved recovery coefficient of this aquifer storage system was approximately 46%.

A hospital near Antwerp that utilised an ATES system coupled with reversible heat pumps for heating and cooling was reported (Vanhoudt et al., 2011). The ATES system consisted of 2 wells with an interval of 100 m at a depth of 65 m under the ground, and it had three operation modes: a heating (winter) mode, a cooling (summer) mode and a regeneration mode. After three years of operation, 81% of the total cooling energy and 22% of the heating of the ventilation were provided by the direct use of groundwater, which saved a total of 1280 tons of CO₂.

Negative impacts on the groundwater system may be caused if the preliminary study is not sufficient, and the reliance on hydro-geological conditions makes aquifer storage quite complex and conditional. In addition, because it is impossible to install heat insulation for an aquifer store, the heat loss problem should be carefully dealt with. Schmidt et al. (2003) suggested that “the surface–volume-ratio of the store unit has to be low in order to keep heat losses in an acceptable range”.

2.2.2. Rock beds

In rock bed heat storage, the rock (pebble, gravel or bricks) bed is usually circulated with a heat transfer fluid (water or air) to exchange heat (gained in summer and released in winter). Compared to water-based systems, rock-based systems can endure much higher temperatures.

A full test of a solar air heating system designed for space heating and heat water supply in a two-story building has been in operation since December 2010 on Qinhuang Island, China (Zhao et al., 2011). It was the first large-scale solar air heating project that was put into practical use in China. The heating area included a 717-m² dormitory and a 2602-m² cafeteria, which each required different heating durations during the heating season, 24 h and 5 h, respectively. A 300-m³ pebble bed was constructed to store surplus heat collected from the 473.2-m² solar collector during the daytime and played the role of heat source to meet the heat load during the night time. Air, a cost-saving option, was selected as the heat transfer material and could be used directly for indoor heating after being heated. As shown in Fig. 6, the mentioned solar air heating system was able to provide heat to the indoor area and store the heat in the pebble bed at the same time. The experimental results revealed that the solar fraction achieved a mean value of 19.1%, and the highest value of 33.6% was observed in the second half of December 2010. A TRNSYS model was also created to optimise the design parameters by evaluating the solar collector area, installation angle, volume of the pebble bed, mass flow rate of air and so on. It was indicated that the designed system could reach an annual average solar fraction of 53.03% using optimum parameters.

However, due to the low energy density, rock bed storage systems require much larger volumes to achieve the same amount of heat storage, approximately three times (Dincer and Rosen, 2002) more space than water-based storage systems.

Some researchers developed a gravel/water (pebble/water, sand/water) storage system by combining the concepts of water tank and rock storage, which can be viewed as a compromise between the high water tank construction expenses and the low thermal capacity problems of rock materials. A gravel-water mixture can slightly reduce the volume of the storage unit yet is still approximately 50% larger than a hot-water heat store in achieving the same heat capacity (Schmidt et al., 2004).

The first large-scale heat storage project based on the gravel/water concept was successfully developed in Stuttgart in 1985 (Hahne, 2000). A hole dug in the ground was lined with 2.5-mm-thick high-density polyethylene (HDPE) foil and filled with 1050 m³ of pebbles. A similar concept was also applied in an office building project at Chemnitz (8000 m³), and the long-term performance was monitored. Fig. 7 illustrates a cross-section of the gravel/water storage unit in Steinfurt (Pfeil and Koch, 2000). The 1500-m³ gravel-water storage unit was sealed with a modified double polypropylene liner and insulated with granulated recycling glass, which had first been used for seasonal stores. It could be operated at temperatures up to 90 °C and had high cost-reduction potential in the long run. According to the design values, the system was able to cover 34% of the annual heating demand by using solar energy.

2.2.3. Ground and soil storage

Ground/soil storage is another application of UTES aside from aquifer systems. There is no need for a separated site because the ground itself is used directly as the storage material. The underground structure can store a large amount of solar heat collected in the summer for later use in winter. In this storage approach, the ground is excavated and drilled to insert vertical or horizontal tubes, so it is also called borehole thermal energy storage (BTES) or duct heat storage in some literatures (Schmidt et al., 2003). The inserted tubes serve as heat exchangers, the free soil is the storage medium (in Sweden, crystalline granite with few fractures is more common (Gustafsson et al., 2010)), and water is used as the transfer fluid. Water-saturated clay and clay stones are suitable for BTES because they have high heat capacities and are capable of preventing ground water flow (Givoni, 1977). However, a BTES system requires 3–5 times more volume to carry the same amount of heat as the hot-water storage system (as in Table 1) due to its lower energy storage density. Small power rate caused by heat transfer in the borehole is another short come of the system; thereby, an auxiliary water buffer store unit is usually necessary in a large-scale plant.

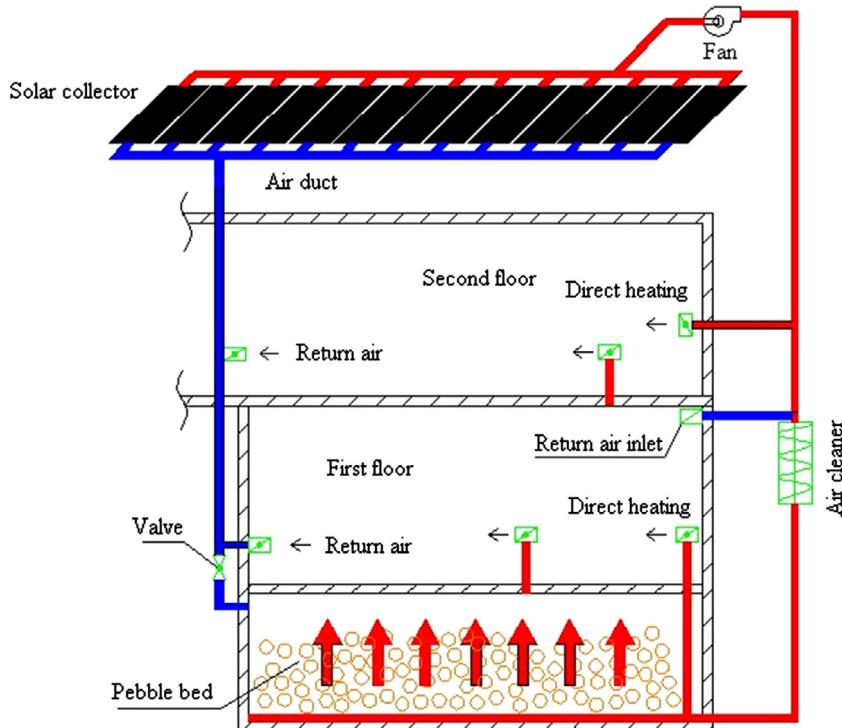


Fig. 6. Schematic diagram of the solar air heating system on Qinhuan Island, China (Zhao et al., 2011).

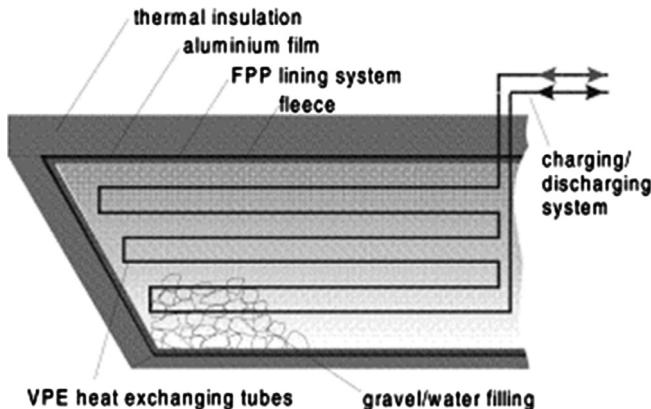


Fig. 7. Cross-section of the gravel/water storage unit in Steinfurt (Pfeil and Koch, 2000).

To provide good thermal contact with the surrounding soil, the space between the pipes and the borehole wall is usually filled with high thermal conductivity grouting material in order to enhance heat transfer. There have been some studies on the grouting material. Some projects have employed bentonite or a high solids composite (such as 9% Blast Furnace Cement, 9% Portland cement, 32% fine silica sand and 50% water in a Canadian project (DLSC, 2012)), while others use water alone, e.g., in Scandinavia (Gustafsson et al., 2010). Gustafsson et al. (2010) simulated the thermal performance in a borehole using water as the grout material. Delaleux et al. (2012) obtained a high thermal conductivity grout material containing 5% wt of graphite whose conductivity reached 5 W/m K, aiming to reduce the thermal borehole resistance.

Based on the theory of BTES, a plant that could seasonally store industrial waste heat was designed (Reuss et al., 1997) in Germany. 15,000 m³ of soil embedded with 140 30-m-deep vertical heat exchangers were designed to store heat to meet a heating demand of 170 kW_{th}. An economic analysis showed that this system cost almost the same price as conventional energy but could save 266 MW h of useful energy annually.

The Drake Landing Solar Community in Okotoks, Alberta, Canada (DLSC, 2012), was the first large seasonal storage community in the world. It consisted of solar collection, the Energy Centre with short-term energy storage, the seasonal Borehole Thermal Energy Storage (BTES) system, the district heating system, and energy efficient homes (shown in Fig. 8). In the BTES system, 144 boreholes were drilled to a depth of 35 m and covered an area 35 m in diameter under the ground. After four years of operation, it met 80% of the community's entire energy demands in the winter, and 52 homes benefitted from it. This project provided a showcase for a BTES-integrated community centre and proved the feasibility of solar energy storage in a high latitude district.

The Anneberg project in Stockholm was the first project to use borehole storage with crystalline rock (Lundh and Dalenbäck, 2008). The system consisted of 2400-m² solar collectors and 100 65-m-deep boreholes that filled with double U-pipes. It was designed to partially meet the heat loads of 50 residential units, and the average solar fraction was found to reach 70% after 3–5 years of operation.

Additionally, the concept of ground/soil storage can be used in agriculture fields for space heating. At Shanghai

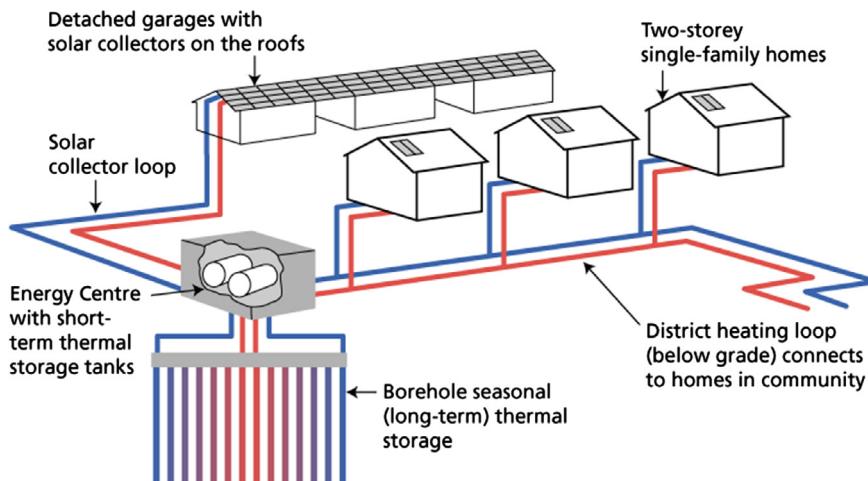


Fig. 8. Solar Seasonal Storage and District Loop of DLSC (2012).

Jiao Tong University, China, a 2304-m² modern greenhouse integrated with a vertical borehole thermal energy storage system was built in 2011. It is designed to store the excess heat from solar radiation in the soil under the greenhouse by utilising water as a heat transfer fluid. The underground stored heat can be extracted when heat is required in the low-temperature season to meet the heat demands of the plants. Together with other technologies, such as the selected cladding material, wet curtains and a floor radiation system, this project aims to provide a suitable growing environment for plants and largely reduce the heating and cooling costs of greenhouse applications. Experiments were initiated in May 2012, and the long-term performance has been monitored.

Although the BTES concept has received considerable attention due to its potential for large-scale applications, it has several drawbacks:

(1) High initial cost

Based on a summary of the investment costs of a plant in Neckarsulm (Schmidt et al., 2003), the borehole exchangers (materials and drilling works) and additional ground works (excavation and refilling) for a borehole heat storage system represented 69% of the total cost. The high installation expense of borehole heat exchangers and complex excavation work are the main obstruction to development to some extent.

(2) Complexity of the underground conditions of water and vapour movement

The thermal conductivity, heat capacity and diffusivity strongly influence the heat transfer performance in the soil and the overall efficiency of the storage system. Many researchers have contributed to studies on underground heat and mass transfer modelling (Cullin and Spitzer, 2011; Gauthier et al., 1997; Gustafsson et al., 2010; Rees, 2002). Olszewski (2004) analysed the possibility of using

the ground as a seasonal heat storage option using numerical study by taking into account such variables as regeneration temperature and geometric size of the pipeline. Reuss et al. (1997) investigated heat and moisture migration in soil by experiment (setup shown in Fig. 9). Diao et al. (2004) established an equation for conduction-advection in porous media by using the Green function analysis to estimate the impact of groundwater flow on the performance of underground heat exchangers.

(3) Long time to reach typical performance

Lundh and Dalenbäck (2008) mentioned that a system with "high-temperature storage" in the ground would need to operate for 3–4 years before achieving a typical performance so that the surrounding ground could reach the designed temperature level. Heat transfer in soil is much slower than in water, so it takes a long time to charge the large storage units in real plants. The DLSC (2012) system was estimated to achieve the target of meeting 90% of heat loads after 5 years of operation.

2.3. Comparison of the investment costs

Investment costs per water equivalent of thirteen realised and planned projects in Germany are presented in Fig. 10 (Schmidt et al., 2003). It is easy to understand that the cost per water equivalent decreases as the storage scale increases. According to the survey, hot water storage project costs most because the construction of the water tank accounts for a large portion. The cheapest types are duct (borehole) and aquifer heat stores, but there are more restrictions on the suitable geological conditions for their use.

Because sensible heat storage easily suffers from heat loss problems in seasonal applications, even if thick insulation is installed, the temperature of the heat source may not allow the extracted heat to be used directly in the heating season. Therefore, the storage unit needs to be assisted with

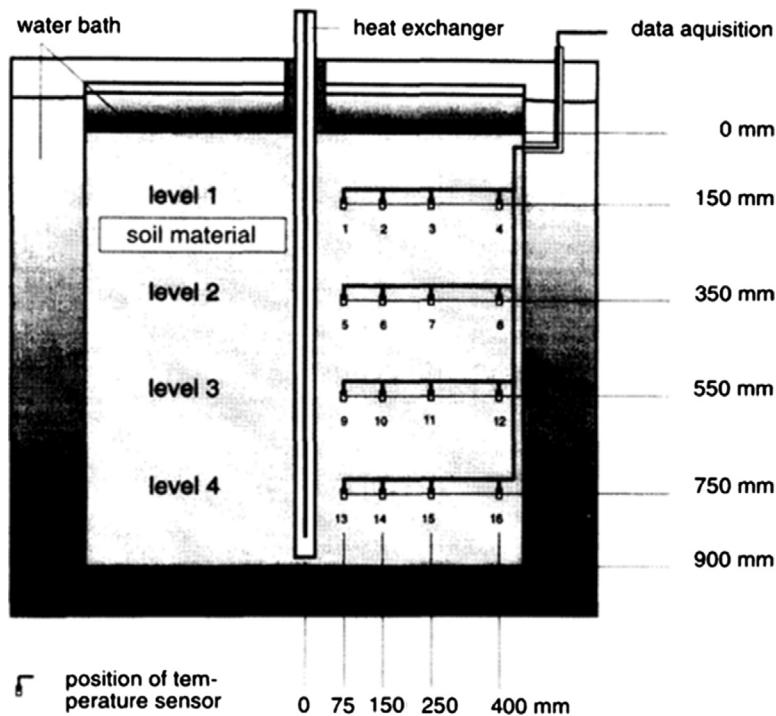


Fig. 9. Setup of the laboratory experiment for determining of heat and moisture migration in soil (Reuss et al., 1997).

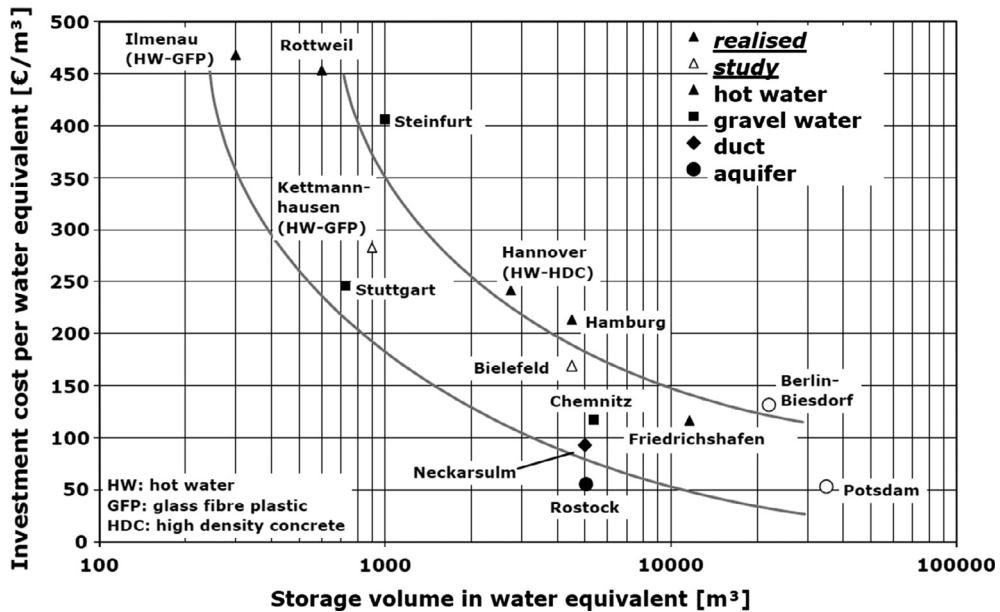


Fig. 10. Investment costs of seasonal heat stores (including design, without VAT) (Schmidt et al., 2003).

additional equipment, such as a heat pump, to upgrade the temperature level to satisfy the required heat load. These extra inputs also increase the total investment cost.

3. Latent heat storage

3.1. Materials research on PCMs

Latent heat storage (LTS) can offer higher energy densities than sensible storage and is considered to be an efficient energy-storing option. Phase change materials (PCMs) are

used in this storage type, and a classification of the materials is listed in Fig. 11.

PCMs undergo phase changing processes by absorbing and releasing heat in the form of latent heat of fusion without the temperature changing in each period. The phase changing temperatures of PCMs differ across a wide range, making them applicable for various situations.

Extensive investigations and improvements in PCMs have been made worldwide. The PCM candidates for storage purposes are $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, paraffins, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, PEG, etc. Veerappan

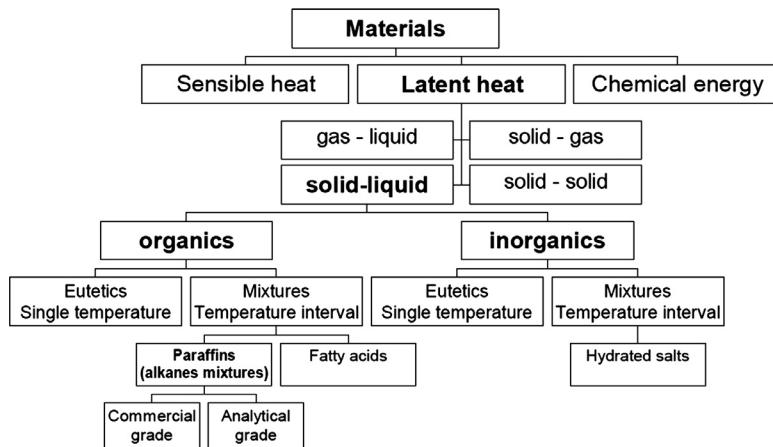


Fig. 11. Classification of energy storage materials for latent heat storage (Streicher, 2008).

et al. (2009) investigated the characteristics of five spherical PCMs: capric/lauric acid, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, n-octadecane, n-hexadecane and n-eicosane. The results indicated that $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ performed excellent in terms of solidification and melting rate. Fukai et al. (2003) inserted carbon-fibre brushes on the shell side of a heat exchanger in order to enhance the thermal conductivity in a PCM so that the charging and discharging rates increased by 10–20% and 30%, respectively. Zhang et al. (2012) used expanded graphite to absorb liquid paraffin. The new composite resulted in a reduction in charging duration compared with using paraffin only.

There are several review papers that summarised previous work on phase change materials (Farid et al., 2004; Kenisarin and Mahkamov, 2007; Sharma et al., 2009; Zalba et al., 2003), heat transfer and phase change problem formulation (Agyenim et al., 2010), and thermal conductivity enhancement methods (Fan and Khodadadi, 2011; Liu et al., 2012). In addition, information about PCMs for cold thermal energy storage (less than 20 °C) has been compiled by Oró et al. (2012), whereas Murat (2010) reviewed PCMs in a temperature range from 120 to 1000 °C to be used in solar heat storage. Cabeza et al. (2011) and Zhou et al. (2012) presented reviews of PCM thermal energy storage studies in the specific field of building applications. The classification of materials and problems, as well as possible solutions during reaction phases, have been discussed and analysed. Moreover, a summarisation of the present state of mathematical modelling of latent heat thermal energy storage systems using PCMs was given by Verma et al. (2008). Both the first and second (exergy) laws of thermodynamics were analysed.

A comparison of the advantages and disadvantages of organic and inorganic materials is shown in Table 4 (Zalba et al., 2003). Organic materials can be further classified into paraffins and non-paraffins. They have the favourable characteristics of being non-corrosive and having chemical and thermal stability. Congruent melting and good nucleating properties also make organic materials an attractive option. However, the low phase change enthalpy, thermal

conductivity and flammability are the main disadvantages of this type of material. Inorganic materials include salt hydrates and metallic materials. They have higher phase change enthalpies and relatively low prices compared to organic compounds. However, the undesirable properties, such as subcooling and corrosion, will severely affect the phase change process. Nucleation agents are necessary to avoid phase segregation, which achieves better thermal stability.

Given the aforementioned reviews of specific phase changing materials, more emphasis will be put on the prototypes and projects for seasonal thermal energy storage in this article.

3.2. Prototypes and projects of PCM thermal energy storage

In past studies and projects, latent heat storage was usually implemented with construction in a passive way. PCMs are frequently mixed with other construction materials, such as concrete, or used alone to play a role in building envelopes (walls, ceilings and floors). Zhang et al. (2007) reviewed the relevant studies of PCM-impregnated materials in building envelopes. In greenhouse applications, north wall storage incorporated with PCMs is the most common technology for increasing the indoor temperature (Berroug et al., 2011). However, most of the passive applications are not highly controllable and have low solar fractions, so they are more favourable for and limited to short-term storage.

For seasonal storage purposes, there seems to be more potential in active storage, which is combined with a solar collector system. Several applications in agriculture greenhouses (Benli and Durmuş, 2009; Öztürk, 2005) (more examples listed in Table 5) and heat pumps have been documented. Qi et al. (2008) simulated the performance of a solar heat pump heating system with seasonal latent heat thermal storage (SHPH-SLHTS) and viewed that as a very promising energy-saving technology. An experimental evaluation of seasonal latent heat storage was performed for the heating system of a 180-m² greenhouse located in

Table 4

Comparison of organic and inorganic materials for heat storage (Zalba et al., 2003).

Organics	Inorganics
<i>Advantages</i>	Greater phase change enthalpy
No corrosives	
Low or none undercooling	
Chemical and thermal stability	
<i>Disadvantages</i>	
Lower phase change enthalpy	Undercooling
Low thermal conductivity	Corrosion
Inflammability	Phase separation
	Phase segregation, lack of thermal stability

Turkey (Öztürk, 2005). This system was composed of five main parts (as shown in Fig. 12): flat plate solar air collectors, a latent heat storage unit, an experimental greenhouse, a heat transfer unit and a data acquisition system. The latent heat storage unit was a cylindrical steel tank filled with 6000 kg of paraffin wax as the phase change material. The system reached an average efficiency of 40.4% for net energy and 4.2% for net exergy.

Esen investigated a solar powered heat pump system that was connected to a cylindrical tank filled with 1090 kg $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as the PCM (Esen, 2000). The experimental set-up (as seen in Fig. 13) was used to supply heat for floor heating of a 75-m² area of a laboratory building in Turkey. When the sunshine was abundant and space heating was required at the same time, the collected heat from the solar collector was first injected into the storage tank and then used as a heat source for the water-source evaporator in the heat pump. When solar radiation was not available, the latent heat storage tank served as a heat supplier for the heat pump system. The ratio of E_{pcm}/Q (energy content of PCM/monthly total space heating load) was analysed based on the experimental outcomes. It was also mentioned that, to obtain the maximum energy that PCM could provide, insufficient isolation, which would lead to the problem of incomplete melting, should be noted.

A project using a ground-source heat pump heating system with a latent heat thermal storage tank, used for space heating in a 30-m² glass greenhouse, was investigated in Turkey (as shown in Fig. 14, Benli, 2011). R-22 was chosen as the refrigerant that cycled in the horizontal ground heat exchanger loop with a length of 246 m, and 300 kg calcium

Table 5

Examples of PCM storage applications in greenhouses.

Storage medium	Heat of fusion (kJ/kg)	Melting temp (°C)	Location	Area (m ²)	Mass of used (kg)	Performance
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	190	29	Nice, France (Jaffrin and Cadier, 1982)	500	13,500	Cover 75% of heating needs with outdoor conditions 8.4 °C and 7.2 °C in Dec. and Jan
			Rosignano, Italy (Balducci, 1985)	200	2800	Satisfy 22% of the thermal needs in winter
			Canberra, Australia (Brandstetter, 1987)	20	100	Raise the indoor temp. by 2–3 °C compared to outdoor (6–8 °C in July and June, 24 h average)
Paraffin wax	173.6	48–60	Turkey (Öztürk, 2005)	180	6000	Average net energy efficiency: 40.4%

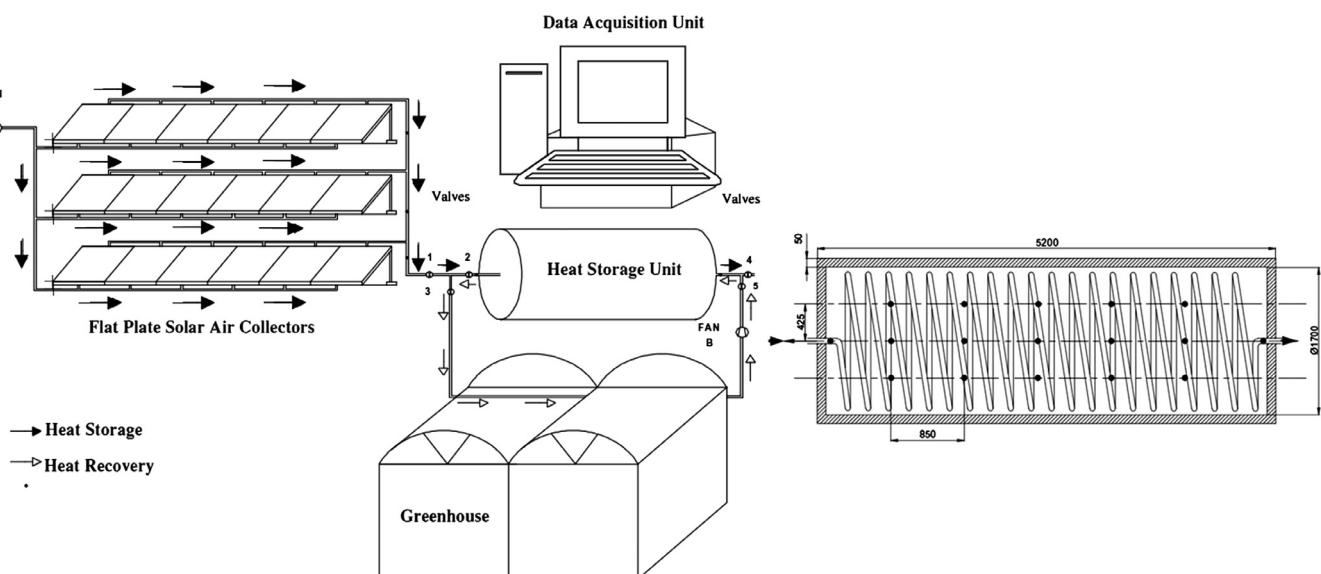


Fig. 12. Scheme for energy storage with paraffin wax in a greenhouse, Turkey (Öztürk, 2005).

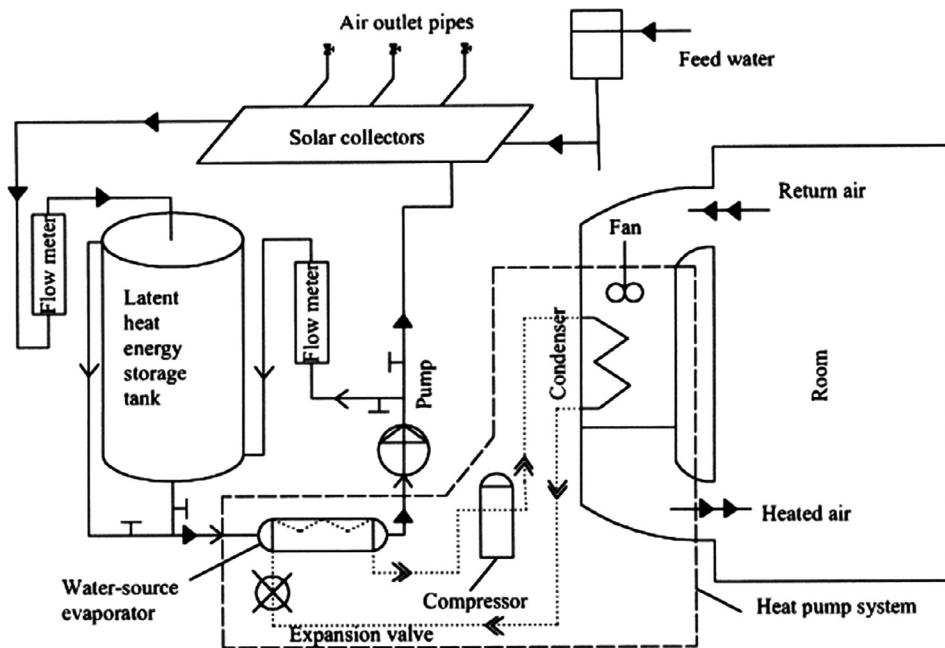


Fig. 13. Solar assisted heat pump system with latent heat storage tank using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Esen, 2000).

chloride hexahydrate was used as the phase change material. Solar radiation and thermal energy from the heat pump provided heat to the indoor air and the PCM storage unit. According to the results obtained from October to May in the heating seasons of 2005 and 2006, the COP (coefficient of performance) of the ground-source heat pump varied from 2.3 to 3.8, and the combined COP of

the whole system was 2–3.5. It was noted that PCM storage contributed to the rational heat distribution in the greenhouse due to its nearly constant phase changing temperature.

The works of five PCM-related projects conducted based on Subtask C, IEA-SHC Task 32, are summarised in Table 6. Among them, only one project (Technical

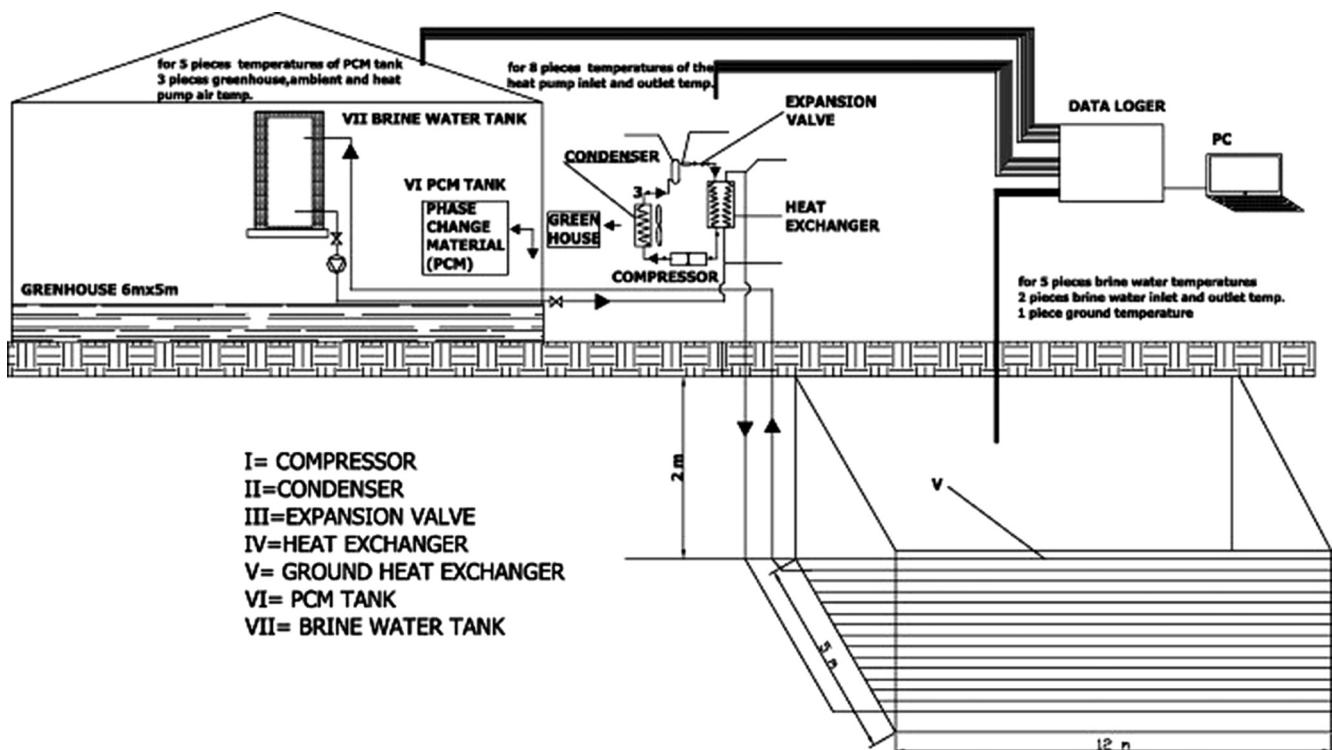


Fig. 14. Main components and schematic of the HGSHP (Benli, 2011).

Table 6
Comparison of the stores with PCM material in IEA SHC Task32 (Streicher, 2008).

Parameter	DTU	LIeida	HEIG-VD	TU Graz	TU Graz
Type of technology	Seasonal storage with subcooled	Macroencapsulated PCM in solar combistore	Macroencapsulated PCM in solar combistore	Macroencapsulated PCM in store for boiler	Immersed heat exchanger in PCM store
Storage materials weight: in kg	Na(CH_3COO) \cdot 3H ₂ O: 60	Na(CH_3COO) \cdot 3H ₂ O + graphite: 4.2	Na(CH_3COO) \cdot 3H ₂ O + graphite: 90	Na(CH_3COO) \cdot 3H ₂ O + graphite: 13.7	Na(CH_3COO) \cdot 3H ₂ O: 45 Water: 0
		Water: 140	Water: 710	Water: 20.8	
Temperature difference in tank	35/70 °C	20/70 °C	25/85 °C	50/70 °C	50/70 °C
Floor space required for prototype	1.3 m ²	0.25 m ²	1.8 m ²	0.4 m ²	0.2 m ²
Energy density of material (NRJ4.1) in kW h/m ³ (ratio to water)	128 (3.2)	56 (0.97)	Water 69,7 SAT 81.2 (1.16) Paraffin RT27 58.3 (0.84)	85 (3.7)	103 (4.44)
Energy density of prototype – heat (NRJ4.2) in kW h/m ³ (ratio to water)	10.9 (0.3)	57 (0.98)	70 (1.0)	40 (1.7)	76 (3.3)
Energy density of material in kW h/m ³ (ratio to water, 15/35 °C)			Water 23.2 Paraffin RT27 57 (2.45)		
Energy density of material in kW h/m ³ (NRJ4.2) (ratio to water, 50/70 °C)			Water 23.2 SAT 51.4 (2.21)		
Charge rate in kW			Auxiliary 20	0.5–1	5–20
Discharge rate in kW			DHW around 30	0.5–1	5–20
Estimated size for 70 kW h in m ³ (energy ratio to water)	2.8 (0.6)	1.2 (1)	1 (1)	1.75 (1.7)	0.92 (3.0)
Estimated size for 1000 kW h in m ³ (energy density ratio to water)	17 (1.4)	17.5 (1)	14.3 (1)	25 (1.7)	13 (3.3)

SAT = sodium acetate trihydrate.

University of Denmark) theoretically proved the possibility of achieving a 100% solar fraction using subcooled liquid PCM for long-term heat storage. Nevertheless, this system might be very complicated to realise because of the requirements that several stores must insulate each other, and a reliable mechanism must be found to activate crystallisation. Furthermore, the report noted that such a seasonal storage was used only once (or a slightly greater number of times), so the investment cost was a key factor to consider. For the rest of the projects, seasonal simulations of the system were performed, and the results were not as good as expected. There appeared to be no significant improvement of PCM stores compared to conventional water stores. According to the suggestions proposed by the task participants, screenings for better PCMs with higher heats of fusion, advancing the storage concepts to attain a higher PCM fraction and a high heat transfer rate should be addressed in future work.

4. Chemical storage

Chemical storage has distinctive advantages of high energy storage and low heat losses over other storage technologies and is regarded as the most promising alternative. The storage volume for 34 m³ of water equivalent (70 °C temperature increase) is only 1 m³ by means of chemical storage (Hadorn, 2008), and Fig. 15 illustrates a comparison of the energy densities among high energy storage methods. Another attractive feature of chemical storage lies in its capability to conserve energy at ambient temperature as long as desired without heat losses. With the above-mentioned merits, chemical storage has become a widely researched technology for seasonal energy storage.

Chemical storage can be separated into chemical reaction and thermochemical sorption storage (Bales, 2005). The principle of chemical reaction is based on the reversible reaction between two substances, A and B, with endothermic decomposition and exothermic synthesis process. A and B can be stored separately by sealing the connection between them during the storage period. Given that the sensible heat effect is negligible when compared with the reaction heat, there are no concerns about heat losses. The sorption storage process includes absorption and adsorption. In the adsorption process, gas bonds to the surface of a solid without creating a new material, while a new compound is formed in the absorption process.

Currently, the studies on chemical storage are at the theoretical and laboratory testing stages, mostly on fundamental materials, modelling and working approaches.

4.1. Materials study

The reaction material is one of the key elements of an entire storage system and should meet criteria such as high storage density, high thermal conductivity, suitable permeability, high uptake of the working pairs, low regeneration temperature for achieving high solar fractions, appropriate operating pressure, long-term stability, low cost and environmental sustainability. Many research groups have done a lot to seek well-behaved working pairs. Abundant materials, such as metal chlorides, metal hydrides and metal oxides, are considered to be promising materials.

Working couples for solid/gas adsorption, gas/liquid absorption and chemical reaction with thermal energy storage potential are listed in Table 7. It is noteworthy that the index “realisation potential” is a comprehensive measure

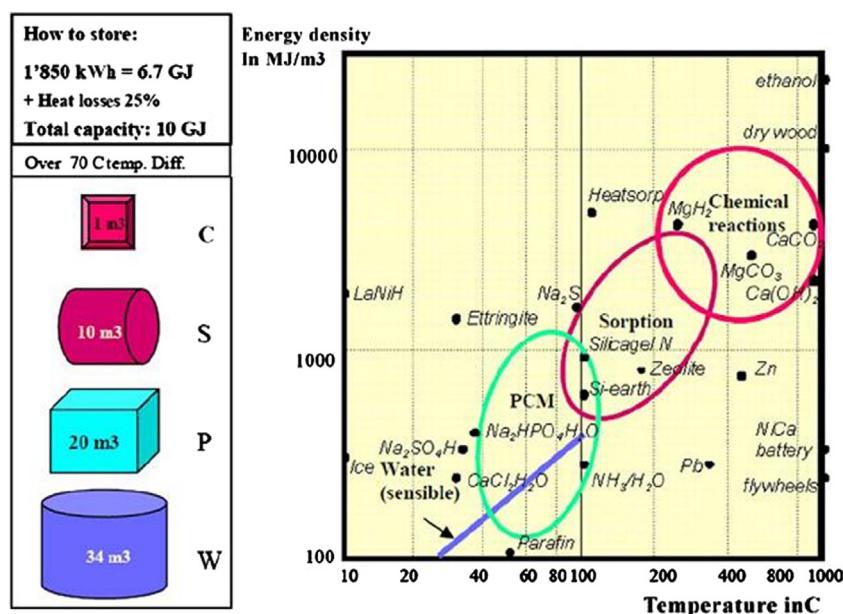


Fig. 15. Energy densities of high energy storage methods (N'Tsoukpo et al., 2009).

Table 7
Potential materials for thermal energy storage.

Material and reaction			Energy storage density (kW h/m ³)	Reaction enthalpy (kJ/mol)	Reaction entropy (J/(mol K))	Turnover temperature (°C)	Realisation potential	Remark	Reference	
	C	A	B							
Pure Material	Solid/Gas	MgSO ₄ ·7H ₂ O	MgSO ₄	H ₂ O	663 (Bertsch et al., 2009); 778	411	1041	122	9.5	Hydrate slowly; Low power density (Visscher et al., 2004)
		MgSO ₄ ·7H ₂ O	MgSO ₄ ·1H ₂ O	H ₂ O	639	336	887	105	1.1	(Visscher et al., 2004)
		MgSO ₄ ·H ₂ O	MgSO ₄	H ₂ O	361	75	154	216	2.7	(Visscher et al., 2004)
		MgCl ₂ ·H ₂ O	MgCl ₂ ·H ₂ O	H ₂ O	689	323	—	178	0.22	Corrosive (Visscher et al., 2004)
		CaCl ₂ ·2H ₂ O	CaCl ₂ ·1H ₂ O	H ₂ O	167	47	104	174	1.1	(Visscher et al., 2004)
		BaCl ₂ ·8NH ₃	BaCl ₂	NH ₃		382.5	232.4	70		(Stitou et al., 2012)
		CaSO ₄ ·2H ₂ O	CaSO ₄	H ₂ O	389	105	290	89	4.3	(Visscher et al., 2004)
		Na ₂ S·5H ₂ O	Na ₂ S·2H ₂ O	H ₂ O	Heating: 780; Cooling: 510	189	—		—	Corrosive; Operate under high vacuum (Boer et al., 2004; N'Tsoukpoe et al., 2009)
Gas/ Liquid		Na ₂ S·2H ₂ O	Na ₂ S·0.5H ₂ O	H ₂ O		111	—		—	(Boer et al., 2004)
		SrBr ₂ ·6H ₂ O	SrBr ₂ ·H ₂ O	H ₂ O	Heating: 250–400; Cooling: 150–240	67.4	—	70–80	—	(Lahmadi et al., 2006)
		LiCl/H ₂ O			Cooling: 253 (Climate well); 438 ^a (44.3 wt.%)	—	—	65.6 (44.3 wt.%)	—	Expensive (Liu et al., 2011; N'Tsoukpoe et al., 2009)
		LiBr/H ₂ O			180–300; 2019 ^a (57.8 wt.%)	—	—	72 (57.8 wt.%)	—	(N'Tsoukpoe et al., 2009; Liu et al., 2011)
Chemical reaction		NaOH/H ₂ O			1558 ^a (34.8 wt.%)	—	—	50 (34.8 wt.%)	—	Corrosive; Crystallize at high concentration (Weber and Dorer, 2008)
		CaCl ₂ /H ₂ O			914 ^a (39.8 wt.%)	—	—	44.8 (39.8 wt.%)	—	(Liu et al., 2011)
		NH ₃ /H ₂ O			1317 ^a (10 wt.%)	—	—	186.6 (10 wt.%)	—	Operate at high pressure (Liu et al., 2011)
		Ca(OH) ₂	CaO	H ₂ O	872 (Visscher et al., 2004)	104.4	135 (Visscher et al., 2004)	505	—	(Schaube et al., 2011)
Mixture		MnO ₂	0.5Mn ₂ O ₃	0.25O ₂	—	42	—	530	—	(Schaube et al., 2011)
		Mg(OH) ₂	MgO	H ₂ O	889 (Visscher et al., 2004)	81	146 (Visscher et al., 2004)	350; 266 (Visscher et al., 2004)	—	(Ishitobi et al., 2013)
		ZnCO ₃	ZnO	CO ₂	694	71	175	133	1.6	(Visscher et al., 2004)
		SiO ₂	Si	O ₂	10,528	859	198	150 (+ hydrofluoric acid)	9	(Visscher et al., 2004)
		Fe(OH) ₂	FeO	H ₂ O	611	58	137	150	4.8	(Visscher et al., 2004)
		FeCO ₃	FeO	CO ₂	722	81	178.3	180	6.3	(Visscher et al., 2004)
		NH ₃	0.5N ₂	1.5H ₂	67 kJ/mol	—	—	400–500	—	(Luo, 2010)
		20 wt% MgSO ₄ and 80 wt% MgCl ₂	1590 ^a , ^b	—	—	130	—		(Posern and Kaps, 2010)	
		6.8 wt% LiCl/	—	—	—	280	—		(Ryu et al., 2008)	

^a kJ/kg.^b Measured by calorimetry at 30 °C/85% RH.

that takes the following characteristics into account (Visscher and Veldhuis, 2005):

1. Energy storage density (thermodynamic).
2. Reactor temperature for storage process.
3. Corrosiveness during storage and/or reaction.
4. Environmental impact and toxicity of the material.
5. Cost of the material (abundance, ability to be mined).
6. Number of material components during synthesis reaction.
7. Reactor pressure.

Based on the above selection criterion, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, SiO_2 , FeCO_3 , Fe(OH)_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are considered to be the top five candidates.

4.1.1. Absorption

For an absorption system, the storage energy density is closely linked with the concentration of the solution. The performance and thermodynamic characteristics of several common absorption couples, such as $\text{LiCl}/\text{H}_2\text{O}$, $\text{NaOH}/\text{H}_2\text{O}$, $\text{CaCl}_2/\text{H}_2\text{O}$, and $\text{LiBr}/\text{H}_2\text{O}$, have been investigated in previous studies (shown in Tables 7 and 8).

According to Liu et al.'s study (2011) on seven absorption couples ($\text{CaCl}_2/\text{H}_2\text{O}$, Glycerin/ H_2O , $\text{KOH}/\text{H}_2\text{O}$, $\text{LiBr}/\text{H}_2\text{O}$, $\text{LiCl}/\text{H}_2\text{O}$, $\text{NaOH}/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{NH}_3$) (listed in Table 8), $\text{LiCl}/\text{H}_2\text{O}$ performs best in terms of storage capacity and efficiency, but its high price might limit its further application in seasonal energy storage systems. $\text{CaCl}_2/\text{H}_2\text{O}$ is a suitable couple in terms of its cost and the appropriate regeneration temperature, but its storage capacity is low. An innovative concept of allowing the solution to reach the crystallisation point during the process was put forward in the study, and an experimental comparison was made. It was found that crystals inside the tanks contributed to the system storage capacity but this phenome-

non would increase the complexity of the system. In addition, the static calculation showed that “the storage capacity increases with the temperature of evaporation and the temperature of the solution before absorption but decreases with the temperature of absorption”.

4.1.2. Adsorption

The energy storage density of a solid/gas couple is determined by several factors, such as the density of the salt, porosity of the composite and properties of the additive. Hydrates and ammoniates can be employed in adsorption processes for seasonal thermal energy storage (listed in Table 8).

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is a potential alternative for seasonal storage (Visscher and Veldhuis, 2005) because of its high energy density (theoretically, 663 kW h/m^3 heptahydrate) (Bertsch et al. 2009) and has attracted lots of interest (Balasubramanian et al., 2010; Bales, 2005; Essen et al., 2006; Hongois et al., 2011; Zondag et al.). MgSO_4 can be dehydrated at temperatures below 150°C , which is achievable by solar thermal collectors. However, some studies show that the hydration speed of pure MgSO_4 decreases strongly at higher temperatures (Zondag et al.). At 40°C , which is the temperature required for space heating, MgSO_4 cannot uptake as much water as supposed, which means that it is not able to release all the stored heat under practical conditions (Essen et al., 2006). Zondag et al. (2008) proposed that the speed of the hydration reaction might significantly increase by operating the reaction at a low pressure. In such conditions, the inert gases in the system can be removed, and the pressure drop between water and salt can be reduced. Essen et al. (2009a,b) conducted hydration experiments under low pressure conditions with two sulphates ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and two chlorides ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). The dehydration TGA (thermo gravimetric analysis) curves during the

Table 8
Evaluation points for the choice of the absorption couples. (Liu et al., 2009, 2011).

	$\text{CaCl}_2/\text{H}_2\text{O}$	Glycerin/ H_2O	$\text{KOH}/\text{H}_2\text{O}$	$\text{LiBr}/\text{H}_2\text{O}$	$\text{LiCl}/\text{H}_2\text{O}$	$\text{NaOH}/\text{H}_2\text{O}$	$\text{NH}_3/\text{H}_2\text{O}$
<i>No crystal</i>							
Mass fraction of absorbent after desorption (%)	39.8	90.0	50.8	58.8	44.3	33.5	0
Storage capacity (kJ/kg material)	914	193	2618	2019	4387	1558	1390
Temperature required of desorption [$^\circ\text{C}$]	44.8	53.0	63	72	65.6	50	186.6
Volume of solution [$\text{m}^3/1000 \text{ kW h}$]	8.4	20.0	3.16	3.2	2.5	6.5	9.6
Pressure absolute [kPa]	1.2–4.2	1.2–4.2	1.2–4.2	1.2–4.2	1.2–4.2	1.2–4.2	615–1167
Efficiency	0.909	0.545	0.83	0.85	0.95	0.75	0.658
<i>20% solution 80% crystal</i>							
Mass fraction of absorbent after desorption (%)	48.5	–	58.8	68.3	52.1	37.8	–
Storage capacity (kJ/kg material)	2023	–	3299	2603	5133	2382	–
Temperature required of desorption [$^\circ\text{C}$]	54.2	–	84	93.3	77.6	57	–
Volume of solution [$\text{m}^3/1000 \text{ kW h}$]	3.8	–	2.5	2.5	2.1	4.3	–
Pressure absolute [kPa]	1.2–4.2	–	1.2–4.2	1.2–4.2	1.2–4.2	1.2–4.2	–
Efficiency	0.885	–	0.856	0.835	0.923	0.767	–
Price [Euro/ton] (purity $\geq 99\%$)	350	500	1200	5000	6000	3000	400

Operation condition: – temperature of condenser (ambient temperature during the summer), $T_c = 30^\circ\text{C}$; – minimum temperature of heat production, $T_a = 20^\circ\text{C}$; – temperature of the storage tanks before the absorption phase, $T_s = 10^\circ\text{C}$; – temperature of the evaporator (temperature of the geothermal heat), $T_e = 10^\circ\text{C}$.

preparation process were presented, and the initial materials for the hydration experiments were $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ and CaCl_2 . The results confirmed the previous finding that low pressure improved water vapour transport in the system. At the same time, it was also found that chlorides presented a larger temperature lift than sulphates (maximum ΔT : $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, 19 °C; CaCl_2 , 11 °C; $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, 4 °C; $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, 1–2 °C) when the reactor and evaporator temperatures were set at 50 and 10 °C, respectively. Unfortunately, the hygroscopic chlorides would form a gel-like material after hydration, which was unfavourable.

In addition to hydrates, ammoniates, such as $\text{BaCl}_2 \cdot 8\text{NH}_3$ and $\text{MnCl}_2 \cdot 6\text{NH}_3$, are well-performing alternatives in the adsorption process. However, because of the safety concerns of using ammonia in a large-scale plant, hydrates that react with water are more preferable for use in energy storage applications.

Another type of thermochemical heat storage material is composites, e.g., salt mixtures and porous materials impregnated with hygroscopic salt hydrates. Salt hydrate mixtures of $\text{MgSO}_4/\text{MgCl}_2$ and $\text{MgSO}_4/\text{LiCl}$ impregnated in porous materials (glass pellets/attapulgite granulates) were studied (Posern and Kaps, 2009, 2010). The results showed that mixing with a lower deliquescence humidity salt (such as chlorides) could increase the capacity for condensation and the sorption heat. Porous binders with high thermal conductivities are often used to improve heat and mass transfer in the reactant. Some are inert materials that do not participate in the reaction, such as expanded graphite, activated carbon or metal foam, while others, such as zeolite, do interact. Hongois et al. (2011) developed a $\text{MgSO}_4/\text{zeolite}$ composite by impregnating MgSO_4 in a zeolite matrix in order to disperse the MgSO_4 for better reaction kinetics but at the cost of energy density. They used micro-calorimetry measurements to prove that the energy density of this composite remained at the same level after three reaction cycles.

4.1.3. Chemical reaction

Apart from the aforementioned sorption storage process, chemical reaction is another interesting method for thermal energy storage. It involves reversible decomposition and synthesis reactions: $\text{C} + \text{heat} \leftrightarrow \text{A} + \text{B}$. Candidates, such as $\text{Ca}(\text{OH})_2$ (Fujii et al., 1985; Schabe et al., 2011, 2012) and $\text{Mg}(\text{OH})_2$ (Ervin, 1977), have been studied in previous research. Those reactions have a common characteristic of high operating temperature (normally higher than 300 °C), so they should usually be used to store high grade heat. No available material is suitable for low-temperature solar applications. One of the solutions for reducing the operation temperature is to add a salt with a lower reaction temperature to the pure one, e.g., LiCl-modified $\text{Mg}(\text{OH})_2$ (Ryu et al., 2008; Ishitobi et al., 2013). It was recorded in the literature that the dehydration temperature of the new mixture dropped to 280 °C from 350 °C when $\text{Mg}(\text{OH})_2$ was used alone. The high storage capacity of

the materials and the high reaction enthalpy is worthy of further study on the chemical reaction storage.

4.2. Existing prototypes and projects

Over the past few years, significant advances have been made not only in material investigation but also in demonstrative prototypes for chemical storage technologies. Relevant experimental results showed the feasibility and great potential, but in the meantime, they unveiled the problems and barriers that researchers need to overcome before going further.

In the following section, descriptions of several projects classified by different reaction processes are given.

4.2.1. Absorption storage prototypes

A prototype of a single-stage closed sorption system with a $\text{NaOH}/\text{H}_2\text{O}$ base was tested (Weber and Dorer, 2008) in Switzerland for long-term heat storage. The results demonstrated the feasibility of the system and showed that the heat storage density was approximately three times higher than water storage for hot water supply (at 70 °C) and six times higher for space heating (at 40 °C). A double-stage concept was also proposed to lower the regeneration temperature during the charging process by adding regenerator 2, condenser 2 and heat exchanger (as shown in Fig. 16). During the charging process, condenser 2 absorbed the vapour from regenerator 2, which was diluted, and then the intermediate concentration solution returned to regenerator 1. Because it had a lower pressure than regenerator 1, the solution from regenerator 2 could increase its concentration at a lower temperature (95 °C), while 150 °C was required for heat supply in a single-stage system (solution concentration of 72 wt.%). Such a double-stage system was more complex, and the charging efficiency would be partially compromised because of the lower supply temperature level and the increased number of transfer processes.

A Watergy Thermo Chemical Storage project was developed in Berlin (Buchholz et al., 2009). It offered an economical absorption system for seasonal heat storage, and the schematic diagram of the reaction process is shown in Fig. 17. MgCl_2 solution was used and represented an energy density of 267 kW h/m³. During the summer, the salt solution was heated by solar radiation and then transferred from the collector to the thermal storage tank. In the meantime, the heated film in the collector increased the temperature of the inside air. The air, together with the water evaporated from the solution, exchanged heat with a colder heat exchanger outside the collector. After condensation occurred, the cooled and dehumidified air went back to the collector, and the released heat from the condensation process was transferred to an open cooling water circuit, which was connected to the storage unit, offering a heat supplement at night or for domestic hot water use. During the winter, air could be heated by exchanging heat with the hot solution in the air–water heat exchanger.

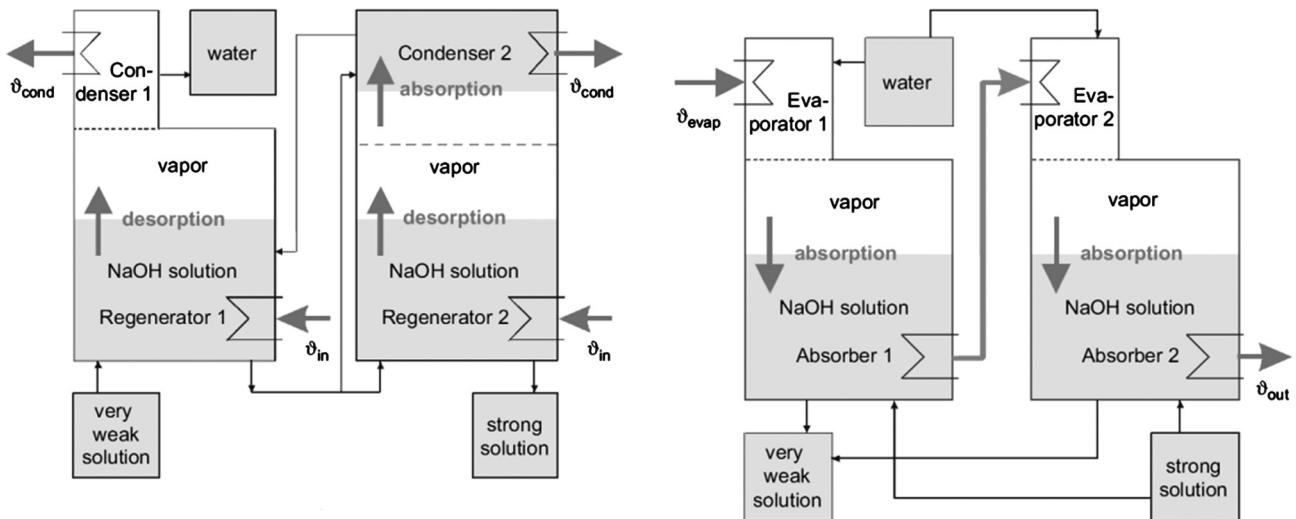


Fig. 16. Operation principle of double-stage closed absorption process (a) charging process, (b) discharging process (Weber and Dorer, 2008).

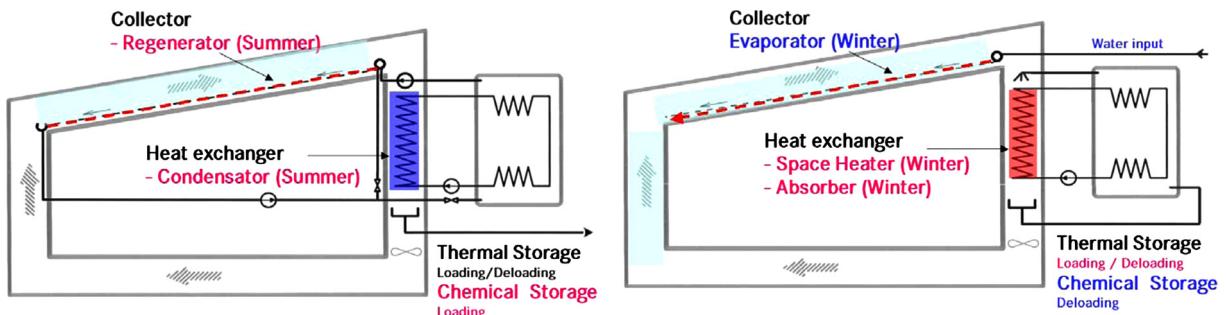


Fig. 17. Schematic diagram of Watergy Thermo Chemical Storage process (Buchholz et al., 2009).

The idea of storing energy in an absorption process, especially for cooling purposes, has been exploited for decades.

The thermo-chemical accumulator (TCA) was an absorption process that involved three phase processes (salt crystals, solution and vapour), and it was principally designed for cooling applications (Bales, 2008a). It had the advantages of a high energy storage density and good heat and mass transfers as the reaction occurred with the solution. According to laboratory test results, the storage energy density reached 253 kW h/m^3 for LiCl salt. This “closed three phase absorption” storage technology has been successfully commercialised by the Swedish company ClimateWell (2012) AB. There are no intentions to develop TCA technology as a pure heat storage system so far, and considering the high price of their chosen salt, alternative salts need to be found prior to implementation in seasonal storage applications.

4.2.2. Adsorption storage prototypes

4.2.2.1. Physisorption (Physical adsorption). Within the framework of the EU-project MODESTORE (Bales, 2008a), a prototype storage module using silica gel/H₂O was developed. It was a closed absorption system with an

adsorber and a spiral heat exchanger in the upper part (shown in Fig. 18). In the lower part, there was a heat exchanger serving as the evaporator and condenser.

The test results showed that the temperature increase for the silica gel/H₂O couple was only sufficient when the water content of the silica gel was below 13%, while the water content must be controlled above 3% in order to guarantee the desorption process under the temperature provided by flat plate solar collectors and available heat sinks. For the above reasons, the material had to be operated in the water content range of 3–13%, and as a result, the material energy density in the experimental prototype was only 50 kW h/m^3 , which was far lower than expected and even less than the value of water storage (70 kW h/m^3 for a temperature difference of 25–85 °C). This study indicated that silica gel/H₂O couples were not suitable for seasonal storage due to their low storage densities.

In another study called Monosorp (Bales, 2008a), zeolite honeycomb structures with a volume of 7.85 m^3 were designed and utilised in an open adsorption system. A small-scale demonstration plant was constructed and tested by the ITW (Institute of Thermodynamics and Thermal Engineering), University of Stuttgart (Germany) (Fig. 19). Its long-term sorption store was built into a

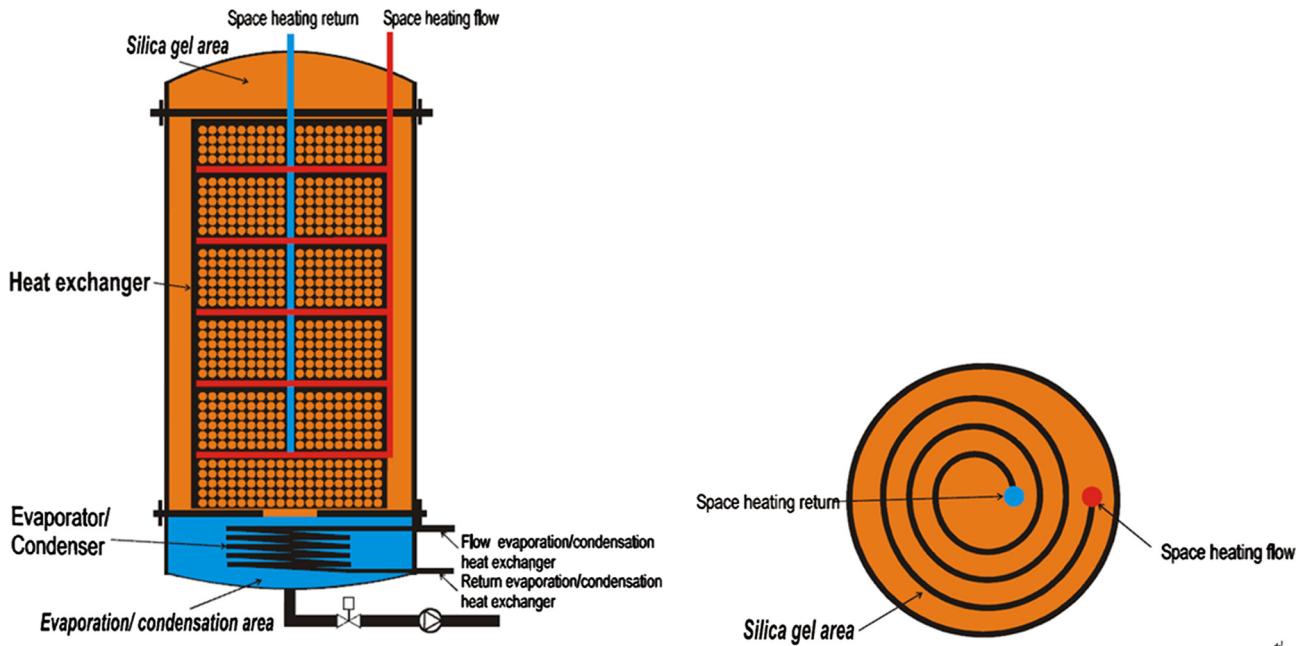


Fig. 18. Scheme of the 2nd generation prototype (Bales, 2008a).

mechanical ventilation system with inherent and efficient heat recovery. Because it was an open system, no vacuum component was required thus making it relatively simple and flexible. During the heat charging phase in the summer, excess solar heat was used to heat the air flow before it entered the storage unit to regenerate zeolite. During the discharging phase, when heat was needed, humid outdoor air was dried by the zeolite in the storage unit. The concurrent heat that was released was then transferred to the ventilation heat exchanger to heat the indoor air for further room heating purposes. The experimental results demonstrated the feasibility of this system under practical condi-

tions. The drawbacks of the system were the limited discharge rate, caused by the natural water content in the building, and the high regeneration temperature of above 150 °C, which makes this idea more challenging to be realised in large-scale applications.

Dicaire and Tezel (2011) conducted a series of adsorption experiments by using an activated alumina and zeolite 13× hybrid as the adsorbent inside a column (as shown in Fig. 20) and water as the adsorbate in order to characterise the factors that might influence the performance. The obtained results showed that flow rate did not significantly affect the performance during the regeneration and adsorption periods, whereas the relative humidity during regeneration greatly influenced the regeneration results. By cycling the experiments many times, the constant performance of the chosen adsorbent was confirmed.

Moreover, Jänenchen et al. (2004) modified zeolites and mesoporous materials by ion exchanging and impregnating them with hygroscopic salts in order to improve heat storage capacity.

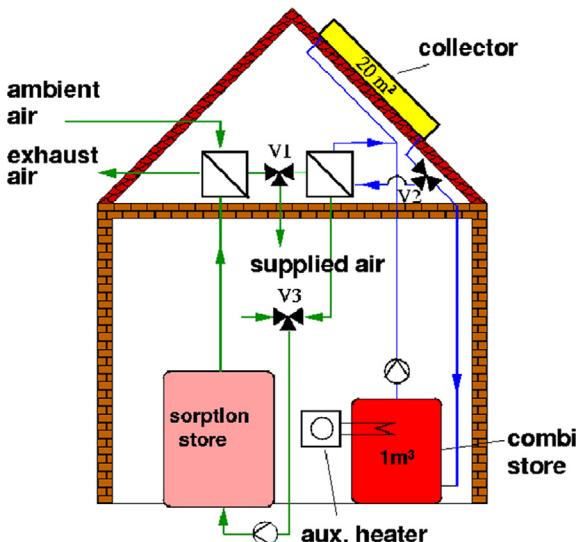


Fig. 19. Schematic sketch of a solar equipped residential building with a sorption store (Bales, 2008a,b).

4.2.3. Chemisorption (chemical adsorption) prototypes

A modular closed solid-sorption cooling with integrated thermal energy storage system was developed by the SWEAT (Salt Water Energy Accumulation and Transformation) project for residential and industrial applications (Boer et al., 2004). Na₂S/H₂O was chosen as the working pair, the regeneration temperature of which had an upper limit of 83 °C due to the eutectic melting point of the salt. To minimise the corrosion problem, vessels were made of stainless steel, and the external surface of the copper heat exchanger was coated with a zero-defect epoxy powder in order to prevent direct contact with Na₂S. The measured

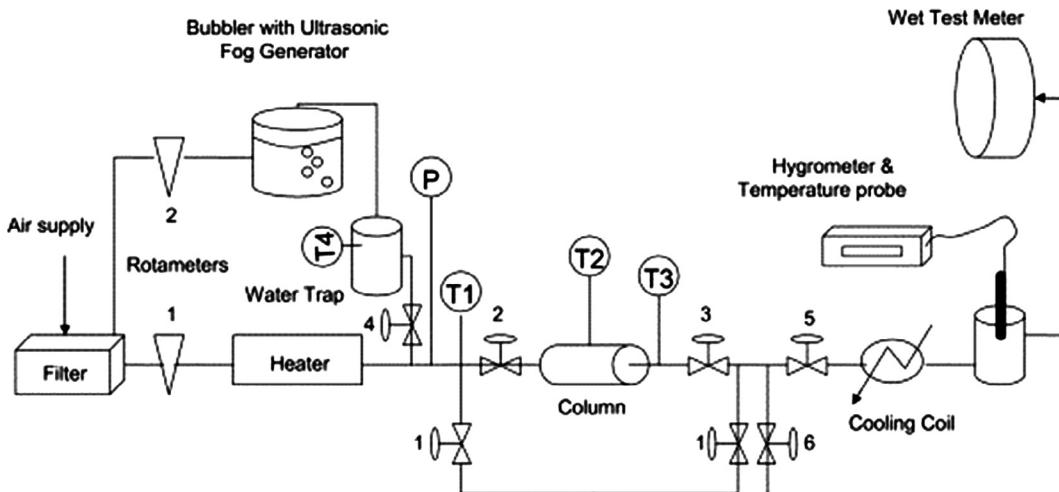


Fig. 20. Schematic diagram of a hybrid adsorbent thermal energy storage system (Dicaire and Tezel, 2011).

cold storage capacity of the SWEAT module was 7.6 MJ (2.1 kW h), and its cooling COP was 0.57, which is 85% of the theoretical maximum value. The obtained heat storage capacity efficiency was 0.84 with 13.3 MJ (3.7 kW h) heat in and 11.5 MJ (3.2 kW h) heat out. Those experimental values were in accordance with the theoretical values and proved that the Na₂S/H₂O couple had intrinsic long-term storage capacities for both heat and cold.

Mauran et al. (2008) designed and tested a chemical heat pump, the thermochemical process of which involved SrBr₂ (implemented with expanded natural graphite) as the reactant and H₂O as the refrigerant fluid. It allowed storage of 60 kW h at 70–80 °C with minimal loss over an indefinite duration and restituted these energy when needed for the floor of the house, either for heating in mid-season (60 kW h at 35 °C) or refreshing in the summer (40 kW h at 18 °C). The author also noted that the method of heat and mass transfer with low pressure (to reach a steady and continuous heat output) in the layers of the reactive composite should be improved. In their case, the heat and mass transfer problem constituted the main limitations of the reaction process, which led to the less than expected experimental results. High energy density and good permeability in porous media are contradictory parameters; hence, additives, such as expanded graphite and vermiculite, are commonly used to enhance the gas permeability and conductivity of the reactant (Michel et al., 2012) without causing side reactions at the same time.

In addition to the aforementioned prototype, there are other studies at the developmental stages of material investigations on chemisorption thermal energy storage systems.

Zondag et al. (2010) achieved a temperature increase of 20 °C at 12 mbar vapour pressure by using MgCl₂·6H₂O as the sorbent in an open sorption reactor and called MgCl₂·6H₂O a material with a large storage capacity. However, a suitable carrier was necessary in case the over-hydration phenomenon of the material occurred.

Other investigations of materials like MgSO₄ have been described in Section 4.1.2.

As noted by Li et al. (2013), a common drawback of conventional thermochemical sorption energy storage systems lies in the lower output temperatures of the released heat during the discharging process, which results from the low ambient temperature in winter. To upgrade the temperature level for the end user, an advanced dual-mode solid-gas thermochemical sorption energy storage system with a heat recovery process was proposed. This novel cycle consisted of two pairs of S/G reactors working at different temperature levels (as shown schematically in Fig. 21). The heating supply is assured by operating in different working modes according to different ambient temperatures, without heat recovery when the ambient temperature was relatively high and with heat recovery when the ambient temperature was low.

Some important achievements of IEA-SHC Task 32 are highlighted in Table 9, and comparisons of the key figures for materials and technologies are made. Four closed systems and one open system are included. The energy densities for the TCA technology, NaOH storage system and Monsorp project were 3.6, 3.6 and 2.3 times greater than that of water. The results obtained in the Modestore project indicated that silica gel was not suitable for seasonal storage.

4.2.4. Chemical reaction storage prototypes

In the previous section, several storage technologies were introduced, and their major goal is to store excess thermal energy in the summer for later low-temperature domestic use, such as space heating and hot water supplying. However, in regard to power generation applications where high temperatures and high reaction enthalpies are required, chemical reaction is the best choice.

Schaube et al. (2009, 2011, 2012) identified the suitability of the decomposition reactions of CaCO₃ and Ca(OH)₂. Calcium hydroxide appeared to be a promising candidate,

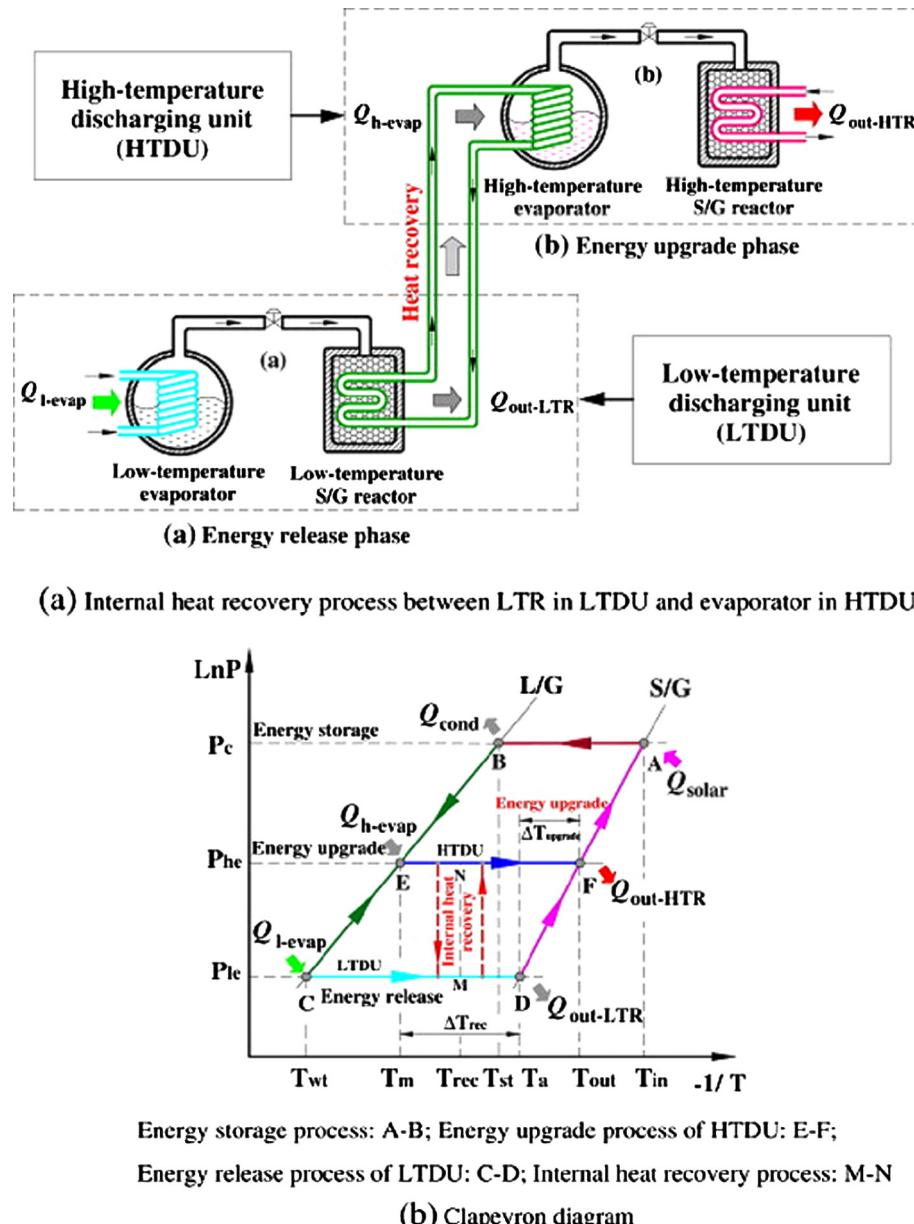


Fig. 21. Schematic diagram of advanced dual-mode solid–gas thermochemical sorption energy storage system with heat recovery process at SJTU, China (Li et al., 2013).

but its cycling stability and low thermal conductivity were the main problems that needed to be addressed. A mixture of nitrogen and steam was proposed as the heat transfer medium in order to improve the direct heat transfer inside the reactor. Thermodynamic and kinetic studies of $\text{Ca}(\text{OH})_2$ were conducted.

Azpiazu et al. (2003) analysed heat recovery from a thermal energy storage system based on the $\text{Ca}(\text{OH})_2/\text{CaO}$ cycle and concluded that carrying out one complete cycle at a higher dehydration temperature was beneficial to the total system reversibility.

Nevertheless, no research studies have so far been reported on chemical reaction storage with long-term durations. In light of the high storage capacity of the material

and the high reaction enthalpy, this option is worthy of further study.

4.3. Other relevant research

Abedin and Rosen (2012) compared the energies and exergies of several selected closed and open thermochemical energy storage projects. Based on their analyses of the existing prototypes, it was found that the overall exergy efficiencies were much lower than the energy efficiencies in both open and closed systems (9% and 50% for closed and 23% and 69% for open storage, respectively), which revealed that there was still a significant margin for reducing heat loss and improving efficiency.

Table 9

Comparison of key figures for materials and technologies for thermochemical and sorption stores studied in IEA-SHC Task 32 (Bales, 2008a).

Parameter	TCA80-100 °C	NaOH 95 °C test 150 °C calculated	Modestore 88 °C	SPF 180 °C	Monsorp 180 °C	ECN 150 °C
Type of technology	Closed three phase absorption	Closed two phase absorption	Closed adsorption	Closed adsorption	Open adsorption	Thermo-chemical
Cost of material	3600 €/m ³	250 €/m ³	4300 €/m ³	2–3000 €/m ³	2500–3500 ^a €/m ³	4870 €/m ³
Storage materials weight:	LiCl salt 54 kg Water 117 kg Steel 47 kg	NaOH 160 kg Water 160 kg	Silica gel 200 kg Water 30 kg Steel 100 kg Copper 50 kg	Zeolite 13 × 7 kg	Zeolite 4A 70 kg Steel 10 kg	MgSO ₄ ·7H ₂ O
Storage capacity for heat	35 kW h	8.9 kW h	13 kW h	1 kW h	12 kW h	–
Floor space required for prototype	0.46 m ²	2 m ²	0.4 m ²	0.09 m ²	0.4 m ²	–
Energy density of material (NRJ4.1) (ratio to water 25/85 °C) kW h/m ³	253 kW h/ m ³ (3.6)	250 kW h/m ³ (3.6)	50 kW h/ m ³ (0.71)	180 kW h/m ³ (~3)	160 kW h/ m ³ (2.3)	420 kW h/ m ³ (6.1)
Energy density of prototype (NRJ4.2) (ratio to water 25/85 °C) kW h/m ³	85 kW h/ m ³ (1.2)	5 kW h/m ³ (0.07)	33.3 kW h/ m ³ (0.48)	57.8 kW h/ m ³ (~1)	120 kW h/ m ³ (1.7)	–
Energy density of prototype – cold (ratio to water 7/17 °C)	54 kW h/ m ³ (4.7)	–	–	–	–	–
Charge rate	15 kW	1 kW	1.0–1.5 kW	–	2.0–2.5 kW	–
Discharge rate heating/cooling [kW]	8 kW	1 kW	0.5–1.0 kW	0.8 kW/1.8 kW	1.0–1.5 kW	–
Estimated size for 70 kW h (ratio to water 25/85 °C) m ³	0.64 m ³ (1.6)	1.3 m ³ (0.75)	1.7 m ³ (0.59)	1.2 m ³ (~1)	0.54 m ³ (1.9)	0.4 m ³ (2.5) ^b
Estimated size for 1000 kW h (ratio to water 25/85 °C) m ³	5.3 m ³ (2.7)	5 m ³ (2.9)	23 m ³ (0.62)	17 m ³ (~1)	7.7 m ³ (1.9)	5.6 m ³ (2.5) ^b

^a Cost for large quantity of extruded material is unknown and is estimated for zeolite 4A.^b Estimations are based on experimental storage density of ~420 kW h/m³ for reaction MgSO₄·6H₂O + heat ↔ MgSO₄·0.2H₂O + 5, 8H₂O.

A life cycle analysis (LCA) methodology was used to evaluate the environmental impacts of the solar thermal system SOLARSTORE, which included a solar heating unit and a thermochemical storage unit during its whole life cycle (Masruroh et al., 2006). The system emissions of CO₂, SO₂, C₂H₄ and phosphate were compared with the conventional solar heating system and a traditional fossil fuel based heating system. The results demonstrated that SOLARSTORE was a promising solution from an ecological aspect.

Although chemical storage has received more and more attention, there are seldom reports on its building scale application. Before being put into practice and commercialised, chemical storage needs to conquer several problems, including low overall efficiency, high cost, corrosion, swelling and clogging, long-term repeatability and stability. Additionally, exploring new materials that are advantageous in terms of storage density and power density is quite necessary.

5. Comparison of available options and prospects

From the storage mechanism aspect, sensible and latent heat storage are direct ways to store heat, whereas chemical storage is indirect by taking advantage of the endothermic and exothermic reaction processes between a pair of substances.

Table 10 provides a summary of the three storage concepts, including a comparison of each one's advantages and disadvantages. Based on the knowledge of the reviewed studies and relevant project performance, the author also suggests work to be concentrated on in the next step.

Sensible heat storage is a well-developed alternative for long-term/seasonal storage. The use of water, rock and ground as sensible heat storage media has been investigated deeply and has proven to be feasible for large-scale district heating. Water-based storage is suitable for residential applications, although it has a limit temperature for operation. A water tank is an easy and acceptable way to store heat. Stratification in a hot water heat store is essential so that layers with different temperature levels do not disturb each other. In recent years, UTES (including aquifer and ground/soil) has become a very popular choice among the sensible storage alternatives. They are relatively cheap in comparison with water tank storage, but careful geological investigations must be made during the pre-design phase to examine whether the site is suitable. The precise simulation of the underground conditions that influence the heat and mass transfers should be emphasised in future work in order to improve the storage efficiency. Furthermore, sensible heat storage systems are now often integrated with heat pump technology in real projects in order to upgrade the temperature level due to its long-term

Table 10

Comparison of the three available technologies for seasonal thermal energy storage.

	Sensible	Latent	Chemical
Storage Medium	Water, gravel, pebble, soil...	Organics, inorganics	Metal chlorides, metal hydrides, metal oxides...
Type	Water based system (Water tank, Aquifer) Rock or ground based system	Active storage Passive storage	Thermal-sorption (Adsorption, Absorption) Chemical reaction (Normally for high-temperature storage)
Advantage	Environmentally friendly cheap material Relative simple system, easy to control Reliable	Higher energy density than sensible heat storage Provide thermal energy at constant temperature	Highest energy density, compact system Negligible heat losses
Disadvantage	Low energy density, huge volumes required for district heating Self discharge and heat losses problem High cost of site construction Geological requirements	Lack of thermal stability Crystallization Corrosion High cost of storage material	Poor heat and mass transfer property under high density condition Uncertain cyclability High cost of storage material
Present status	Large-scale demonstration plants	Material characterization, laboratory-scale prototypes	Material characterization, laboratory-scale prototypes
Future Work	Optimisation of control policy to advance the solar fraction and reduce the power consumption Optimisation of storage temperature to reduce heat losses Simulation of ground/soil based system with the consideration of affecting factors (e.g. Underground water flow)	Screening for better suited PCM materials with higher heat of fusion Optimal study on store process and concept Further thermodynamic and kinetic study, noble reaction cycle	Optimisation of the particle size and reaction bed structure to get constant heat output Optimisation of temperature level during charging/discharging process Screening for more suitable and economical materials Further thermodynamic and kinetic study, noble reaction cycle

self-discharging, so efforts must be made to eliminate this heat loss problem to further cut down on the investment costs. Because the amount of stored heat depends on the temperature increase and the specific heat of the storage material, it seems that, in order to store more heat with the same mass of material, the storage unit should reach a higher temperature. Yet, as a consequence, it has greater risks of heat losses at high temperature levels. It is essential to determine the optimal storage temperature of a system by comparing and balancing the load demands and stored heat.

Latent heat storage with phase change materials has a higher energy density than sensible storage and features the ability to provide thermal energy at a constant temperature during the phase changing processes. Currently, projects that utilise PCM stores are mainly used in agriculture areas or for short-term storage purposes. Because of the complicated control strategies and the uncertainty of the long-run performance of phase change materials, there are seldom LTS-integrated building projects reported or commercial products in the market thus far. IEA-SHC Task 32 mentioned that the improvement of seasonal storage by latent heat was very limited to water stores for most current applications. Searching for novel phase change materials and gaining better understandings of their physicochemical mechanisms are quite necessary for further

technical developments. Critical points, such as latent heat of fusion, long-term thermal behaviour, flammability, melting temperature, and compatibility with building materials, should be taken into account. Corrosion problems caused by crystallisation and water-PCMs, which affect the technical lifetimes of systems, should be solved. Experiments with realistic boundary conditions will be unavoidable prior to large-scale practical use. In addition, active systems assisted with passive storage methods are the developing trend in seasonal latent heat storage.

Chemical storage is characterised by its high storage potential with negligible heat losses during the storing period. Current studies are mainly on the selection and modification of working pairs in accordance with the thermodynamic requirements and operating conditions. The feasibility of heat storage has been demonstrated in some chemical heat pumps and short-term storage systems, though no large-scale seasonal project has yet been completed. Seasonal storage requires a large amount of storage materials and requires a steady and continuous heat output when discharging. The entire chemical storage system can be more compact than other alternatives, but subsequent heat and mass transfer problems must be solved. Finding the proper particle size of the sorbent and optimising the reaction bed structure to guarantee a constant flow rate, which leads to stable heat output, without compromising

system compaction at the same time are critical steps. Furthermore, noble reaction cycles considering heat recovery can be introduced into the design to reduce the charging temperature and to achieve higher solar fractions. During the discharging phase, sensible heat loss resulting from the temperature increase of the sorbent from ambient temperature to the discharging reaction point is another problem to be addressed (Jaehnig et al., 2006). Storage materials, storage equipment and control strategies of the whole system are also important issues to consider.

For both latent and chemical storage, the processes must be reversible and maintain constant performance without severe degradation after a large number of cycles. Because the cost of materials for seasonal storage is far more important than for short-term storage, further investigation into economical materials is pivotal and necessary.

Seasonal thermal storage is an extremely promising technology for saving energy, yet the cost is currently too high to be acceptable for most people, even by using the sensible storage concept. Among all the available technologies, chemical heat storage is regarded as the idea with greatest potential in the long run due to its high energy density. Once the technical bottlenecks are overcome, and the investment costs are lowered, it should be implemented in large-scale applications. Before that, a small, detached house might be a good choice for investigating the performance of chemical storage systems. On the other hand, in the short run, sensible heat storage, such as water tanks and ground/soil storage will still be dominant in district heating fields because of its reliability and cost-effectiveness.

6. Conclusions

The concept of seasonal/long-term heat storage presents great opportunities for making the utmost use of solar energy. Stored “excess” heat can compensate for the heat shortage when necessary. Seasonal storage offers the possibility that solar energy can cover all the heating loads without an extra heating system. As a result, there will be less and less dependency on fossil fuel resources, and the world's carbon footprint will surely be reduced in the near future.

Three different technologies for seasonal heat storage (sensible, latent and chemical) and related projects are reviewed in this article. Different technologies have different levels of development: sensible heat storage has been demonstrated in large-scale district heating plants, while latent and chemical heat storage systems remain in the laboratory study stages. All of these technologies should conform to the requirements of cost-effectiveness, environmental sustainability, reliability, stability and well cycling behaviours. In terms of the current state of development of each concept, sensible heat storage is more applicable and acceptable for practical use. As research proceeds, technologies with high energy storage densities (latent and chemical heat storage) will be the main trend in the future. In short, efforts need to be made to optimise the technical and economic aspects

so that seasonal thermal storage concepts can be further popularised.

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References

- Abedin, A.H., Rosen, M.A., 2012. Closed and open thermochemical energy storage: Energy- and exergy-based comparisons. *Energy* 41, 83–92.
- Agyenim, F., Hewitt, N., Eames, P., Smyth, M., 2010. A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renew. Sustain. Energy Rev.* 14, 615–628.
- Alkilani, M.M., Sopian, K., Alghoul, M.A., Sohif, M., Ruslan, M.H., 2011. Review of solar air collectors with thermal storage units. *Renew. Sustain. Energy Rev.* 15, 1476–1490.
- Azpiazu, M.N., Morquillas, J.M., Vazquez, A., 2003. Heat recovery from a thermal energy storage based on the Ca(OH)₂/CaO cycle. *Appl. Therm. Eng.* 23, 733–741.
- Bakema, G., Snijders, A.L., Nordell, B., 1995. Underground Thermal Energy Storage, State of the Art Report 1994. Arnhem, The Netherlands, 83p.
- Balasubramanian, G., Ghommem, M., Hajj, M.R., Wong, W.P., Tomlin, J.A., Puri, I.K., 2010. Modeling of thermochemical energy storage by salt hydrates. *Int. J. Heat Mass Transf.* 53, 5700–5706.
- Baldacci, M., 1985. Thermal performance of a solar heat storage accumulator used for greenhouses. Solar Agricultural Greenhouse Flag Brochure EEC. FAO, Roma, pp. 17–24.
- Bales, C., 2005. Thermal Properties of Materials for Thermo-chemical Storage of Solar Heat, A Report of IEA Solar Heating and Cooling programme – Task 32.
- Bales, C., 2008a. Laboratory Tests of Chemical Reactions and Prototype Sorption Storage Units, A Report of IEA Solar Heating and Cooling programme – Task 32.
- Bales, C., 2008b. Final report of Subtask B – “Chemical and Sorption Storage”, The overview, IEA solar heating and cooling programme – Task 32.
- Bauer, D., Marx, R., Nußbicker-Lux, J., Ochs, F., Heidemann, W., Müller-Steinhagen, H., 2010. German central solar heating plants with seasonal heat storage. *Sol. Energy* 84, 612–623.
- Benli, H., Durmus, A., 2009. Performance analysis of a latent heat storage system with phase change material for new designed solar collectors in greenhouse heating. *Sol. Energy* 83, 2109–2119.
- Benli, H., 2011. Energetic performance analysis of a ground-source heat pump system with latent heat storage for a greenhouse heating. *Energy Convers. Manage.* 52, 581–589.
- Berroug, F., Lakhal, E.K., El Omari, M., Faraji, M., El Qarnia, H., 2011. Thermal performance of a greenhouse with a phase change material north wall. *Energy Build.* 43, 3027–3035.
- Bertsch, F., Mette, B., Asenbeck, S., Kerskes, H., Müller-Steinhagen, H., 2009. Low temperature chemical heat storage – an investigation of hydration reactions. EFFSTOCK'2009. In: 11th International Conference on Thermal Energy Storage, Stockholm, Sweden.
- Boer, R.de., Haije, W.G., Veldhuis, J.B.J., Smeling, S.F., 2004. Solid sorption cooling with integrated storage: The SWEAT prototype. ECN-RX-04-080.

- Bokhoven, T.P., Kratz, J., Van Dam, P., 2001. Recent experience with large solar thermal systems in The Netherlands. *Sol. Energy* 71 (5), 347–352.
- Brandstetter, A., 1987. Greenhouse heating using phase changing material. In: Bilgen, E., Hollands, K.G.T. (Eds.), Proceedings of ISES Solar World Congress, Hamburg, pp. 3353–3356.
- Breger D.S., Michaels A.I., 1984. A seasonal storage solar heating system for the charlestown, Boston Navy Yard National Historic Park. In: First E.C. Conference on Solar Heating; pp. 858–863.
- Bricault, M., 1982. Use of heat surplus from a greenhouse for soil heating. In: Proceedings of the International Conference on Energex 82, Regina, pp. 564–568.
- Buchholz, M., Schmidt, M., Buchholz, R., Geyer, P., Steffan, C., 2009. Heating and cooling with sun and salt - a thermo-chemical seasonal storage system in combination with latent heat accumulation. In: Rio 9- World Climate and Energy Event, Rio de Janeiro, Brazil.
- Cabeza, L.F., Castell, A., Barreneche, C., de Gracia, A., Fernández, A.I., 2011. Materials used as PCM in thermal energy storage in buildings: a review. *Renew. Sustain. Energy Rev.* 15, 1675–1695.
- Cullin, J.R., Spitler, J.D., 2011. A computationally efficient hybrid time step methodology for simulation of ground heat exchangers. *Geothermics* 40, 144–156.
- Delaleux, F., Py, X., Olives, R., Dominguez, R., 2012. Enhancement of geothermal borehole heat exchangers performances by improvement of bentonite grouts conductivity. *Appl. Therm. Eng.* 33–34, 92–99.
- Diao, N., Li, Q., Fang, Z., 2004. Heat transfer in ground heat exchangers with groundwater advection. *Int. J. Therm. Sci.* 43, 1203–1211.
- Dicaire, D., Tezel, F.H., 2011. Regeneration and efficiency characterization of hybrid adsorbent for thermal energy storage of excess and solar heat. *Renewable Energy* 36, 986–992.
- Dickinson, J.S., Buik, N., Matthews, M.C., Snijders, A., 2009. Aquifer thermal energy storage: theoretical and operational analysis. *Geotechnique* 59, 249–260.
- Dincer, I., Rosen, M., 2002. Thermal Energy Storage – Systems and Applications. John Wiley & Son, New York.
- Ervin, G., 1977. Solar heat storage using chemical reactions. *J. Solid State Chem.* 22, 51–61.
- Essen, V.M.v., Zondag, H.A., Schuitema, R., Helden, W.G.J.v., Rindt, C.C.M., 2006. Materials for thermochemical storage: characterization of magnesium sulfate. *EuroSun*.
- Essen, V.M.V., Cot G.J., Bleijendaal, L.P.J., Zondag, H.A., Schuitema, R., Helden W.G.J.V., 2009a. Characterization of salt hydrates for compact seasonal thermochemical storage. *EFFSTOCK'2009*. In: 11th International Conference on Thermal Energy Storage, Stockholm, Sweden (May).
- Essen, V.M.V., Cot G.J., Bleijendaal, L.P.J., Zondag, H.A., Schuitema, R., Bakker, M., Helden, W.G.J., 2009b. Characterization of salt hydrates for compact seasonal thermochemical storage. In: Proceedings of the ASME 3rd International Conference on Energy Sustainability 2009 San Francisco, USA, pp. 825–830 (July).
- Esen, M., 2000. Thermal performance of a solar-aided latent heat store used for space heating by heat pump. *Sol. Energy* 69, 15–25.
- Fan, L., Khodadadi, J.M., 2011. Thermal conductivity enhancement of phase change materials for thermal energy storage: a review. *Renew. Sustain. Energy Rev.* 15, 24–46.
- Farid, M.M., Khudhair, A.M., Razack, S.A.K., Al-Hallaj, S., 2004. A review on phase change energy storage: materials and applications. *Energy Convers. Manage.* 45, 1597–1615.
- Fernandez, A.I., Martínez, M., Segarra, M., Martorell, I., Cabeza, L.F., 2010. Selection of materials with potential in sensible thermal energy storage. *Sol. Energy Mater. Sol. Cells* 94, 1723–1729.
- Fisch, M.N., Guigas, M., Dalenbäck, J.O., 1998. A review of large-scale solar heating systems in Europe. *Sol. Energy* 63, 355–366.
- Fujii, I., Tsuchiya, K., Higano, M., Yamada, J., 1985. Studies of an energy storage system by use of the reversible chemical reaction: $\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca}(\text{OH})_2$. *Sol. Energy* 34, 367–377.
- Fukai, J., Hamada, Y., Morozumi, Y., Miyatake, O., 2003. Improvement of thermal characteristics of latent heat thermal energy storage units using carbon-fiber brushes: experiments and modeling. *Int. J. Heat Mass Transf.* 46, 4513–4525.
- Gauthier, C., Lacroix, M., Bernier, H., 1997. Numerical simulation of soil heat exchanger-storage systems for greenhouses. *Sol. Energy* 60, 333–346.
- Givoni, B., 1977. Underground longterm storage of solar energy – an overview. *Sol. Energy* 19, 617–623.
- Gustafsson, A.M., Westerlund, L., Hellström, G., 2010. CFD-modelling of natural convection in a groundwater-filled borehole heat exchanger. *Appl. Therm. Eng.* 30, 683–691.
- Hahne, E., 2000. The ITW solar heating system: an oldtimer fully in action. *Sol. Energy* 69, 469–493.
- Han, Y.M., Wang, R.Z., Dai, Y.J., 2009. Thermal stratification within the water tank. *Renew. Sustain. Energy Rev.* 13, 1014–1026.
- Hasnain, S.M., 1998. Review on sustainable thermal energy storage technologies, Part I: heat storage materials and techniques. *Energy Convers. Manage.* 39, 1127–1138.
- Heller, A., 2000. 15 Years of R&D in central solar heating in Denmark. *Sol. Energy* 69, 437–447.
- Hongois, S., Kuznik, F., Stevens, P., Roux, J.-J., 2011. Development and characterization of a new MgSO_4 – zeolite composite for long-term thermal energy storage. *Sol. Energy Mater. Sol. Cells* 95, 1831–1837.
- Ishitobi, H., Uruma, K., Takeuchi, M., Ryu, J., Kato, Y., 2013. Dehydration and hydration behavior of metal-salt-modified materials for chemical heat pumps. *Appl. Therm. Eng.* 50, 1639–1644.
- Hadorn, J.-C., 2008. Advanced storage concepts for active solar energy-IEA SHC Task 32 2003–2007. In: Eurosun – 1st International Conference on Solar Heating, Cooling and Buildings.
- Jaehnig, D., Hausner, R., Wagner, W., Isaksson, C. Thermo-chemical storage for solar space heating in a single-family house. *ECOSTOCK'2006*. In: 10th International Conference on Thermal Energy Storage, Stockton, USA.
- Jaffrin, A., Cadier, P., 1982. Latent heat storage applied to horticulture. *Sol. Energy* 28, 313–321.
- Jänen, J., Ackermann, D., Stach, H., Brösicke, W., 2004. Studies of the water adsorption on Zeolites and modified mesoporous materials for seasonal storage of solar heat. *Sol. Energy* 76, 339–344.
- Jegadheeswaran, S., Pohekare, S.D., Kousksou, T., 2010. Exergy based performance evaluation of latent heat thermal storage system: a review. *Renew. Sustain. Energy Rev.* 14, 2580–2595.
- Kabus, F., Wolfgamm, M., 2009. Aquifer thermal energy storage in Neubrandenburg -Monitoring throughout three years of regular operation. *EFFSTOCK'2009*. In: 11th International Conference on Thermal Energy Storage, Stockholm, Sweden.
- Kavin, J., Kurtan, S., 1987. Utilization of solar energy in greenhouse, Greenhouse Heating with Solar Energy. REU Technical Series 1. FAO, ENEA, Roma, 178–185.
- Kenisarin, M., Mahkamov, K., 2007. Solar energy storage using phase change materials. *Renew. Sustain. Energy Rev.* 11, 1913–1965.
- Khalifa, A.J.N., Abbas, E.F., 2009. A comparative performance study of some thermal storage materials used for solar space heating. *Energy Build.* 41, 407–415.
- Lahmudi, H., Mauran, S., Goetz, V., 2006. Definition, test and simulation of a thermochemical storage process adapted to solar thermal systems. *Sol. Energy* 80, 883–893.
- Li, T., Wang, R., Kiplagat, J.K., Kang, Y., 2013. Performance analysis of an integrated energy storage and energy upgrade thermochemical solid–gas sorption system for seasonal storage of solar thermal energy. *Energy* 50, 454–467.
- Liu, H., Le Pierres, N., Luo, L.A., 2009. Seasonal storage of solar energy for house heating by different absorption couples. In: EFFSTOCK'2009, 11th International Conference on Thermal Energy Storage, Stockholm, Sweden (May).
- Liu, H., N'Tsoukpoe, K.E., Le Pierres, N., Luo, L., 2011. Evaluation of a seasonal storage system of solar energy for house heating using different absorption couples. *Energy Convers. Manage.* 52, 2427–2436.
- Liu, M., Saman, W., Bruno, F., 2012. Review on storage materials and thermal performance enhancement techniques for high temperature

- phase change thermal storage systems. *Renew. Sustain. Energy Rev.* 16, 2118–2132.
- Luo L.A., 2010. Solar energy storage systems. In: 9th International Conference on Sustainable Energy Technologies, Shanghai, China (August).
- Lottner, V., Schulz, M.E., Hahne, E., 2000. Solar-assisted district heating plants: status of the german programme solarthermie-2000. *Sol. Energy* 69, 449–459.
- Lundh, M., Dalenbäck, J.O., 2008. Swedish solar heated residential area with seasonal storage in rock: initial evaluation. *Renewable Energy* 33, 703–711.
- Masruroh, N.A., Li, B., Klemeš, J., 2006. Life cycle analysis of a solar thermal system with thermochemical storage process. *Renewable Energy* 31, 537–548.
- Mauran, S., Lahmidi, H., Goetz, V., 2008. Solar heating and cooling by a thermochemical process. First experiments of a prototype storing 60 kW h by a solid/gas reaction. *Sol. Energy* 82, 623–636.
- Michel, B., Mazet, N., Mauran, S., Stitou, D., Xu, J., 2012. Thermochemical process for seasonal storage of solar energy: characterization and modeling of a high density reactive bed. *Energy* 47 (1), 553–563.
- Murat, M.K., 2010. High-temperature phase change materials for thermal energy storage. *Renew. Sustain. Energy Rev.* 14, 955–970.
- N'Tsoukpo, K.E., Liu, H., Le Pierrès, N., Luo, L., 2009. A review on long-term sorption solar energy storage. *Renew. Sustain. Energy Rev.* 13, 2385–2396.
- Novo, A.V., Bayon, J.R., Castro-Fresno, D., Rodriguez-Hernandez, J., 2010. Review of seasonal heat storage in large basins: water tanks and gravel-water pits. *Appl. Energy* 87, 390–397.
- Olszewski, P., 2004. The possibility of using the ground as a seasonal heat storage—the numerical study. In: ASME Heat Transfer/Fluids Engineering Summer Conference, July 11–15, Charlotte, North Carolina USA.
- Olivetti, G., Arcuri, N., Ruffolo, S., 1998. First experimental results from a prototype plant for the interseasonal storage of solar energy for the winter heating of buildings. *Sol. Energy* 62, 281–290.
- Oró, E., de Gracia, A., Castell, A., Farid, M.M., Cabeza, L.F., 2012. Review on phase change materials (PCMs) for cold thermal energy storage applications. *Appl. Energy* 99, 513–533.
- Öztürk, H.H., 2005. Experimental evaluation of energy and exergy efficiency of a seasonal latent heat storage system for greenhouse heating. *Energy Convers. Manage.* 46, 1523–1542.
- Paksoy, H.O., Andersson, O., Abaci, S., Evliya, H., Turgut, B., 2000. Heating and cooling of a hospital using solar energy coupled with seasonal thermal energy storage in an aquifer. *Renewable Energy* 19, 117–122.
- Pfeil, M., Koch, H., 2000. High performance-low cost seasonal gravel/water storage pit. *Sol. Energy* 69, 461–467.
- Pinel, P., Cruickshank, C.A., Beausoleil-Morrison, I., Wills, A., 2011. A review of available methods for seasonal storage of solar thermal energy in residential applications. *Renew. Sustain. Energy Rev.* 15, 3341–3359.
- Posern, K., Kaps, C., 2009. Influence of salt hydrate mixtures and pore sizes on the sorption heat of composite TES material. EFFSTOCK'2009. In: 11th International Conference on Thermal Energy Storage, Stockholm, Sweden (May).
- Posern, K., Kaps, C., 2010. Calorimetric studies of thermochemical heat storage materials based on mixtures of MgSO₄ and MgCl₂. *Thermochim. Acta* 502, 73–76.
- Qi, Q., Deng, S., Jiang, Y., 2008. A simulation study on a solar heat pump heating system with seasonal latent heat storage. *Sol. Energy* 82, 669–675.
- Raab, S., Mangold, D., Heidemann, W., Müller-Steinhagen, H., 2004. Solar assisted district heating system with seasonal hot water heat store in Friedrichshafen (Germany). In: The 5th ISES Europe Solar Conference, Freiburg, Germany (20–23 June).
- Rees, D.A.S., 2002. The onset of Darcy–Brinkman convection in a porous layer: an asymptotic analysis. *Int. J. Heat Mass Transf.* 45, 2213–2220.
- Reuss, M., Beck, M., Müller, J.P., 1997. Design of a seasonal thermal energy storage in the ground. *Sol. Energy* 59, 247–257.
- Reuss, M., Beuth, W., Schmidt, M., Schoelkopf, W., 2006. Solar district heating with seasonal storage in Attenkirchen. ECOSTOCK'2006. In: 10th International Conference on Thermal Energy Storage, Stockton, USA.
- Ryu, J., Hirao, N., Takahashi, R., Kato, Y., 2008. Dehydration behavior of metal-salt-added magnesium hydroxide as chemical heat storage media. *Chem. Lett.* 37, 1140–1141.
- Santamouris, M., Balaras, C.A., Dascalaki, E., Vallindras, M., 1994. Passive solar agricultural greenhouses: a worldwide classification and evaluation of technologies and systems used for heating purposes. *Sol. Energy* 53, 411–426.
- Schaube, F., Wörner, A., Müller-Steinhagen, H., 2009. High temperature heat storage using gas–solid reactions. EFFSTOCK'2009. In: 11th International Conference on Thermal Energy Storage, Stockholm, Sweden (May).
- Schaube, F., Wörner, A., Tamme, R., 2011. High temperature thermochemical heat storage for concentrated solar power using gas–solid reactions. *J. Sol. Energy Eng.* 133 (031006), 1–7.
- Schaube, F., Koch, L., Wörner, A., Müller-Steinhagen, H., 2012. A thermodynamic and kinetic study of the de- and rehydration of Ca(OH)₂ at high H₂O partial pressures for thermo-chemical heat storage. *Thermochim. Acta* 538, 9–20.
- Schmidt, T., Mangold, D., Müller-Steinhagen, H., 2003. Seasonal thermal energy storage in Germany. In: ISES Solar World Congress, 14–19 June, Göteborg, Schweden.
- Schmidt, T., Müller-Steinhagen, H., 2004. The central solar heating plant with aquifer thermal energy store in Rostock—results after four years of operation. In: The 5th ISES Europe Solar Conference, 20–23 June, Freiburg, Germany.
- Schmidt, T., Mangold, D., Müller-Steinhagen, H., 2004. Central solar heating plants with seasonal storage in Germany. *Sol. Energy* 76, 165–174.
- Schmidt, T., Mangold, D., 2006. Status of solar thermal seasonal storage in Germany. ECOSTOCK '2006. In: 10th International Conference on Thermal Energy Storage, Stockton, USA.
- Seibt, P., Kabus, F., 2006. Aquifer thermal energy storage – projects implemented in Germany. ECOSTOCK '2006. In: 10th International Conference on Thermal Energy Storage, Stockton, USA.
- Sethi, V.P., Sharma, S.K., 2008. Survey and evaluation of heating technologies for worldwide agricultural greenhouse applications. *Sol. Energy* 82, 832–859.
- Sharma, A., Tyagi, V.V., Chen, C.R., Buddhi, D., 2009. Review on thermal energy storage with phase change materials and applications. *Renew. Sustain. Energy Rev.* 13, 318–345.
- Shukla, A., Buddhi, D., Sawhney, R.L., 2009. Solar water heaters with phase change material thermal energy storage medium: a review. *Renew. Sustain. Energy Rev.* 13, 2119–2125.
- Snijders, A.L., 2000. Lessons from 100 ATES projects—the developments of aquifer storage in Netherlands. In: Proceedings of TERRASTOCK 2000, Stuttgart, Germany, August 28–September 1, 2000. p. 147–152.
- Stitou, D., Mazet, N., Mauran, S., 2012. Experimental investigation of a solid/gas thermochemical storage process for solar air-conditioning. *Energy* 41, 261–270.
- Streicher, W., 2008. Final report of Subtask C “Phase Change Materials” The overview. A Report of IEA Solar Heating and Cooling programme – Task 32.
- Turgut, B., Paksoy, H., Bozdağ Ş., Evliya, H., Abak, K., Dasgan, H.Y., 2006. Aquifer Thermal Energy Storage Application in Greenhouse Climatization. ECOSTOCK '2006. In: 10th International Conference on Thermal Energy Storage, Stockton, USA.
- Vanhoudt, D., Desmedt, J., Van Bael, J., Robeyn, N., Hoes, H., 2011. An aquifer thermal storage system in a Belgian hospital: long-term experimental evaluation of energy and cost savings. *Energy Build.* 43, 3657–3665.
- Veerappan, M., Kalaiselvam, S., Iniyan, S., Goic, R., 2009. Phase change characteristic study of spherical PCMs in solar energy storage. *Sol. Energy* 83, 1245–1252.

- Verma, P., Varun, Singal, S.K., 2008. Review of mathematical modeling on latent heat thermal energy storage systems using phase-change material. *Renew. Sustain. Energy Rev.* 12, 999–1031.
- Visscher, K., Veldhuis, J.B.J., Oonk, H.A.J., Ekeren, P.J., van Blok, J.G., 2004. *Compacte Chemische Seizoensopslag Van Zonnewarmte*. ECN Report C-04-074.
- Visscher, K., Veldhuis, J.B.J., 2005. Comparison of candidate materials for seasonal storage of solar heat through dynamic simulation of building and renewable energy system. In: Ninth International IBPSA Conference. Montréal, Canada.
- Weber, R., Dorer, V., 2008. Long-term heat storage with NaOH. *Vacuum* 82, 708–716.
- Zalba, B., Marín, J.M., Cabeza, L.F., Mehling, H., 2003. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl. Therm. Eng.* 23, 251–283.
- Zhang, Y., Zhou, G., Lin, K., Zhang, Q., Di, H., 2007. Application of latent heat thermal energy storage in buildings: state-of-the-art and outlook. *Build. Environ.* 42, 2197–2209.
- Zhang, Z., Zhang, N., Peng, J., Fang, X., Gao, X., Fang, Y., 2012. Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material. *Appl. Energy* 91, 426–431.
- Zhao, D.L., Li, Y., Dai, Y.J., Wang, R.Z., 2011. Optimal study of a solar air heating system with pebble bed energy storage. *Energy Convers. Manage.* 52, 2392–2400.
- Zhou, D., Zhao, C.Y., Tian, Y., 2012. Review on thermal energy storage with phase change materials (PCMs) in building applications. *Appl. Energy* 92, 593–605.
- Zondag, H., Essen, M.V., He, Z., Schuitema, R., Helden, W.V., Characterization of MgSO₄ for Thermochemical Storage.
- Zondag, H., Essen, M.V., Blijendaal, L., Cot, J., Schuitema, R., Helden, W.V., Planje, W., Epema, T., Oversloot, H., 2008. Comparison of reactor concepts for thermochemical storage of solar heat. In: Third International Renewable Energy Storage Conference, IRES 2008, 24–25 November, Berlin, Germany.
- Zondag, H., Essen, M.V., Blijendaal, L., Kikkert, B.W.J., Bakker, M., 2010. Application of MgCl₂·6H₂O for thermochemical seasonal solar heat storage. In: 5th International Renewable Energy Storage Conference IRES 2010 Berlin, Germany.

Web references

- ClimateWell, 2012. <http://www.climatewell.com>.
- Dalenbäck, 2012. Available from: <http://www.solar-district-heating.eu/SDH/LargeScaleSolarHeatingPlants.aspx>.
- Drake Landing Solar Community, 2012. Borehole thermal energy storage (BTES). Available from: <http://dlsc.ca>.
- SOLARGE. Available from: <http://www.solarge.org/index.php?id=1631>.