

Review article

## Research progress of seasonal thermal energy storage technology based on supercooled phase change materials



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### ABSTRACT

Seasonal thermal energy storage (STES) is a highly effective energy-use system that uses thermal storage media to store and utilize thermal energy over cycles, which is crucial for accomplishing low and zero carbon emissions. Sensible heat storage, latent heat storage, and thermochemical heat storage are the three most prevalent types of seasonal thermal energy storage. In recent years, latent heat storage based on phase change materials (PCMs) has made great progress in solar energy utilization. However, the inherent defects of phase change materials have become resistant, limiting their further development, including low thermal conductivity, phase separation, and susceptibility to leakage. Supercooling is frequently considered a negative to be avoided in short-term usage. In seasonal thermal energy storage, however, supercooling of PCMs becomes an advantage. The paper begins with a brief overview of existing methods of seasonal thermal energy storage. Afterward, a brief description of the research on PCMs capable of storing seasonal heat is provided. A detailed discussion of the current state of research into supercooled PCMs for seasonal thermal energy storage and systems is presented. Finally, we present a detailed outline of the future directions of seasonal thermal energy storage using PCMs. According to current researches, finding and preparing PCMs with stable supercooling, designing suitable trigger crystallization devices and seasonal thermal energy storage systems with high performance will be the three directions for future research.

### 1. Introduction

As science and technology advance, fossil fuel consumption is on an upward trend, posing many problems, such as global warming and non-renewable energy depletion. A low and zero carbon goal is being implemented globally to respond to such a situation. Reducing primary energy use and increasing renewable energy use has become increasingly important. As a result, many countries conduct research primarily focusing on developing clean and green alternatives to energy production, such as wind, solar, biomass, and geothermal energy. As opposed to conventional energy sources, these sources are sustainable and do not increase greenhouse gas emissions [1]. As the most promising green energy source, solar energy is a renewable, inexhaustible, and resourceful source of energy on Earth [2]. By using solar energy efficiently and rationally, we can reduce the use of fossil fuels, alleviating the environmental problems caused by fossil fuel use [3]. Globally, solar energy will generate 27 % of electricity in 2050, while PV solar and concentrated solar power plants (CSPs) will produce 60 % and 40 %, respectively [4]. Currently, solar energy is used in low-, medium-, and

high-temperature areas. However, solar energy also has disadvantages, such as intermittent and uneven distribution.

Thermal energy storage (TES) offers a viable solution to the problem of intermittent, uneven distribution of solar energy. TES was first introduced and studied during the energy crisis of the 1970s. By storing solar energy, intermittent solar energy can meet space heating and domestic water needs and provide high-grade heat year-round, regardless of time or season. In terms of storage time, it can be categorized as short-term storage or long-term storage. The concept of seasonal thermal energy storage (STES), which uses the excess heat collected in summer to make up for the lack of heating in winter, is also known as long-term thermal storage [4]. Seasonal thermal energy storage was proposed in the United States in the 1960s, and research projects were carried out in the 1970s. In the late 1970s, Nordic researchers also began studying seasonal solar thermal energy storage systems [5]. In addition to preventing energy shortages during periods without sunlight, this stored seasonal energy can reduce energy costs significantly. Research has shown that seasonal storage is more energy efficient and reduces fossil fuel consumption to protect the environment. Despite seasonal storage's

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potential for practical applications is more technically challenging than short-term storage. The materials chosen to implement it must be reliable, affordable, and ecological, as it requires a large storage volume and a greater risk of heat loss [4]. Currently, the most common seasonal thermal energy storage methods are sensible heat storage, latent heat storage (phase change heat storage), and thermochemical heat storage. The three's most mature and advanced technology is sensible heat storage, which has been successfully demonstrated on a large scale in recent years. Sensible heat storage is primarily used to store heat based on the specific heat capacity of the material and the temperature change. Pollution-free and low-cost make it a good choice. However, sensible heat storage also has disadvantages, such as low heat storage density and high heat loss. Latent heat storage is also known as energy stored by phase change [6]. Latent heat storage has a higher energy density than sensible heat storage, and PCMs can store 5–14 times more heat than sensible heat [7]. Latent heat storage relies on the study of PCMs. PCMs can be divided into organic, inorganic, and eutectic materials. Organic PCMs are currently the most commonly used PCMs. Their non-toxicity, non-supercooling requirement, and non-phase separation make them excellent choices. Disadvantages such as low storage density, low thermal conductivity, and flammability are the main factors limiting the widespread use of organic PCMs. Compared to organic PCMs, inorganic PCMs usually have a high thermal storage capacity and a wide melting point and are cheap and non-flammable. However, inorganic phase changes commonly suffer from problems such as supercooling and phase separation [8]. Eutectic PCMs are usually a composite of several organic or inorganic PCMs. They have the advantages of both organic and inorganic materials. The greatest advantage of eutectic PCMs lies in their tailored properties. Thermal conductivity is one of the main disadvantages of eutectic materials [9]. As the highest heat storage density of the three technologies, thermochemical heat storage is three times larger than latent heat storage and ten times larger than sensible heat storage [10]. Chemical reactions and chemisorption are typical mechanisms for thermochemical heat storage. In addition, thermochemical heat storage can achieve long-term storage without heat loss, get high-grade thermal energy safe, non-toxic, inexpensive, and easy to handle, with no supercooling and phase separation problems, and the instantaneous release of thermal energy with great power. However, at present, thermochemical thermal storage is only in its infancy and has not been applied on a large scale.

In PCMs, supercooling is a common phenomenon, and many scholars are interested in reducing the supercooling of PCMs for their short-term applications. One common solution to supercooling problem is adding nucleating agents to PCMs. At the same time, however, supercooling can also be used for seasonal thermal energy storage. As a result, latent heat stored in the PCMs can be loaded by melting it using, for example, solar collectors or industrial waste heat. After melting, the PCMs can be supercooled well below the equilibrium phase change temperature. If spontaneous crystallization does not occur, thermal energy can be stored as latent heat and released when required by initiating crystallization [11]. PCMs used in seasonal thermal energy storage can be classified as supercooled or direct based on whether supercooling is utilized or not. Of these, the supercooling-type is the more common. Using supercooling for heat storage can significantly reduce insulation costs. Stable supercooling is one of the critical technologies for developing supercooled seasonal thermal energy storage. To achieve stable supercooling researchers usually consider three perspectives: the supercooling stabilizer, the design of the container, and the external environment [12–14]. Inorganic materials are usually given preference due to their considerable supercooling degree. Among them, sodium acetate trihydrate is more studied in supercooled seasonal thermal energy storage due to its suitable supercooling potential, suitable phase change temperature, and large latent heat value, and it is also the main object of research at present. In addition, erythritol and calcium chloride hexahydrate have also been researched and applied in recent years.

Its main purpose is to help scholars understand the current research

difficulties and directions. Initially, this paper provides a comprehensive overview of the existing approaches to seasonal thermal energy storage. Then, a brief review and introduction of some existing PCMs that can be used for seasonal heat storage in low and medium temperature solar energy is-temperature solar energy are presented. Then, a review of the key technology research difficulties and seasonal thermal energy storage system cases based on supercooled PCMs in the existing literature is highlighted. Finally, the future research directions of using PCMs as thermal storage media are prospected.

## 2. Types of seasonal thermal energy storage

Seasonal thermal energy storage is an effective way to improve the comprehensive energy utilization rate. Solar energy and natural cold heat can be efficiently utilized through seasonal thermal energy storage, and the consumption of electricity and fossil fuels can be reduced. Generally speaking, seasonal thermal energy storage can be used by storing summer heat for winter use or storing winter cold for summer use, i.e., summer heat for winter use and winter cold for summer use. Common seasonal heat storage includes seasonal sensible heat storage, seasonal latent heat storage, and seasonal thermochemical heat storage. Among them, both sensible and latent heat are used to store solar energy directly in the material. Thermochemistry is used to store solar energy indirectly by using solar energy to drive the thermochemical reaction. This chapter focuses on the seasonal thermal energy storage methods that are currently available.

### 2.1. Sensible heat storage (SHS)

Sensible heat storage converts solar energy into sensible heat in the selected material and releases it when needed. A material's specific heat and temperature increase determine the amount of heat it can store. It is a simple, low-cost, and relatively mature seasonal energy storage technology compared to the other two methods. Due to its affordability and reliability, it has been used in various projects. Aquifer thermal storage (ATES), pit thermal storage (PTES), and borehole thermal storage (BTES) are common types of sensible heat storage [15]. The construction costs of TTES and PTES are generally higher than those of ATES and BTES, as well as their suitability for hydrogeological conditions. However, TTES and PTES can also provide a higher power of charging and discharging than ATES and BTES. A comparison of the four forms of sensible thermal storage can be seen in Fig. 1 [16].

#### 2.1.1. Tank thermal energy storage(TTES)

A tank thermal energy storage system generally consists of reinforced concrete or stainless-steel tanks as storage containers, with water serving as the heat storage medium. For the outside of the tank, extruded polystyrene (XPS) is used as an insulation material, and stainless steel is used for the interior to prevent water vapor from spreading. In addition, a layer of PVC protects the insulation from moisture in the soil [17]. Natural stratification occurs in tank thermal energy storage due to the different densities of water at different temperatures; hot water flows towards the top while cold water remains at the bottom, called thermal stratification. As a result of the thermocline, there are no mixing effects, heat is lost less, and the system as a whole is more efficient in storing heat [18]. Therefore, in recent years, the research on tank thermal energy storage has mainly focused on studying the thermocline and the insulation of tanks. In general, by adding diffusers and baffles inside a tank or adding stratifies at its mouth, the velocity and momentum of fluids entering and leaving the tank can be reduced to reduce the mixing effect and increase the thermal stratification of the tank, thereby improving its thermal efficiency [19–22]. However, adding a physical barrier or diffuser to a system typically increases its complexity and cost [23]. Furthermore, research has demonstrated that poorly performing solar collectors will negatively affect the performance of a solar power system [24].

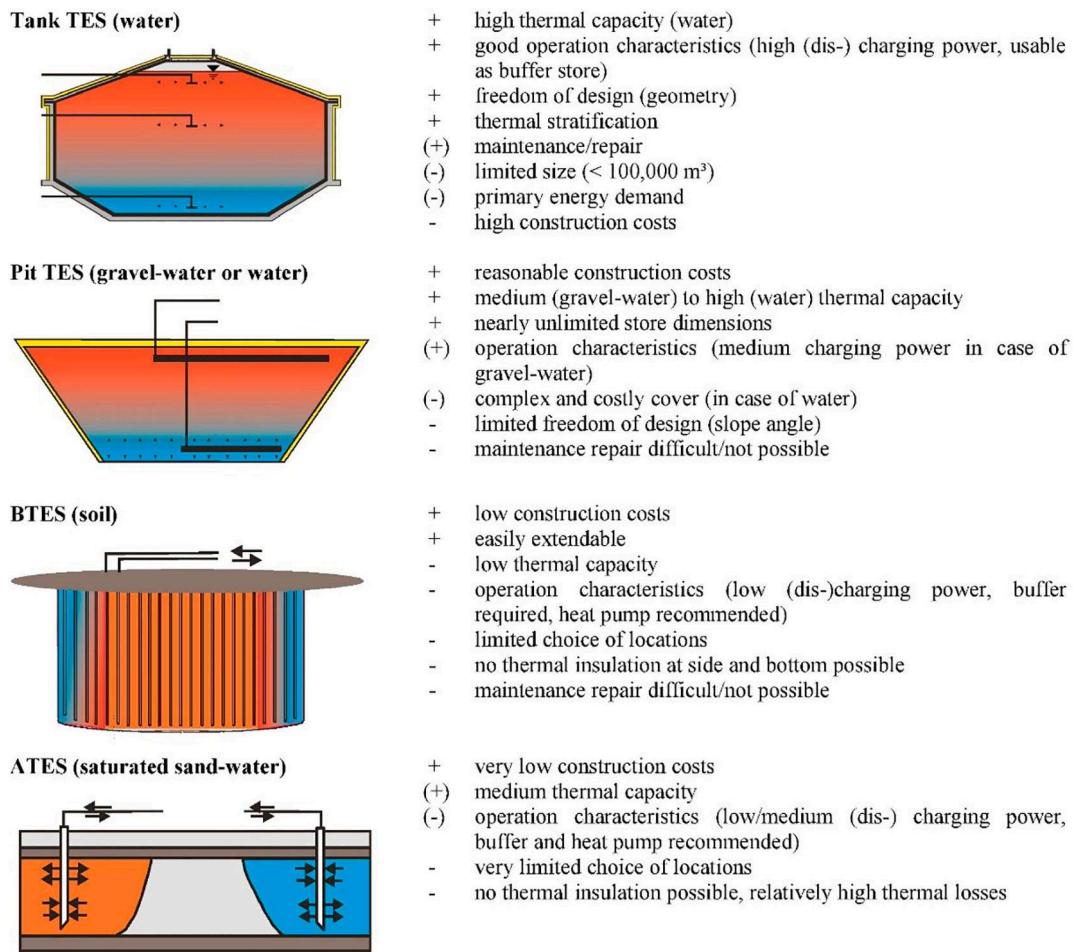


Fig. 1. Construction concepts for large or seasonal thermal energy storage systems and their advantages and disadvantages [16].

### 2.1.2. Aquifer thermal energy storage (ATES)

In aquifer thermal energy storage, geological strata serve as the storage medium and groundwater serves as the heat transport fluid. Aquifer thermal storage can be divided into two types: high-temperature aquifer thermal storage and conventional aquifer thermal storage. In comparison with conventional ATES, high-temperature aquifer thermal energy storage (HT-ATES) can significantly enhance the capacity, storage temperature, and efficiency of renewable energy sources (RES) [25]. ATES systems generally rely on three main site-specific physical characteristics: aquifers with high flow rates; seasonal changes in heating and cooling demand (preferably fairly balanced); and relatively large thermal loads, usually  $>250$  kW [26]. Aquifer thermal storage systems require drilling at least two wells (one called a warm well and the other a cold well), and larger systems may have multiple wells. The temperature difference between the cold and warm wells ( $\Delta T$ ) and the flow rate of the wells ( $Q$ ) determine the heat capacity of the ATES system [27]. An aquifer thermal storage system's performance is closely linked to its location strategy and the geometry of its recirculating injection wells [28,29].

### 2.1.3. Pit thermal energy storage (PTES)

In-pit thermal energy storage, water is a common storage medium. A mixture of water and rock can also be used as a storage medium in PTES. Typically, PTES systems require two elements: simple and cost-effective large storage units; and ecological, reliable, and inexpensive materials for filling, lining, and insulation [30]. PTES systems are currently undergoing research on natural convection and temperature stratification. In addition, weather conditions, inlet and outlet flow arrangement, shape, geometrical parameters, and insulation measures can all affect

PTES thermal stratification and heat loss [31,32]. According to Xie et al., 60 % of the annual heat loss occurs from the top cover and 38 % from the side walls, and 2 % from the bottom of PTES systems. The type of soil significantly influences the thermal performance of the suspension. A PTES surrounded by dry soil can achieve a storage efficiency of 90 %, whereas a PTES surrounded by wet gravel can achieve a storage efficiency of 7 % [33].

### 2.1.4. Borehole thermal energy storage (BTES)

Borehole thermal storage utilizes soil as the storage medium and can store large amounts of solar energy collected during the summer for use during the winter. Considering that borehole thermal storage uses soil as its storage medium, it is essential to correctly estimate the soil's thermal properties when designing a BTES system. However, the difficulty of evaluating heterogeneous soils' thermal conductivity and volumetric heat capacity introduces considerable uncertainty to the design and operation of BTES systems [34]. There are usually four components in a BTES system: a heat source, a borehole heat accumulator, a borehole heat exchanger (BHE), and a buffer tank. An effective BTES system is determined by the design and arrangement of the BHE, the material characteristics, the ground characteristics, and the operating parameters [35]. There are three types of bore heat exchangers: the single-tube U-shaped BHE (SBHE), the double-tube U-shaped BHE (DBHE), and the coaxial bore heat exchanger. During operation, bored heat exchangers typically reach temperatures exceeding 50 °C, resulting in thermal buckling of buried tubes under high-temperature loads. It has been demonstrated that such problems may be mitigated by increasing the initial envelope pressure [36]. Moreover, the heat source injection location in BTES systems is usually fixed at the inlet. Lim et al. showed

that by changing the location of the heat inlet, it was possible to minimize conventional types of energy loss and increase heat storage efficiency [37].

## 2.2. Latent heat storage (LHS)

Phase change heat storage is primarily carried out using the absorption and release of energy that accompanies the transformation of a material state. The general heat storage process does not involve a change in phase state. As the phase change occurs under isothermal or near isothermal conditions, this allows phase change energy storage to provide a constant output temperature and heat flow. For latent heat storage systems based on PCMs, the storage capacity is given by Eq. (1) [38]:

$$Q = \int_{T_i}^{T_m} mC_{md}dT + a_m\Delta H_m + \int_{T_m}^{T_f} mC_{pd}dT \quad (1)$$

where  $a_m$  = melted part,  $\Delta H_m$  = heat of melting per unit mass(J/Kg).

Latent heat storage relies mainly on the properties of PCMs. Phase change material's application field is determined mainly by the temperature range in which it operates. Their low thermal conductivity, easy leakage, and corrosion problems also limit PCMs. The PCMs can be classified into the direct and supercooled types according to whether they use supercooling for thermal storage.

### 2.2.1. Direct type

In direct seasonal latent heat storage, supercooling is considered as a defect to be avoided and needs to be suppressed by adding nucleation agents. In general, the basic principle of direct latent heat storage can be expressed in Fig. 2 [39]. During the summer, the PCMs are heated by solar heat pumps, etc. Adding insulation keeps the heat from dissipating during the storage process, and then it is released in the winter when needed. The insulation method is similar to sensible heat storage, either by insulation or by storage in the ground, etc. However, this type of heat storage has proven to have many shortcomings [40]. Direct seasonal thermal energy storage is more complicated because of the large number of PCMs storage units installed inside the tank and the high cost of heat insulation. Therefore, most of the current direct latent heat storage is based on short-term heat storage, and very few studies are aimed at long-term heat storage.

### 2.2.2. Supercooling type

**2.2.2.1. Principle and model establishment of supercooling.** Normally, in this state, liquid PCMs does not solidify immediately on cooling below the freezing temperature but begins to crystallize only after reaching a temperature well below the melting temperature. During supercooling,

sensible heat is lost, but latent heat is released immediately upon crystallization. In general, supercooling can be observed through a supercooling curve. Standard supercooling curves are usually the following (Fig. 3): Fig. 3(a) and (b) depict the supercooling due to poor nucleation, in (b) the  $T_m$  is reached more quickly due to the higher thermal diffusion coefficient. The temperature rises after crystallization and stabilizes immediately at the melting point ( $T_m$ ). Fig. 3(c) shows the supercooling due to the poor crystal growth rate. The supercooled liquid in Fig. 3(d) starts to solidify at  $T_m$ , indicating no nucleation problem. In the case of the supercooled liquid in curve Fig. 3(e), the temperature takes a long time to drop to  $T_m$ , which means that the thermal diffusivity of the liquid is low [41]. Supercooling is the temperature difference between the melting and freezing points (crystallization). According to classical nucleation theory, supercooling can also be referred to as the crystallization driving force, which is the additional energy required for the liquid to crystallize. In general, in seasonal heat storage, the ambient temperature of the storage reflects the supercooling of the PCMs in the unit [42]. The degree of supercooling varies with almost all material and system parameters: geometry, volume, material, microstructure, purity, emission rate, etc. In general, the degree of supercooling can be expressed by the following Eq. (2) [43]:

$$\Delta T_s = T_m - T_f \quad (2)$$

where  $\Delta T_s$  is the degree of supercooling,  $T_m$  is the melting temperature and  $T_f$  is the freezing temperature. It is feasible to increase the effective heat capacity of the supercooled liquid by reducing the interval between the melting and freezing temperature ranges.

The uncertainty of supercooling makes most numerical models completely ignore the effects of supercooling, which leads to large errors in model building. The main difficulty in modeling supercooling is correctly representing the thermal behavior during cooling while ensuring continuity of enthalpy, temperature, and liquid fraction within the PCMs [44]. Huang et al. used the implicit finite difference method to develop a two-dimensional PCMs heat transfer model that considers the crystal growth process in detail. They verified the model's accuracy with experimental results obtained from melting, cooling, and triggered crystallization under steady supercooling and during cooling. Furthermore, this model found that large supercooling would accelerate the heat release rate of the PCMs heat exchanger after triggered crystallization [45]. Thonon et al. analytically modeled the thermal behavior of PCMs undergoing supercooling and phase change hysteresis, including complete and partial phase change cycles, based on a heat source term. There is good agreement between the experimental and numerical results for the complete heating and cooling cycles. In addition, the solidification behavior laws used to model the supercooling and re-fusion processes are validated over the range of cooling rates tested. However, the model needs to be further validated for hydrated salts and sugar

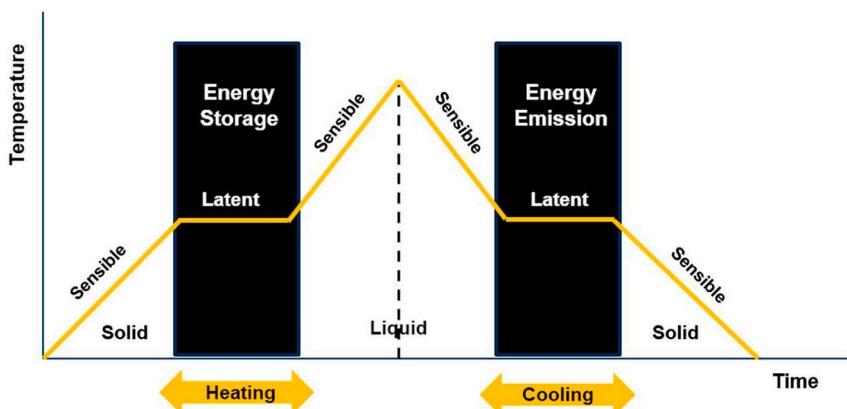
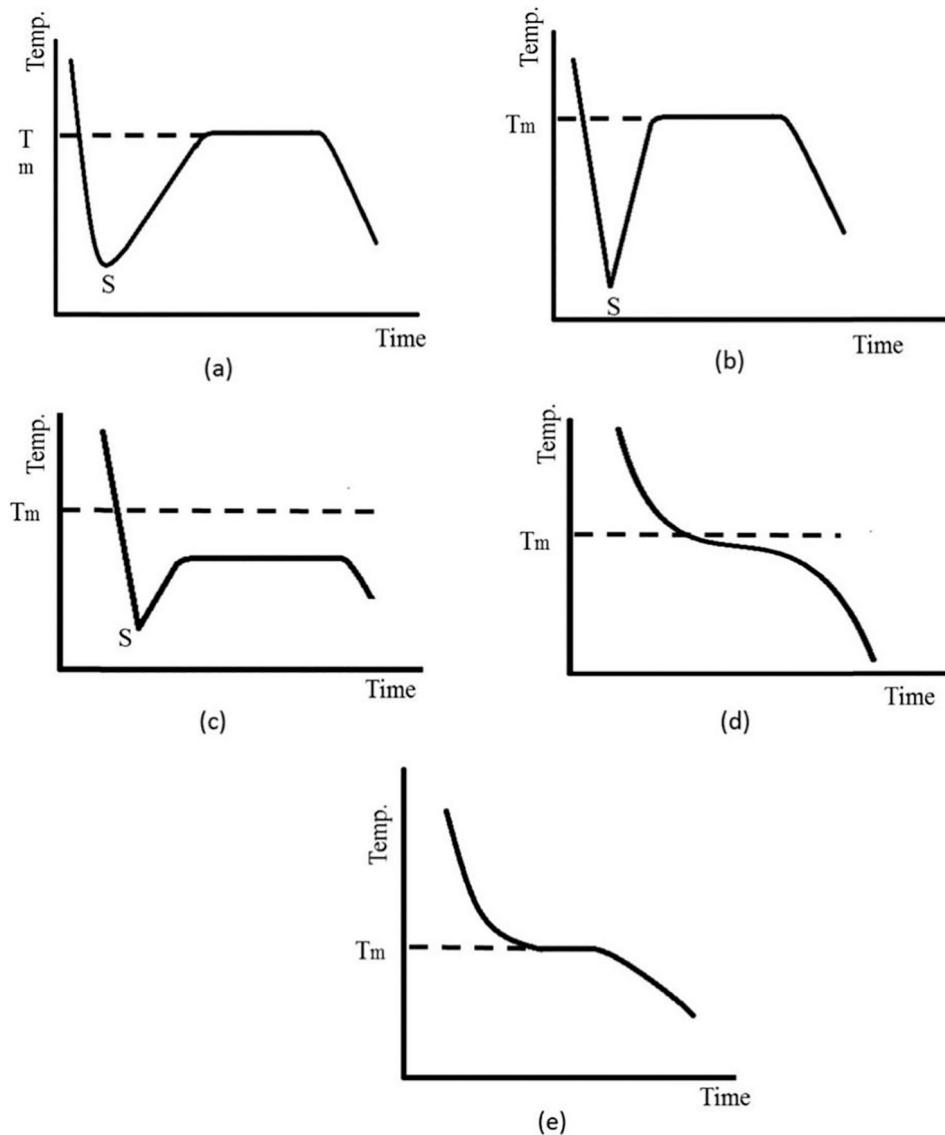


Fig. 2. Schematic diagram of the phase transition of PCMs [39].



**Fig. 3.** Supercooling curve [41].

alcohols [44]. Lilley et al. developed a theoretical framework for predicting supercooling in generalized systems using experimental characterization techniques for supercooling in thermal energy storage applications. The model uses a small sample of laboratory-scale data to quantitatively predict the performance of supercooling in generalized thermal energy storage applications of any size, including the possibility of considering temperature gradients. In addition, by taking into account thermal gradients, the model avoids the approximately 2-fold error caused by the centralized approximation [46]. Ma et al. established a mathematical model of the exothermic process of the storage system based on the experimentally obtained SAT crystal growth rate and the enthalpy change of the solidified supercooled SA aqueous solution, i.e., the solidification process of the supercooled SA aqueous solution, based on the heat transfer between the PCMs in a single heat storage tube. Numerical simulations analyze the discharge temperature and thermal power of the storage system. The effects of ambient temperature, mass flow rate, and the heat transfer coefficient of the HTF on the heat dissipation performance are discussed [47]. Waser et al. proposed a new modeling method that can optimize complex heat exchanger designs and predict supercooling effects with high accuracy [48].

**2.2.2.2. Seasonal latent heat storage based on supercooling.** Supercooled latent heat storage, i.e., using the supercooling of the PCMs for insulation to prevent heat loss during storage. Usually, due to the high degree of supercooling, the molten PCMs can remain liquid at lower temperatures without losing any stored latent heat, and only sensible heat is lost throughout the storage period, so the system is not necessarily adiabatic, but still releases most of the stored thermal energy [47]. This will greatly reduce the cost of insulation. In general, it is better to have the actual crystallization temperature below the ambient temperature of the storage, which is more conducive to heat storage. Placing the system in the basement is a common choice. In supercooled seasonal latent heat storage, inorganic PCMs are preferred, and some organic materials with supercooling, such as sugar alcohols, have also been studied in recent years. Taking SAT as an example, its heat storage principle can be expressed in Fig. 4 [49]. At present, the hot spots of supercooled latent heat storage are stable supercooling and trigger crystallization, of which stable supercooling is the more critical. Most systems have not yet achieved stable operation because stable supercooling has not yet been fully guaranteed. Generally, most current systems usually have both short-term and long-term thermal storage. The supercooling type is more advantageous in seasonal thermal energy storage than the direct type, so it has received more research. So far, it is

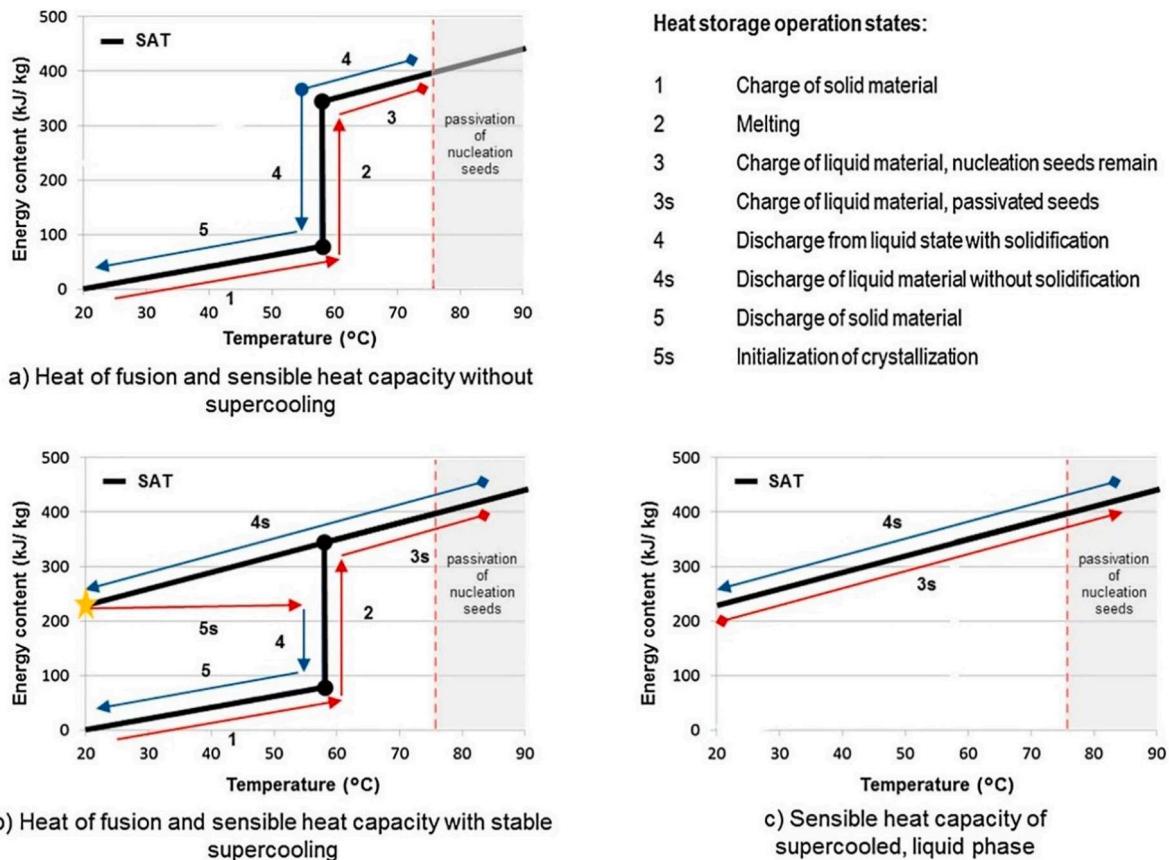


Fig. 4. Thermal storage operation with SAT composites [49].

mainly dominated by the research of Englmair's team, who has made a significant contribution in this area and whose prototype diagram of thermal storage can be represented in Fig. 5 [49].

In addition, supercooled PCMs can also be used for short-term solar energy utilization, battery thermal management, etc. Kutlu et al. developed a solar-assisted heat pump system for DHW applications.

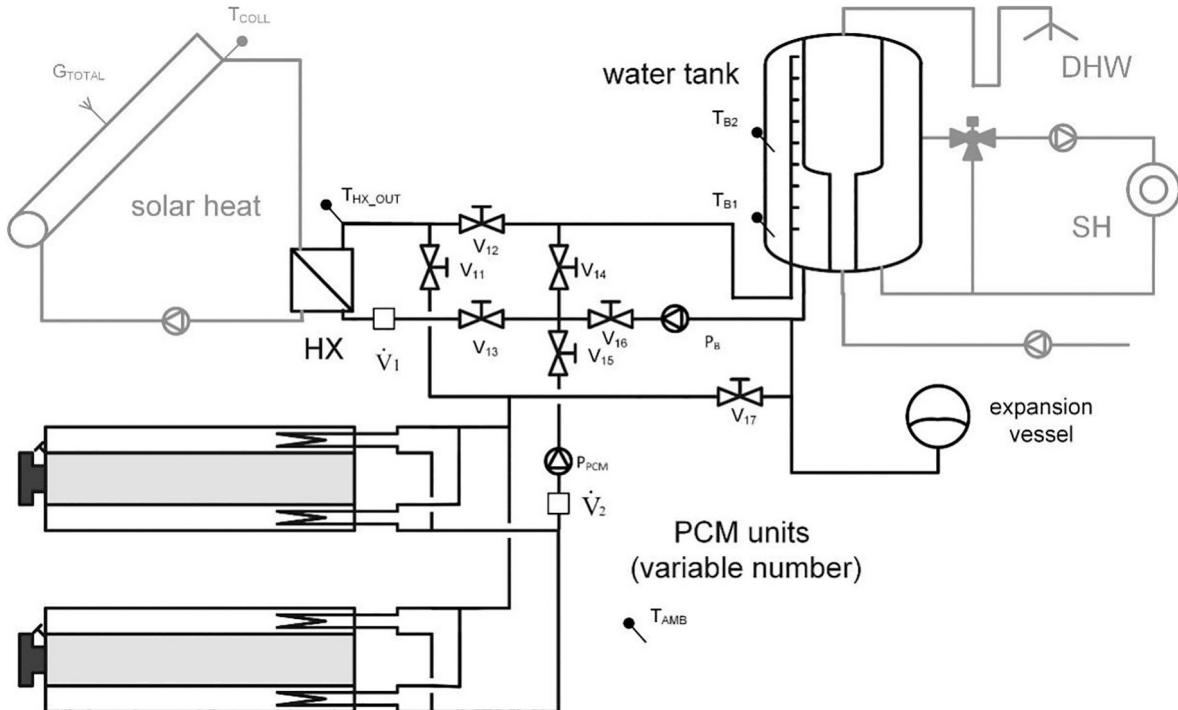


Fig. 5. Configuration diagram of the thermal storage prototype [49].

They developed a transient thermodynamic model of the entire system, including the solar collector, heat pump, tank with PCMs, and DHW demand curve. The system improves energy efficiency by controlling the heat release time of the supercooled PCMs. The study shows that the PCMs tubes effectively compensate for the morning peak hot water demand, reducing daily energy consumption by approximately 12.1 % and 13.5 % and improving energy efficiency [50].

### 2.3. Thermochemical heat storage (TCHS)

Thermochemical thermal storage can be achieved using two different approaches: thermochemical adsorption and thermochemical reaction. The effectiveness of a thermochemical thermal storage system is typically determined by several design parameters, including the thermochemical material, the process design, the reactor design, and the ambient humidity conditions [51]. The preparation and selection of thermochemical materials are essential. For thermochemical thermal storage materials (TCM) to be viable for seasonal heat storage, they must undergo multiple dehydration/hydration cycles, and the choice of TCM is usually determined not only by their recyclability but also by their physicochemical properties such as energy storage density, volume, cost, and toxicity [52].

#### 2.3.1. Thermochemical adsorption thermal storage

As the name suggests, thermal adsorption storage involves using adsorbent and adsorbent in the desorption/adsorption process, along with the absorption and release of a large amount of thermal energy, namely water in the hydrated salt system and ammonia complex in the ammonia complex system. Fig. 6 shows its operational and

thermodynamic processes [53]. Its TES efficiency strictly depends on the reaction rate, reactor design, and selected materials [54]. In thermochemical adsorption thermal storage, common pairs of workpieces include  $\text{SrCl}_2\text{-NH}_3$ ,  $\text{MnCl}_2\text{-NH}_3$ ,  $\text{CaCl}_2\text{-NH}_3$ , etc. [55–57]. In addition, the hydration/dehydration cycle of  $\text{MgSO}_4$  zeolite composites has been applied to seasonal thermochemical adsorption thermal storage [56,58]. The thermochemical adsorption thermal storage system typically consists of a reactor and a storage unit. The storage unit is used alternatively as a condenser or evaporator. Generally speaking, there are three modes of operation for thermochemical adsorption thermal storage systems: direct heat supply, thermal energy upgrading, and combined heat and cold supply [59]. The current research in thermochemical heat storage focuses on materials research, system performance research, etc.

#### 2.3.2. Reversible chemical reactions

Thermal reaction heat storage involves the storage and release of thermal energy through the disruption and reorganization of molecular bonds in reversible chemical reactions, which require the application of high temperatures, usually above 200 °C. The amount of heat storage is determined by the extent of the chemical reaction, the mass of the heat storage material, and the heat of the chemical reaction. For reversible thermochemical reaction heat storage, the heat storage and release processes can usually be described as in Eq. (3), where compound A is split into chemicals B and C through an endothermic dissociation reaction, with the resulting chemicals B and C [60]:



Currently,  $\text{CaO}/\text{Ca}(\text{OH})_2$  and  $\text{MgO}/\text{Mg}(\text{OH})_2$  are two key thermochemical systems in the solid gas range, as well as two typical reactants

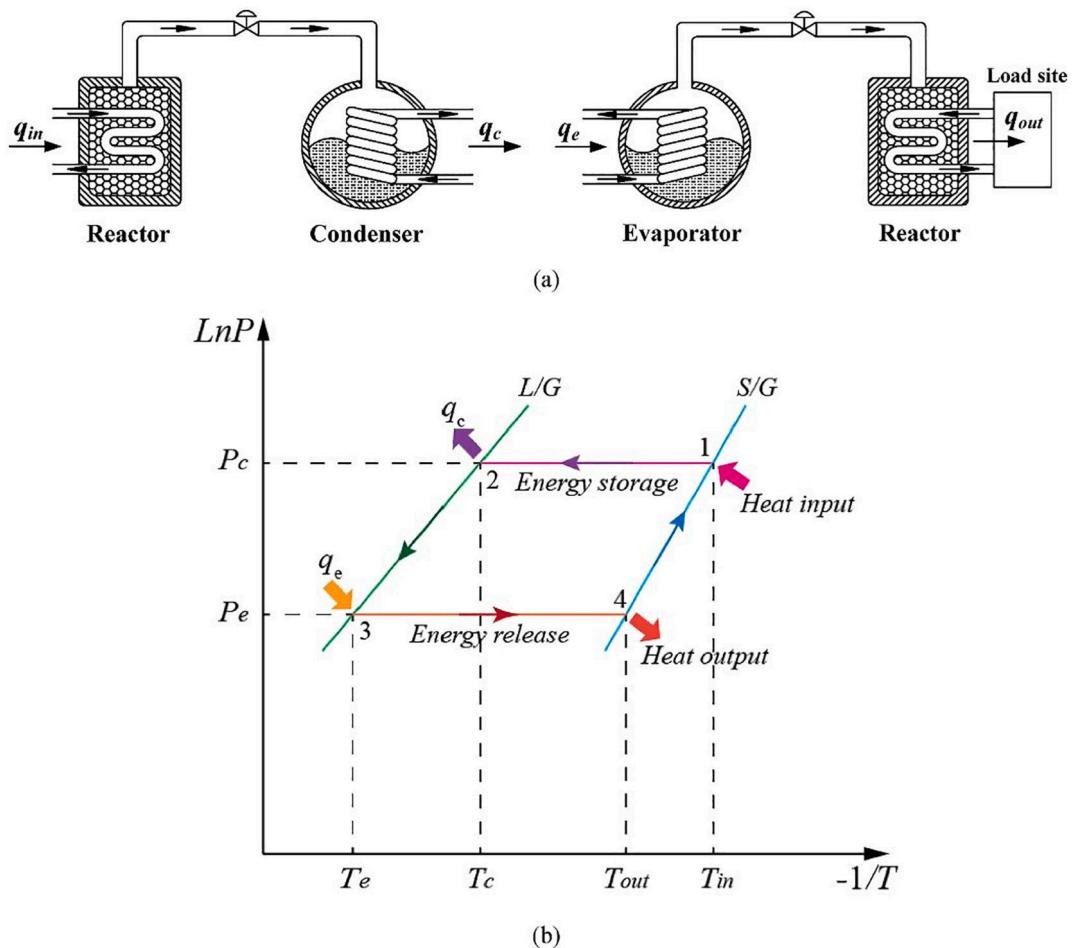


Fig. 6. Schematic diagram of thermal chemisorption heat storage: (a) operational process; (b) thermodynamic process [53].

in candidate hydroxide pairs [61]. In addition to these two systems, there are also  $\text{NH}_3/\text{N}_2/\text{H}_2$  chemical reaction heat storage systems,  $\text{SO}_3/\text{O}_2/\text{SO}_2$  chemical reaction heat storage systems,  $\text{CH}_3\text{OH}/\text{H}_2/\text{CO}$  chemical reaction heat storage systems, etc. [62,63].  $\text{CaO}/\text{CaCO}_3$  reversible carbonation/calcination energy storage is one of the most attractive options due to its high energy density, high temperature, and low material cost [64]. The reactor usually determines TCES systems. The fluidized bed reactor (FBR) is a new type of reactor that has gained much popularity since it is not limited by the material's low effective thermal conductivity. Yan et al. investigated the performance of FBR with  $\text{MgO}/\text{Mg}(\text{OH})_2$  as the reaction material by numerical modeling and experimental validation. According to sensitivity analysis, the main factors that affected the temperature of the bed were the reactor's inner diameter, material mass, and inlet gas velocity [62].

**Table 1** shows a comparison chart of different technologies for seasonal heat storage [65]. A comprehensive comparison reveals that latent heat storage with PCMs possesses a greater storage density than sensible heat storage. Although its storage density is not as high as chemical reaction storage, the system is simpler, more robust and more reliable than chemical reaction systems. Regarding technical maturity, seasonal latent heat storage is more likely to achieve large-scale promotion and application. And among direct-type latent heat storage and supercooling-type latent heat storage, supercooling-type latent heat storage has more promising development prospects.

### 3. Phase change materials with seasonal thermal energy storage potential

There are three types of PCMs: inorganic, organic, and eutectic (**Fig. 7**). When selecting PCMs, the thermal properties, physical properties, kinetic properties, chemical properties, and economics of PCMs should be considered. Direct-type latent heat storage generally requires a suitable phase change temperature, high enthalpy, etc. In the case of using supercooled latent heat storage, the PCMs also need a reasonable supercooling degree to ensure the realization of stable supercooling. Since the focus of this thesis is on supercooled PCMs. The study of stable supercooling will be explicitly described in Chapter 4. In addition, the largest possible latent heat value not only reduces the size of the system and thus the cost but also makes the material more conducive to achieving stable supercooling.

#### 3.1. Inorganic

Inorganic PCMs are dominated by crystalline hydrate salts, composed of crystalline water and salts such as sulfate and nitrate [66]. Typically, crystalline hydrated salts store and exert heat through the release and absorption of crystalline water during melting and solidification. Inorganic PCMs have the advantage of a large enthalpy of phase change, a wide temperature range, and a high thermal conductivity. However, at the same time, there are disadvantages to short-term thermal energy storage, such as phase separation, high supercooling,

high corrosion, and easy leakage [67]. The phase separation problem can be alleviated by adding thickeners, moderate excess water, and shaking to the PCMs. Common thickeners are carboxymethyl cellulose, xanthan gum, acrylic acid, silica gel, etc. Related studies have shown that the addition of suitable EG and graphene nanoflakes (CNF) to SAT can also reduce phase separation [68,69]. In addition, the type of thickening agent, the amount added and the viscosity all affect the solution of phase separation [70,71].

In recent years, many scholars have fabricated salt hydrate-based shape-stabilized PCMs by impregnating them in porous materials. This approach can simultaneously improve low thermal conductivity, phase separation and leakage [43]. The support materials used include biomass-derived carbonaceous flakes (BDCSs) (**Fig. 8**), expanded graphite, graphite oxide/expanded graphite, etc. [72,73]. In addition, enhancing the photothermal conversion of inorganic PCMs in solar energy applications is currently an important research hotspot. Incorporating carbon fibers (CF), graphene nanoplates (GNPs), carbon nanotubes (CNT), Ni-MOF, etc. are proven to enhance the photothermal conversion of inorganic PCMs [74–76].

Among all inorganic PCMs, sodium acetate trihydrate (SAT) has been studied extensively in seasonal heat storage due to its advantages of suitable phase change temperature, high latent heat, low coefficient of phase change expansion, high chemical stability, non-toxicity, low cost, and easy accessibility. The large supercooling degree of SAT is advantageous for long-term or even seasonal thermal energy storage through careful design of thermal storage and controlled crystallization [77]. In addition, sodium thiosulphate pentahydrate and calcium chloride hexahydrate have also been investigated in seasonal thermal energy storage due to their suitable phase change temperature, latent heat and stable supercooling capacity. Of these, calcium chloride hexahydrate is mainly used as a supercooling PCM in battery thermal management [14,42].

#### 3.2. Organic

Organic PCMs are widely used for energy storage due to their high latent heat and wide phase change temperature range. Compared to inorganic PCMs, organic PCMs also have the advantages of no supercooling and no phase separation [78]. At present, paraffin waxes, fatty acids, and sugar alcohols are the three most widely used organic PCMs for storing thermal energy at medium to low temperatures. However, organic PCMs have obvious drawbacks in practical applications, i.e., low thermal conductivity, easy leakage in the molten state, etc. [79]. In addition, organic materials can also be divided into paraffin and non-paraffin, as paraffin is more widely used in organic materials.

##### 3.2.1. Paraffin wax

Paraffin waxes have the most flexible melting temperature range of any organic PCMs. Typically, the chemical formula for paraffin wax can be expressed as  $\text{CnH}_{2n+2}$ . By increasing the number of carbon atoms, PCMs can increase its high melting temperature and latent heat of

**Table 1**  
Technical comparison of different STES concepts [65].

Storage concept	Maturity level	Thermal storage media	Advantages	Limitations
SHS	Commercialization	Water, rock, soil, etc.	<ul style="list-style-type: none"> <li>Unhazardous and low-cost material</li> <li>Relatively simple system</li> <li>Reliable</li> <li>Easy to control</li> <li>High energy density</li> <li>Provide heat at almost constant temperatures</li> </ul>	<ul style="list-style-type: none"> <li>Low energy density</li> <li>Large volume required</li> <li>Heat loss</li> <li>Geological requirements</li> <li>Lack of thermal stability</li> <li>Potential degradation</li> <li>Potential corrosion</li> <li>Material instability</li> <li>Cyclability problems</li> <li>Complex system</li> </ul>
LHS	Demonstration and deployment	Inorganic, organic and eutectic PCMs	<ul style="list-style-type: none"> <li>High energy density</li> <li>Compact system</li> <li>Negligible heat loss</li> <li>Potentially non-toxic materials</li> </ul>	
TCHS	Research and development	Metal chlorides, Metal hydrides, etc.		

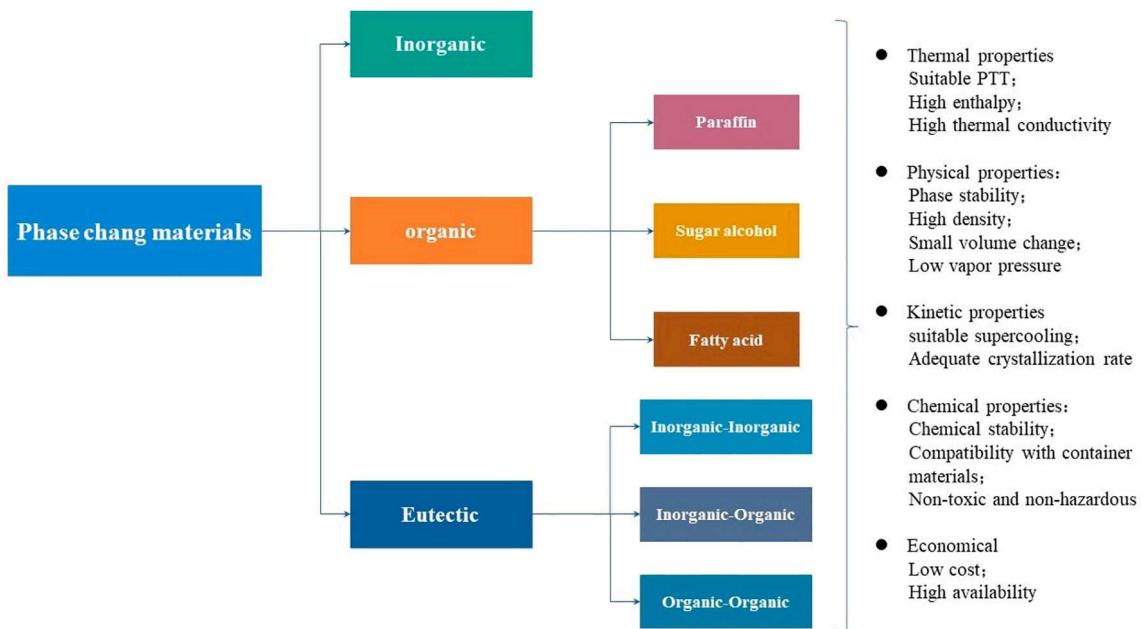


Fig. 7. Classification of solid-liquid PCMs.

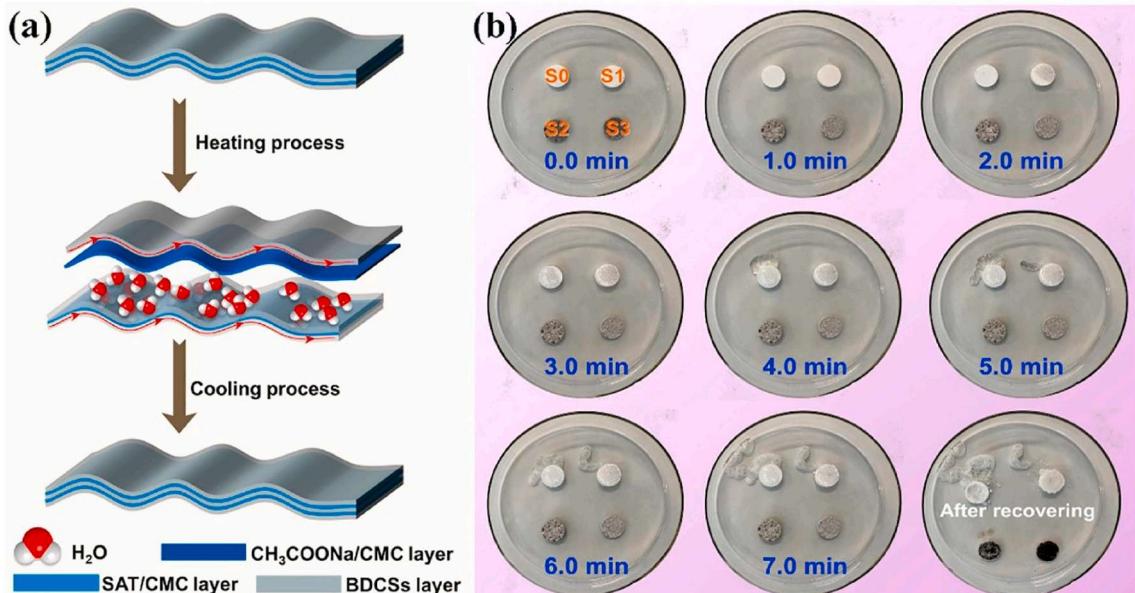


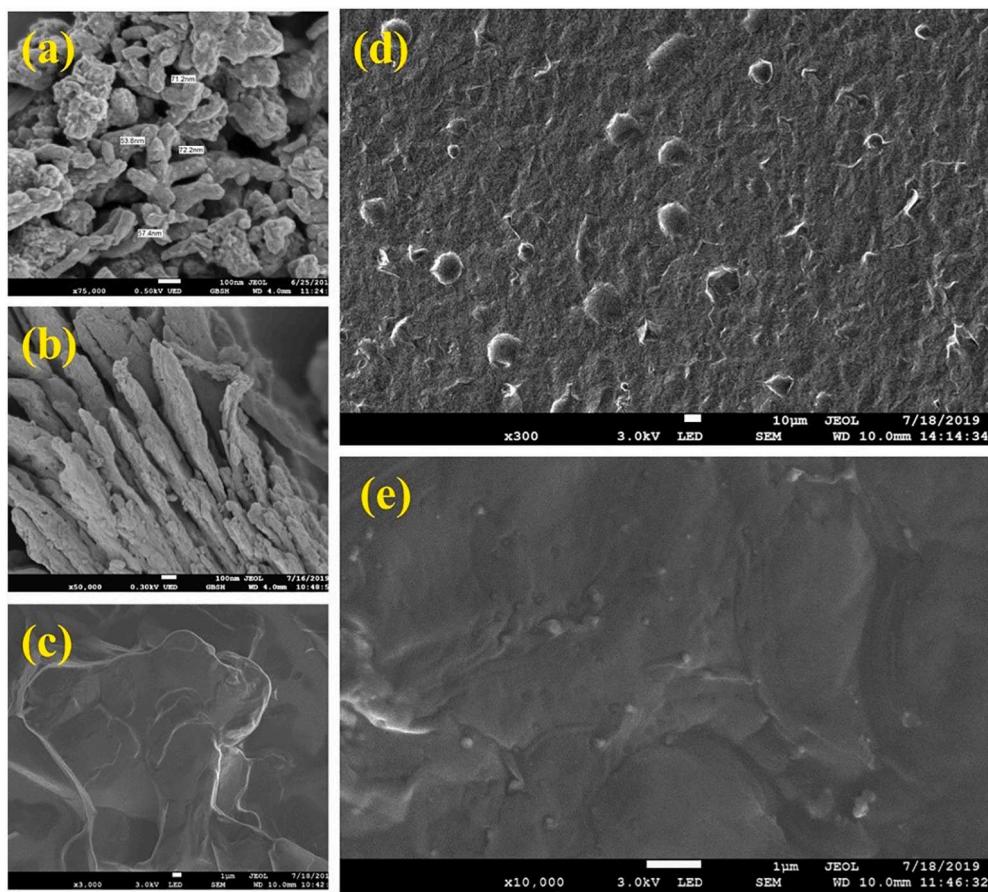
Fig. 8. (a) Schematic diagram of the mechanisms of heat transfer and shape stability of SAT/BDCSs and SAT/CMC/BDCSs composites. (b) Digital photographs of (S0) pure SAT and (S1) SAT/CMC, (S2) SAT/BDCSs and (S3) SAT/CMC/BDCSs composites obtained during isothermal heating at 90 °C [72].

melting [80]. Paraffin waxes are chemically and physically stable and can be produced on an industrial scale and at low prices. In addition, paraffin waxes are safe, non-corrosive, and have low vapor pressure. However, paraffin waxes also suffer from low thermal conductivity, high flammability, easy leakage and large volume change [7]. Compared to paraffin wax, polyethylene glycol shows slight volume shrinkage when mixed with water. Nazir et al. also reported supercooling of paraffin waxes with a melting point of around 55 °C [66]. Paraffin waxes have not been widely studied in seasonal heat storage. At the same time, its application in solar energy utilization is limited due to its weaker optical and thermal properties [81]. Lin et al. improved the solar absorption capacity of EG-paraffin composite PCMs by adding carbon nanotubes. The prepared composite PCMs contain 5 wt% EG and 2 wt% CNTs were shown to exhibit excellent thermal conductivity (2.05 W/m·K), high

solar absorption capacity (94.2 %), excellent cycling stability and at the same time, maintain a high latent heat of 159 kJ/kg [82].

Low thermal conductivity is one of the more researched problems with paraffin waxes. To improve the thermal conductivity of paraffin waxes, researchers usually add various types of nanoparticles ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{CuO}$ ,  $\text{Fe}_3\text{O}_4$ ), carbon nanotubes, graphene, conductive polyaniline and other thermal conductivity enhancers to paraffin waxes [67,83,84]. Fig. 9 shows the SEM images of conductive polyaniline, copper nanoparticles and composite with paraffin waxes. However, at the same time, the addition of nanomaterials reduces the control volume and increases the dynamic viscosity, further reducing the energy storage capacity of the LHTES system.

In addition, simultaneous improvement of leakage and low thermal conductivity can also be achieved by sealing paraffin waxes in some



**Fig. 9.** FESEM images of (a) PANI nanoparticles (b) CuO particles (c) paraffin (d) paraffin/CuO (PWC) and (e) paraffin/PANI (PWP) composites [67].

porous supports to make shape-stable PCMs, such as metal foams, porous carbon supports, ethylene propylene monomer (EPDM) rubber networks, etc. [85,86].

### 3.2.2. Sugar alcohols

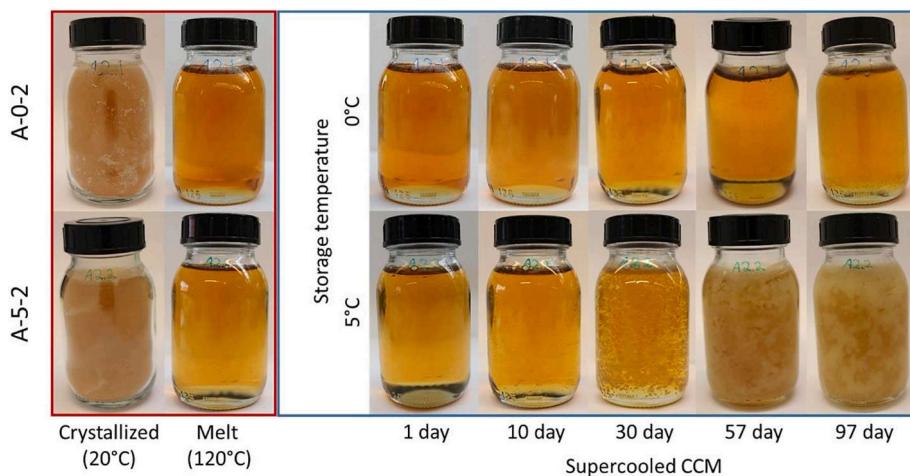
In addition to inorganic materials such as sodium thiosulfate pentahydrate and sodium acetate trihydrate, sugar alcohols such as xylitol and erythritol are among the important materials for seasonal thermal energy storage and have become the subject of research by researchers in recent years—sugar alcohols (SA), also known as polyols. Generally, polyols have as much as twice the volume latent heat value of other organic materials. In addition, sugar alcohols are characterized by low cost, availability and natural origin, non-toxicity and non-corrosiveness, high energy density, and significant but stable supercooling [87]. Such properties allow sugar alcohols to be used as thermal storage media for seasonal thermal energy storage. Of these, erythritol has received more research as a major sugar alcohol [12,88]. In 2015, Puupponen et al. successfully prepared novel microencapsulated PCM-polystyrene composites based on erythritol and xylitol, with PCM mass fractions of 62 wt % and 67 wt%, respectively, and an average void diameter of ~50 μm. The material can be used for long-term thermal storage or protection applications [89]. In 2018, Puupponen et al. prepared another new supercooled PCM-polymer blend consisting of a supercooled polyol (erythritol or D-mannitol) dispersed in a cross-linked sodium polyacrylate (PAANa) matrix. The PAANa in the material prevents the PCMs from cooling and crystallizing, making it less prone to spontaneous crystallization during storage. The material also exhibits good long-term performance, allowing long-term storage of heat in the milligram range [11]. In 2020, Puupponen et al. scaled up a previously developed cold crystalline material, CCM, to a volume size of 160 g and analyzed its supercooling and crystallization properties for long-term thermal

storage. It was found that the CCM samples remained in storage mode at a constant temperature between 0 and 10 °C for up to 97 days (Fig. 10). In addition, the heat release in cold crystallization exceeded 70 % of the heat of melting. This heat can be stored for at least 97 days without reduction, demonstrating the reliable performance of long-term heat storage. The material has a maximum volumetric storage capacity of 250 MJ/m<sup>3</sup> and has excellent properties for further thermal storage applications [90]. However, sugar alcohols suffer from poor thermal reliability, low thermal conductivity, and easy leakage [91]. The addition of EG can effectively increase the thermal conductivity and freezing temperature of erythritol and at the same time, can reduce the melting temperature and supercooling degree of composite PCMs, but also low its latent heat [92–94].

In addition, related studies have shown that both the melting point and the latent heat of the fusion of sugar alcohols decrease with increasing heating time and that higher superheats lead to faster degradation. The reduction in the range of hydrogen bonding shifts the melting point of sugar alcohols. The decrease of latent heat may be associated with the disruption of the hydrogen bonding network and incomplete crystallization. The introduction of nitrogen can effectively improve thermal endurance [95].

### 3.2.3. Fatty acids

Fatty acids, whose chemical formula can usually be expressed as  $C_nH_{2n+1}COOH$ , are organic substances containing long aliphatic hydrocarbon chains based on carboxy lauric and myristic acids. They remain thermally stable at ambient temperature and pressure [79]. They can be obtained from animals and plants and are used in several industries. In general, fatty acids have a high thermal energy storage capacity and an alternative phase change temperature determined by their carbon chain length. However, leakage problems, low thermal



**Fig. 10.** Pictures of supercooled samples after the storage period, including melted and crystallized samples for comparison [90].

conductivity, and low light absorption capacity are limitations to their viable long-term application [96]. Capric, lauric, palmitic, and stearic acids are the fatty acids commonly used in space heating applications [41]. Typically, fatty acids are applied in eutectic or non-eutectic form with other PCMs.

### 3.2.4. Others

Besides paraffin waxes, sugar alcohols, and fatty acids, organic PCMs include ketones, fatty alcohols, and esters [66]. Typically, these materials are flammable and unstable at high temperatures, have a high enthalpy of phase change, low thermal conductivity values, and are toxic. Most of the research on these materials has focused on improving thermal conductivity and photothermal conversion. Table 2 shows some studies on these PCMs in recent years. The application of these materials in seasonal thermal energy storage is very little in the current studies, and their feasibility needs to be further explored. Among them, polyethylene glycol (PEG) has become an essential branch of the new PCMS because of its molecular designability, high energy storage density, wide melting temperature range, non-toxicity, chemical stability, and low price [95]. And PEG has two familiar drawbacks in the practical application of energy storage: low thermal conductivity and easy leakage [97].

### 3.3. Eutectic

Eutectic PCMs are usually composed of two or more PCMs. Still, where the phase change temperature is a fixed value and differs from every single component in the eutectic system, the phase change temperature is called the eutectic temperature. The Schrader equation can

determine the eutectic point of a eutectic mixture. Defects in single-PCMs can be effectively mitigated by eutectic crystallization. In general, eutectic materials can be classified as inorganic-inorganic eutectic, organic-organic eutectic, and inorganic-organic eutectic [105]. Eutectic PCMs developed by mixing two or more PCMS and adjusting the ratio of a single component can be customized for melting temperatures and enthalpies, thus making them suitable for target TES applications [9]. Generally, eutectic PCMS the advantages of no phase separation, eutectic phase change and high bulk heat storage density. Still, the disadvantage is that the information on thermophysical properties is limited [106]. The lack of thermal property test data, low total latent heat, high material cost, low thermal conductivity and poor cycling stability are the main reasons why eutectic PCMs are difficult to use in seasonal thermal energy storage [66]. Table 3 shows some prepared PCMs with suitable phase change temperatures and latent heat for medium-temperature solar energy utilization. The potential for application in seasonal thermal energy storage needs to be further proven. Wu et al. prepared a series of CPCMs with 2 phase change temperatures (PTT) using five single-PCMs: capric acid (CA), lauric acid (LA), stearic acid (SA), 62# paraffin (62#), and octadecanoic (OA), which can be used for seasonal thermal energy storage. Thermal performance analysis showed stable performance, higher latent heat, and lower price for this type of PCMs compared to its single component. The critical parameters of the developed materials can be found in Table 3 [107].

Sugar alcohols have a huge latent calorific value, but their high temperature limits their application. Sugar alcohols have great potential for supercooled seasonal thermal energy storage, and by combining multiple sugar alcohols, the temperature of sugar alcohols can be lowered and their applications can be expanded to have more suitable

**Table 2**  
Study of some other organic materials.

Basic PCMs	Year	Additives	Melting temperature (°C)	Latent heat (kJ·kg <sup>-1</sup> )	Objectives	Refs
PEG	2022	PVP, CuS	58.95–59.63	156.1–175.7	Improving photothermal conversion(87.36 %)	[98]
PEG	2022	TaON nanoparticles, metal-organic frameworks	52.8–3.9	146.3–150.2	Improved thermal conductivity (126.7 %) and photothermal conversion (89.9–94.6 %)	[99]
PEG	2022	Luminous particles	61.7	163.9	Realization of light energy thermal energy storage	[100]
Myristyl alcohol	2017	Metal foam (nickel foam, copper foam)	41.1–41.9	155.1–211.53	Improved thermal conductivity	[101]
1-Octadecanol	2020	SiC, EG	58.6	210	Improved thermal conductivity(0.996 W/(m·K))	[102]
Octadecanol	2022	EG, CuS, @ZnO	53.34	202.97	Improved thermal conductivity(11.77 W/(m·K))and absorptivity	[103]
Tetradecyl amine (TDA)	2020	Porous 3D graphene sponge(GS)	39	293	Improved thermal conductivity	[104]
Octadecyl amine (ODA)	2020	Porous 3D graphene sponge(GS)	51.9	303	Improved thermal conductivity	[104]

**Table 3**

Thermal properties of different eutectic and non-eutectic PCMs.

PCMs	Composite ratio	Year	Melting temperature(°C)	Latent heat(kJ·kg <sup>-1</sup> )	Refs
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O-LiNO <sub>3</sub>	60:40	2022	72.35	170.32	[108]
CA - OA	90:10	2022	28.12/32.22	170.52	[107]
Urea - NaNO <sub>3</sub>	71.25:28.75	2021	85	172	[109]
Palmitic acid (PA) - Stearic acid (SA)	64:36	2022	53.93	177.77	[110]
LA - SA	4:1	2022	34.76/38.56	184.38	[107]
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O-Glutaric acid(GA)	60:40	2020	66.7	189	[111]
Stearic acid - Myristyl alcohol	80:20	2009	61–65	190.87	[112]
CA/62	10:90	2020	29.55/58.98	192.54	[113]
PW48-PW62	10:90	2020	58.77	192.84	[113]
LA-62#	50:50	2022	39.94/55.94	194.55	[107]
LA-HD	60.17:39.83	2022	41.82	196.98	[114]
LA-OA	75:25	2022	38.81/42.74	199.46	[107]
MA-HD	45.98:54.02	2022	48.35	201.67	[114]
Stearic acid-Acetamide	83:17	2017	67	205.5	[115]
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O-KCl	90:10	2021	66.25	206.4	[105]
LA-62#	75:25	2022	38.75/42.56	209.56	[107]
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O - CH <sub>3</sub> COONa·3H <sub>2</sub> O	72:28	2021	41.58	211.9	[116]
1-Hexadecanol(1-HD)-Palmitic acid(PA)	64.5:35.5	2018	48	217.7	[117]
Acetamine-Stearic acid	50:50	2009	65	218	[7]
PA-HD	36.64:63.36	2022	52.35	219.71	[114]
SA-HD	22.90:77.10	2022	55.15	222.54	[114]
LA/OA-62#	1:1	2022	33.77/53.46	223.46	[107]
Arabinitol -Erythritol	60:40	2016	86	225	[118]
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O-KNO <sub>3</sub>	88:12	2021	67.71	231.5	[105]
Arabinitol - xylitol	44:56	2016	77	243	[118]
Erythritol - xylitol	64:36	2021	82	270	[87]
Erythritol - Mannitol	87:13	2018	114.4	322.8	[119]

thermal properties. Palomo Del Barrio et al. identified four eutectic mixtures with long-term TES potential at around 80 °C, namely: adenitol-erythritol, containing 30 mol% erythritol, melting at 87 °C, with a latent heat of fusion of 254 J/g; 2) arabinitol-erythritol, containing 40 mol% erythritol, melting at 86 °C and latent heat of fusion of 225 J/g; 3) xylitol-erythritol, containing 36 mol% erythritol, melting at 82 °C and latent heat of fusion of 270 J/g; and 4) arabinitol-xylitol, containing 56 mol% xylitol, melting at 77 °C and latent heat of fusion of 243 J/g [118].

In conclusion, the current PCMs are still mainly studied for short-term thermal storage, and only a few researchers are studying the PCMs for seasonal utilization. Currently, there are two main directions for modification of PCMs, the first is modification by traditional additives, and the second is the preparation of shape-stable PCMs. Among all PCMs, inorganic PCMs are more suitable for supercooled seasonal heat storage, among which sodium acetate trihydrate is the most researched and used in supercooled seasonal thermal energy storage as well as the more mature technology. Sodium thiosulfate pentahydrate and calcium chloride hexahydrate also have greater potential. Among organic PCMs, sugar alcohols have been widely studied in recent years for supercooled seasonal thermal energy storage. Among other organic materials, some of them have supercooling degree. Still, they do not achieve stable supercooling, such as paraffin waxes, fatty acid and other organic PCMs. However, they also have a certain supercooling degree, but their supercooling stability has not been studied, and their application feasibility needs further confirmation. Eutectic PCMs also have great potential, and compounding some single materials has the potential to increase the overall supercooling stability of the material. In addition, there are fewer studies on supercooling stabilizers, which are basically based on supercooling inhibition. The application of the PCMs listed in this chapter for seasonal thermal energy storage needs further study.

#### 4. Supercooled seasonal thermal energy storage technology and system

Seasonal solar thermal storage using PCMs as the thermal storage medium is usually done in two ways. One is to store the PCMs directly in the thermal storage unit, similar to the seasonal thermal energy storage

of sensible heat, i.e., the direct-type. One is to use the supercooling of the PCMs for thermal storage, i.e., the supercooling-type. Among them, the supercooling-type is also the main direction of current research. This section will review the application of supercooling-type PCMs in seasonal thermal energy storage, including the technical keys (stable supercooling, triggered crystallization, insulation) and system research cases (direct-type, supercooling-type).

##### 4.1. Technical keys

###### 4.1.1. Stable supercooling

Stable supercooling is a prerequisite for developing long-term thermal storage systems and must be carefully considered and designed. Therefore, the PCM's Autonomous crystallization is to be avoided in seasonal heat storage. If the PCMs crystallizes too early, this will lead to ineffective modules and additional energy consumption [120]. In addition, external stimuli can cause nucleation, such as low temperatures, vibrations and impurities, so preventing crystallization from keeping the PCMs in a stable supercooled state is necessary [121]. Stable supercooling can usually be achieved by adding additives, selecting and designing the thermal storage container, and controlling the external environment. Generally, researchers evaluate the stability of supercooling by the duration of stable supercooling. Stable supercooling has been achieved for as short as a few hours and as long as a hundred days. Moreover, in the last century some researchers proposed the use of the hydrochemical potential as an indicator of the stability of supercooled hydrated salt solutions, as shown in Eq. (4). The supercooled solution is stable when  $\Delta\mu_{H_2O} > 0$ . The degree of hydration is only related to the water activity at a given temperature. The lower the water activity of the supercooled solution, the more stable the supercooling is.

$$\Delta\mu_{H_2O} = \mu_c - \mu_m = \mu_s - \mu_m = RT \ln \frac{a_s}{a_m} \quad (4)$$

where  $a_m$  = supercooled water activity,  $a_s$  = water activity of saturated solution,  $T$  = temperature,  $\Delta\mu_{H_2O}$  = difference in water chemical potential,  $\mu_c$  = chemical potential of hydrated salt crystals,  $\mu_m$  = chemical potential of the supercooled solution, and  $\mu_s$  = chemical potential of saturated hydrated salt solution.

**4.1.1.1. Additives.** To achieve stable supercooling, crystallization inhibitors such as mono-, di- and tri-alcohols can be added to PCMs as these compounds enhance the internal stability of the supercooled liquid and facilitate the fabrication of thermal storage modules [122]. However, crystallization inhibitors are currently not common in PCMs and are mostly targeted at additives reducing supercooling. Recently Ribezzo et al. discussed in their paper the most important PCMs for long-term thermal energy storage and discussed the role of additives on the thermophysical and stability properties of PCMs [123]. Yuan et al. demonstrated that acetic acid, ethanol, ethylene glycol, glycerol, and urea effectively extended the supercooling time of saturated aqueous mixtures. Acetic acid, ethanol, and glycerol can extend the supercooling time of SAT solutions from 6 h to >9 days. Acetic acid at 10 % by mass had the strongest stabilizing effect on the supercooled solution in the cycling test. It can be seen from Fig. 11 that SAT with or without acetic acid exhibited similar morphology, being mainly rod-shaped and flattened crystals. However, the crystals of SAT with acetic acid (b) were more dispersed and smaller in size compared to those without acetic acid (a), verifying that the growth and agglomeration of the crystals were inhibited by acetic acid [122]. Puupponen et al. found that cross-linked sodium polyacrylate (PAANa) was effective in preventing conventional cooling crystallization of erythritol and D-mannitol, facilitating the achievement of supercooling of both PCMs [11]. Li et al. showed that the addition of NaOH to erythritol can make erythritol keep the supercooled state and preserve the latent heat (about 200 J/g) for several months at room temperature or very low temperature. This is due to the fact that the alkali hydroxide can form hydrogen bonds with ET molecules, which increase the barrier to formation and hinder the orderly arrangement of the sugar alcohol PCMs during cooling, allowing them to achieve stable supercooling [12].

Moreover, Jana et al. prepared composite carbon foams based on sucrose-based carbon matrix and graphite filler and treated them with hydrophobic properties. It has been shown that the most hydrophobic carbon foam is able to induce significant supercooling of the bearing PCMs. In addition, grafting fluorine atoms or depositing silica onto the carbonaceous surface is an effective way to increase its hydrophobicity and prevent nucleation of heterogeneous PCMs, thus promoting longer thermal storage (Fig. 12) [87].

In seasonal thermal energy storage with supercooled PCMs as the storage medium, problems such as phase separation and poor thermal conductivity remain. Related studies have shown that phase separation in supercooled SAT is facilitated by repeated heating and activation as well as low ambient temperatures. Long-term supercooled samples generally have more intense phase separation problems than short-term ones [124]. The presence of phase separation makes the latent heat much lower, while the poor thermal conductivity leads to the risk of homogeneous nucleation with incomplete melting of PCMs. These can

be solved by adding thickening agents, high thermal conductivity particles, etc. However, the addition of these additives improves the physical properties of PCMs on the one hand and increases the chance of spontaneous nucleation and destroys the supercooling stability of supercooled PCMs on the other hand. Therefore, these problems need to be solved while also considering whether it is beneficial to achieve stable supercooling. Adding additional water proved to be a better option. Still, the PCMs with the addition of water did not exhibit as good cyclic stability as with the addition of other thickeners. By adding additional water to SAT, Dannemand et al. not only alleviated the phase separation problem of SAT but also kept it in the supercooled state for 8 weeks. In contrast, those containing the thickener CMC remained supercooled for 5 weeks. However, the latent heat of the unit with water added gradually decreased with the increase of the number of cycles [70]. Kong, et al. also mitigated the phase separation problem by adding 45 % and 46 % additional water in their experiments. It stabilized the SAT for 131 days, as can be seen in Fig. 13(a), where the phase separation of 40 % water was less after 131 days of supercooling. In addition, it was also demonstrated that the SAT solution with the addition of CMC and xanthan gum also achieved stable supercooling [124]. Zhou et al. indicated that stable supercooling was favored when the brine mass ratios were 3:2:1:1 and 2:3 [13]. In general, small ratios of CMC can improve the supercooling stability of PCMs, as CMC is a thickening agent that restricts the molecular movement of liquid PCMs. However, too much CMC may reduce its stability, because excess CMC increases the number of impurity particles in the solution, which become nucleation substrates and promote the heterogeneous nucleation process, thus making PCMs more prone to solidification [14]. Zhou et al. also stated that adding too much CMC to SAT is not conducive to achieving stable supercooling, and the temperature versus time in the container with different proportions of CMC can be seen in Fig. 14 [13]. Johans et al. not only enhanced the thermal conductivity of SAT when adding 5 wt% graphite powder but also made SAT stable for supercooling for at least 5 months with no signs of spontaneous solidification (Fig. 13(b)) [125]. In addition, adding oil can also improve the heat transfer ability of PCMs without affecting its supercooling stability [70].

**4.1.1.2. Selection and design of the thermal storage container.** The geometry and material of the thermal storage container are important factors in the stability of supercooling. For seasonal thermal energy storage, the thermal storage container is generally closed. This is to prevent airborne impurities from affecting stable supercooling. In addition, the size of the PCMs container has a direct effect on the supercooling, and the decrease in the volume of the sample usually increases the supercooling. In seasonal thermal energy storage, it is generally recommended to use a small volume of the thermal storage container to reduce the chance of spontaneous crystallization. For SAT,

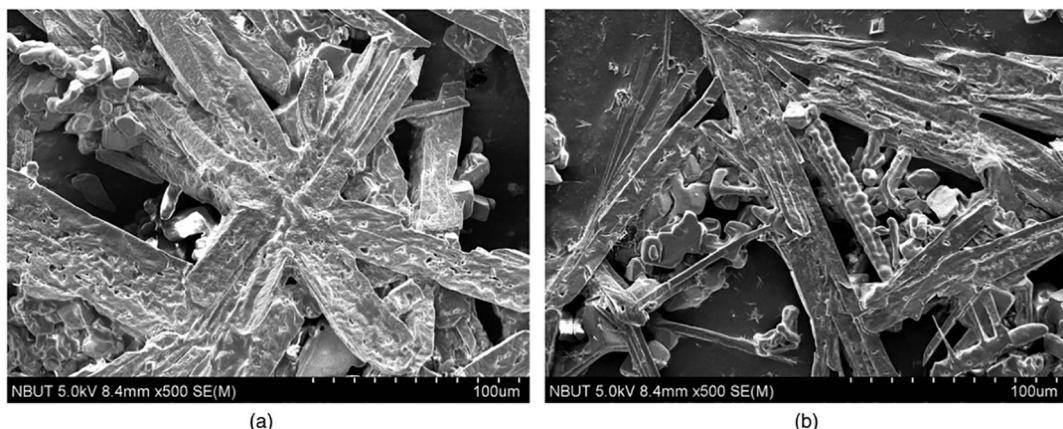
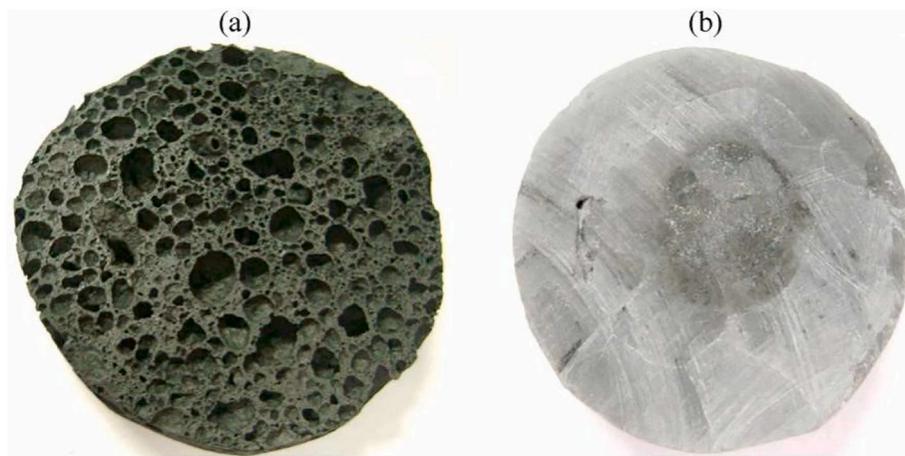


Fig. 11. SEM images of SAT crystals: (a) SAT after the first cycle; (b) SEM image of SAT after the first cycle with 10 % acetic acid [122].

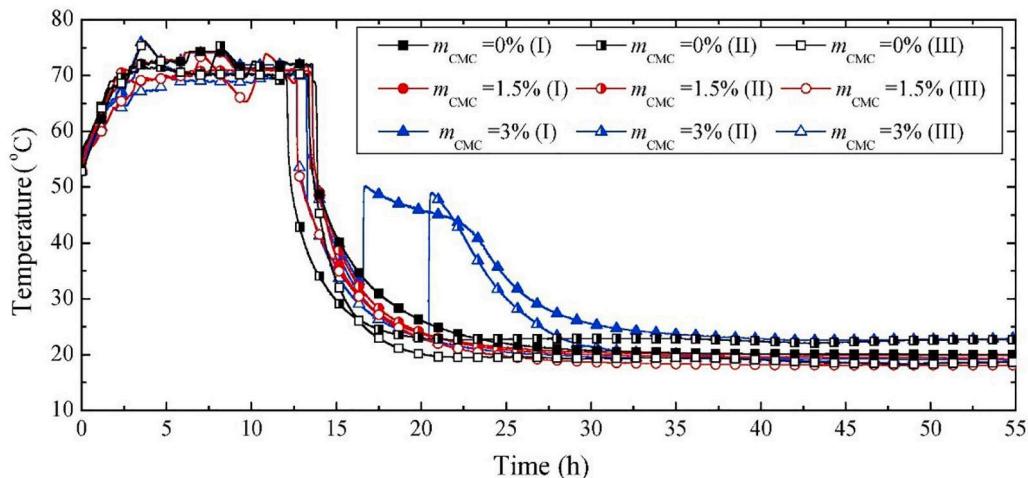


**Fig. 12.** Photographs of the composite carbon foam: (a) before MASA impregnation; (b) after a single MASA impregnation [87].



(a) Status of different proportions of brine mixtures after 131 days of supercooling. (b) Supercooled five-month SAT containing graphite powder.

**Fig. 13.** Supercooling conditions for different additives [124,125].



**Fig. 14.** Temperature versus time for thermal storage containers with different CMC content [13].

Dannemand et al. state that in seasonal heat storage, the thermal storage container usually needs to meet three requirements: (a) avoiding pressure changes in the PCMs container (e.g., by using a membrane expansion container); (b) a smooth inner container surface; (c) heating the entire PCMs volume to a minimum temperature of 77 °C [126]. In the design, attention should also be paid to avoiding geometrical designs

prone to incomplete melting, where incomplete areas of melting will provide nucleation points for supercooled PCMs and affect stable supercooling. Currently, flat rectangles, cylindrical shapes, and rounded rectangles have been shown to work for seasonal thermal energy storage containers, and other related aspects of the research have been based on these three shapes. Hirano et al. experimentally encapsulated threitol in

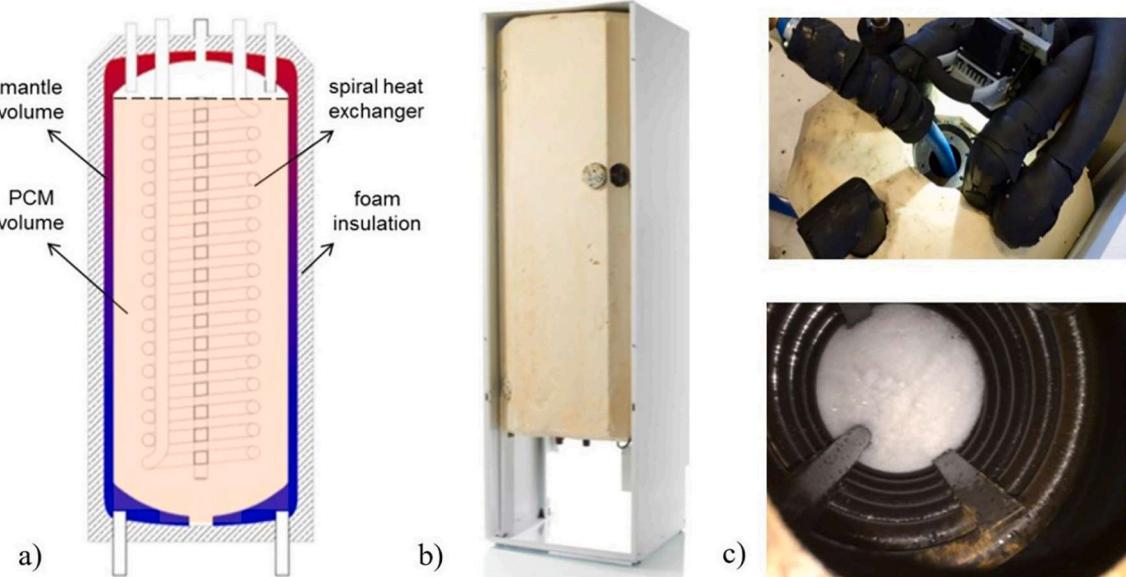
a thin, long, cylindrical copper container, and successfully extracted 12.7 MJ of sensible heat from it. After 56 h of supercooled storage, 27.1 MJ of heat was extracted [127]. While all three shapes of thermal storage materials are feasible, they also differ. For example, flat cell designs are better able to induce convection of molten PCMs than cylindrical heat storage, and flat cells have less phase separation due to their lower height [126]. Whereas cylindrical cell design exchangers may flat cell designs are better able to cope with internal pressures and have lower manufacturing costs [70]. Englmaier et al. designed a cylindrical in-tank storage heater with an internal spiral heat exchanger (Fig. 15) for short and long-term heat storage using a composite material of sodium acetate trihydrate (SAT) with 2 % wt. Additional water and 3 % wt. Liquid polymer solution, and suggested a well-sealed opening design with no temperature sensor in the liner [128]. Zhou et al. demonstrated that of the three shapes of thermal storage containers, pointed rectangular, rounded rectangular, and cylindrical, sodium acetate trihydrate in a rounded rectangular container was more likely to be stably supercooled than in a pointed rectangular container. In addition, longer filling times, lower cooling rates, and lower internal surface roughness resulted in more stable supercooling [13]. The aspect ratio ( $A/V$ ) in a rounded rectangle should be as large as possible (considering the container strength) to improve the heat transfer rate. Fig. 16 shows the effect of aspect ratio on supercooling [42]. At the same time, however, the large surface-to-volume ratio of individual PCMs containers will also lead to unfavorably high heat loss coefficients [49].

Furthermore, a numerical study of a storage heater utilizing sodium acetate trihydrate (SAT) as a PCM was carried out by Wang et al. The numerical study showed that by moving the inlet from the bottom to the top of the reservoir, the time required for the complete melting of the PCM could be reduced by 50 %. The top inlet is used for charging and the bottom inlet for discharging energy is advocated. Small inlet sizes (3.0–8.0 mm) can be used to achieve a uniform temperature distribution within the thermal store. Fig. 17 shows the temperature distribution for different sizes of inlet outlets. Typically, the addition of a porous plate with a 10 % porosity eliminates the short circuit. The addition of the porous plate reduced the charging time of the thermal storage container by 28 % [129].

The compatibility of the PCMs with the unitary material is also an important factor in the ability of the PCMs to achieve stable supercooling. Generally, low-indicated energy materials are advocated. Peng

et al. used droplet free fall experiments to investigate the supercooling behavior of sodium thiosulphate pentahydrate under different surface free energy conditions, both dynamically and statically. It was found that PCMs droplets could remain supercooled on substrates with low surface free energy, while phase transition occurred after 20 cm of free fall on substrates with higher surface free energy. The experimental results show that lower surface free energy provides a larger contact angle at the solid-liquid interface, expanding the free energy required for heterogeneous nucleation and making it difficult for PCMs to crystallize and that cells made from materials with a lower surface free energy are more conducive to stable PCMs supercooling. Stainless steel coatings with PTFE on the inner surface can be used for long-term TES [121]. The effect of corrosion of PCMs is more prominent in seasonal thermal energy storage than in short-term thermal storage. When the surface of the thermal storage container becomes rough due to corrosion, this will result in some of the unmelted crystal particles remaining in the grooves of the rough surface becoming induced to solidify; in addition, the critical nucleation energy may be lower due to the lower contact angle between the crystalline phase and the rough inner surface [13]. Rusty steel profiles or materials with rough surfaces lead to higher and more uniform crystallization temperatures [130]. Cabeza et al. tested the corrosion resistance of five commercial metals in contact with  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ . The results indicated that brass and copper should be avoided in long-term applications in contact with  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ . Still, aluminum, steel, and stainless steel had better corrosion resistance for SAT [13]. Punniakod et al. stated that organic and inorganic PCMs container materials should preferably be stainless steel and aluminum to avoid corrosion [131]. The temperature at which the PCMs are stably supercooled varies between containers of different materials. Laboratory studies have shown that sodium acetate trihydrate can be stably supercooled to approximately  $-24^\circ\text{C}$  in glass containers and to  $-9\text{--}15^\circ\text{C}$  in iron containers [132].

**4.1.1.3. Other factors.** The ambient temperature, cooling rate, and heating temperature are also important factors affecting the supercooling stability. In general, the ambient temperature should be higher than the actual crystallization temperature of the PCMs, because the lower the ambient storage temperature, the more latent heat needs to be released to raise the system temperature to the melting point, which requires more PCMs to transition from the liquid to the solid state. So the



**Fig. 15.** (a) Schematic diagram of the accumulator; (b) picture of the cylindrical accumulator; (c) inner tank of the accumulator filled with melted SAT composite (top); view of the inner tank, partially filled with melted SAT composite (bottom) [128].

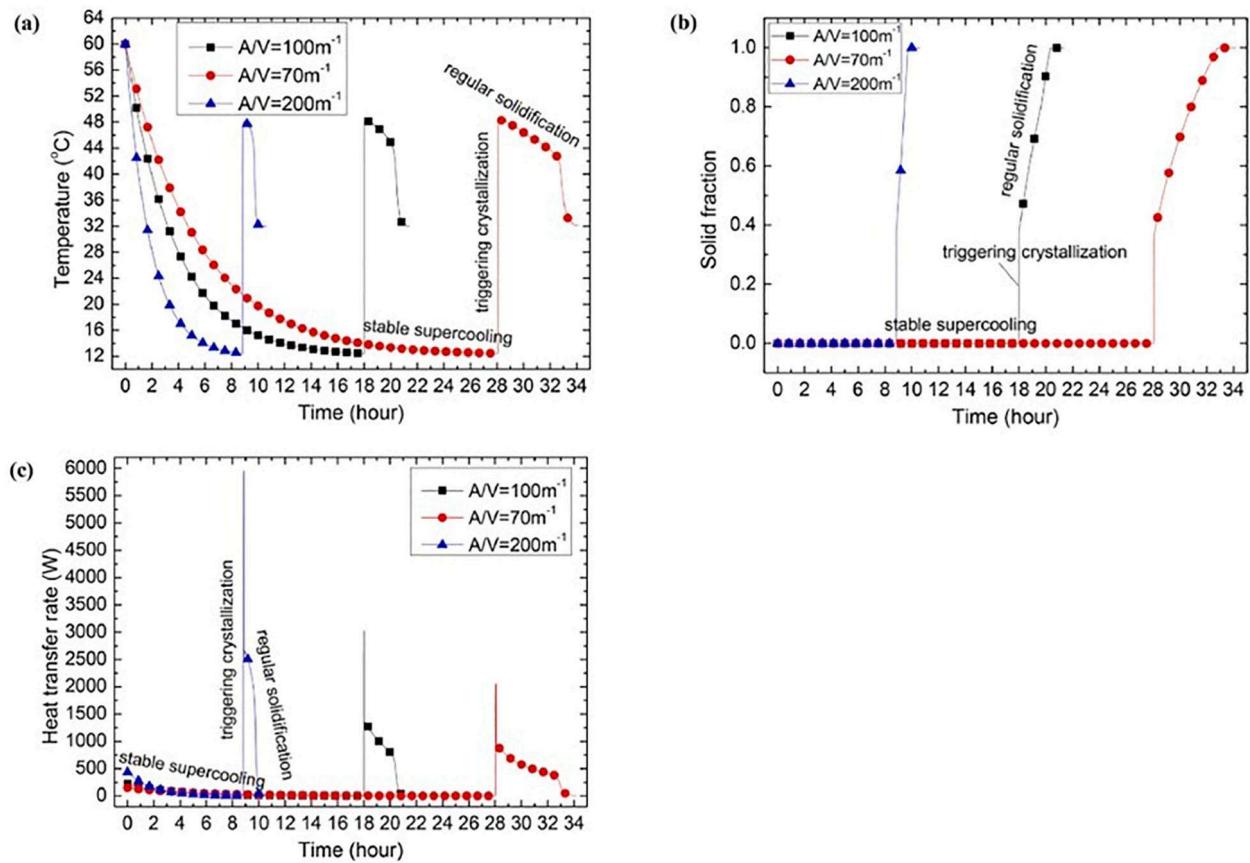


Fig. 16. Effect of container aspect ratio on the emission characteristics of supercooled PCM [42].

storage temperature should be as high as possible to reduce the latent heat loss during the trigger crystallization process [42]. Ling et al. investigated the effect of cooling rate on the stability of supercooling by covering the surface of the device with different thicknesses of insulation, which showed that the faster the cooling rate, the more difficult it was to stabilize the supercooling [14]. In addition, the higher the heating temperature and the longer the heating time, the more favorable the stability of the supercooling. This is because when the temperature is too low, the solubility of PCMs is not high enough to dissolve all anhydrous salts in the crystalline water. The undissolved anhydrous salts act as nuclei for crystallization. For SAT, the heating temperature is at least 77 °C [133]. In addition, it has been shown that STP dissolves more completely than SAT at the same heating temperature and time, which helps maintain the supercooled state's stability [134]. Of course, the purer the PCMs, the easier it is to achieve stable supercooling.

#### 4.1.2. Trigger crystallization

Another problem that needs to be solved in systems where the supercooled PCMs are used as the heat storage medium is the triggering of crystallization. Incomplete crystallization will result in a large proportion of heat being lost. In general, trigger crystallization can be divided into two categories: passive (supercooling reduction) or active (on-demand trigger crystallization) devices [135]. In seasonal thermal energy storage, on-demand triggered crystallization is more common. Currently, the common ways to trigger crystallization in seasonal heat storage include adding seeds, mechanical vibration, applying electric fields, and cooling down crystallization. In addition, the bubbling method has also been shown to be effective in triggering crystallization. In addition, bubbling is effective in triggering crystallization.

##### 4.1.2.1. Seeding and bulging

Seeding, also known as adding a crystal

seed, is the simplest way to trigger the nucleation of a supercooled material by providing a stable solid crystal of the same material. The surrounding liquid will rapidly grow around this seed as this change in structure increases stability and heat is released [135]. Englmair et al. designed and fabricated a triggered crystallization device using acrylonitrile butadiene styrene (ABS) as the material through 3D printing (Fig. 18). The principle is the addition of a crystalline seed triggers that crystallization. Crystallization is triggered by inserting solid SAT crystals into the supercooled SAT via a hollow needle, and the material used to fabricate the device generally needs to be highly heat resistant. In this case 220 kg of modified SAT can release approximately 10.3 kW·h of heat [49]. In their experiments, Kong, et al. induced solidification of supercooled SAT samples by adding solid SAT crystals to a plastic bottle from the top or bottom. Solidification of supercooled SAT samples was induced from the bottom by dipping a needle into the solid SAT and then pushing the needle into the plastic vial from the bottom [124]. But seeding does not work for all supercooled PCMs. Xylitol is one such material where local cooling cannot trigger nucleation due to the very high activation energy for atomic diffusion and rearrangement at the solid-liquid interface in xylitol. Although crystalline seeds allow activation of xylitol crystallization, the effect of crystalline seeds on crystallization is too localized and their crystal growth rates are too low for the application. This technique leads to low exothermic rates and long discharge times and is not conducive to subsequent applications [136]. Therefore, some researchers have chosen to achieve trigger crystallization of sugar alcohols by bubbling in their experiments. The ones that have been validated so far are xylitol and erythritol. Typically, bubbles are injected into the PCMs through injection, and high pressure is induced after the bubbles have collapsed. Generally, this pressure is sufficient to raise the melting point and produce homogeneous nucleation-evaporation of the cavitation effect reduces the stress at the bubble's surface to a very low temperature. Thus homogeneous

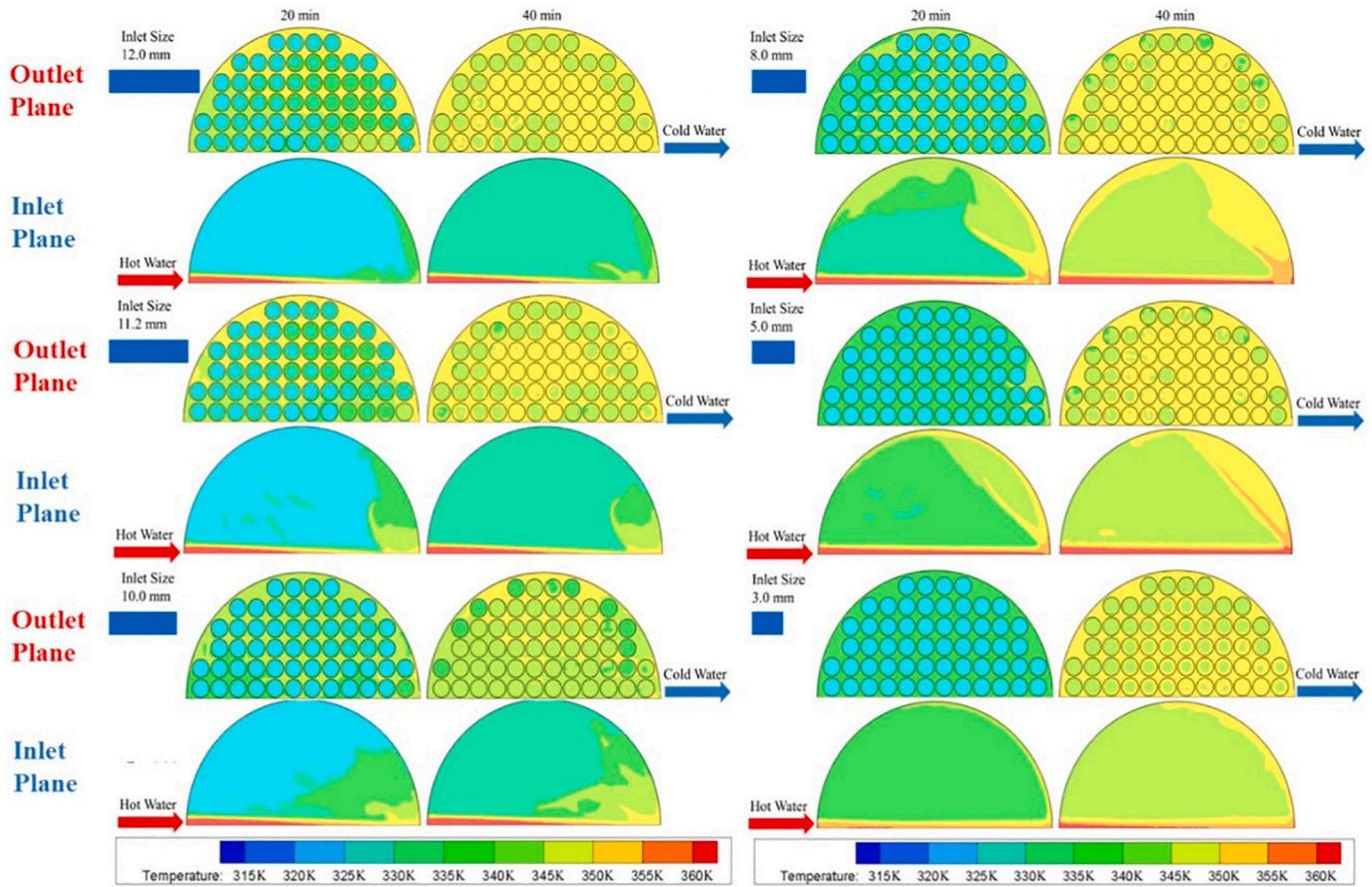


Fig. 17. Temperature distribution for different inlet sizes on the inlet and outlet surfaces [129].

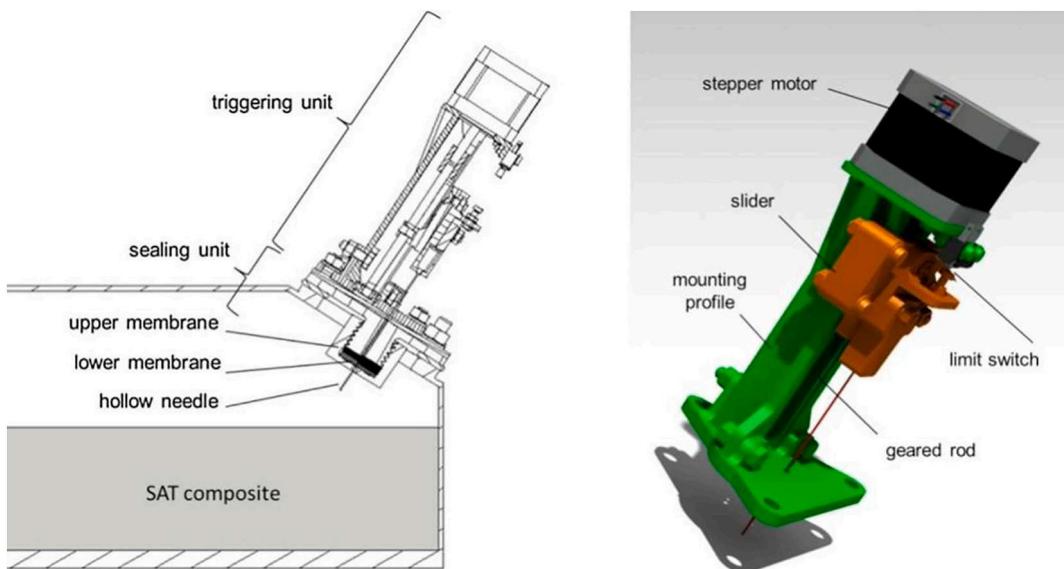


Fig. 18. Schematic diagram of the trigger device [49].

nucleation occurs [135]. The bubbles can be used to trigger crystallization and enhance convective heat transfer and improve the exothermic performance of latent heat energy storage systems (LHTES) [137]. Godind et al. used gas to bubble supercooled xylitol to activate the crystallization of highly viscous supercooled xylitol. This less invasive technique is easily implemented in standard storage containers. Experiments have shown that the rupture of the original bubbles on the

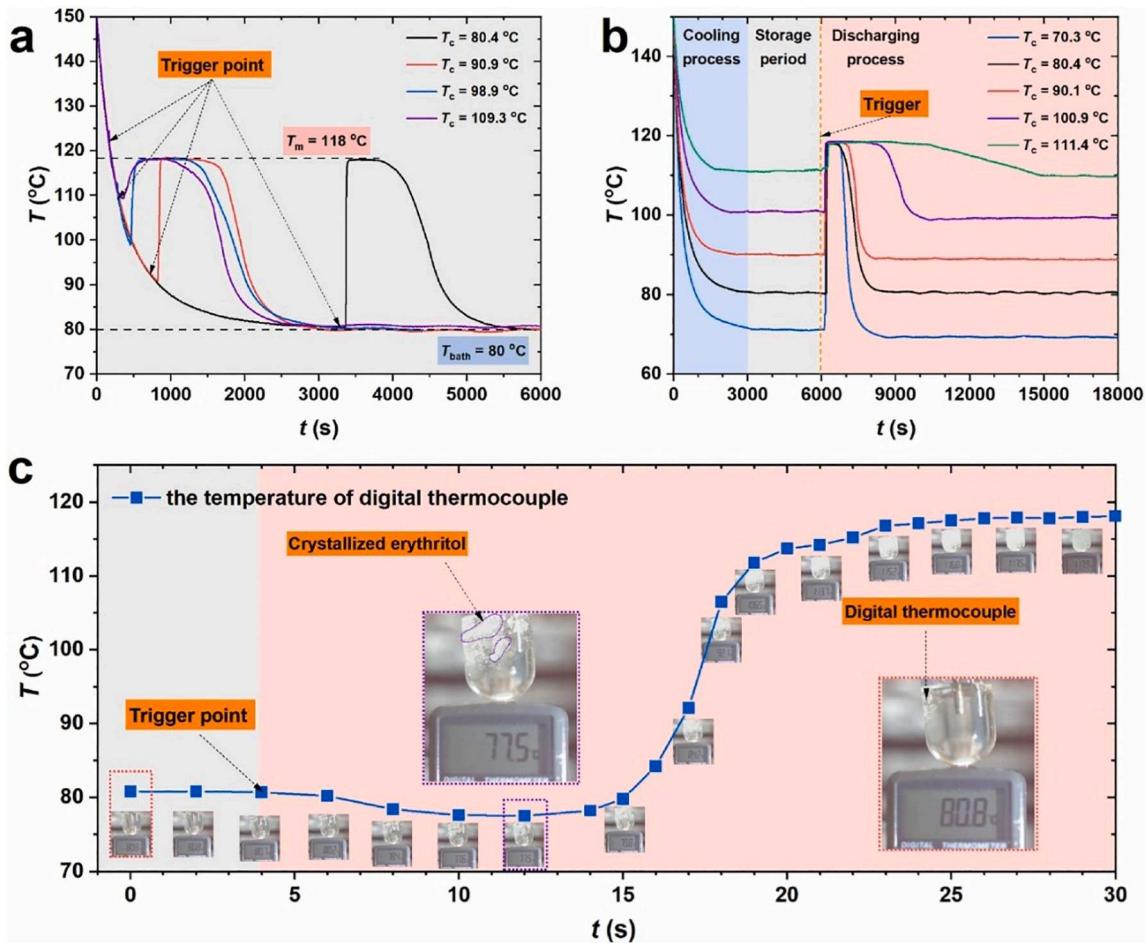
surface of the free liquid and the generation of offspring are necessary for the crystallization of xylitol. Furthermore, the efficiency of the crystallization process will depend on the number of nucleation-generating sites and the extent and homogeneity of their dispersion in the melt. Also, as the bubbles are injected at ambient temperature there is a certain amount of heat loss [136]. Yang et al. indicated that the injection of bubbles is also an effective method to actively trigger the

crystallization of erythritol in a controlled manner. In general, the size of the bubbles varies with the flow rate and the triggering effect. The injection of bubbles not only reduces the supercooling of erythritol to promote nucleation but also increases the latent heat of the crystallization of erythritol. The latent heat of crystallization increases to 290.5  $\pm$  3.8 kJ/kg at a supercooling of 58 °C, triggered by large bubbles, and up to 322.3 kJ/kg at a supercooling of 8 °C. In addition, the use of nitrogen bubbles protects the erythritol from oxidation during the heating process and prolongs the life of the erythritol. Fig. 19 shows the different stages of the controlled crystallization process [88].

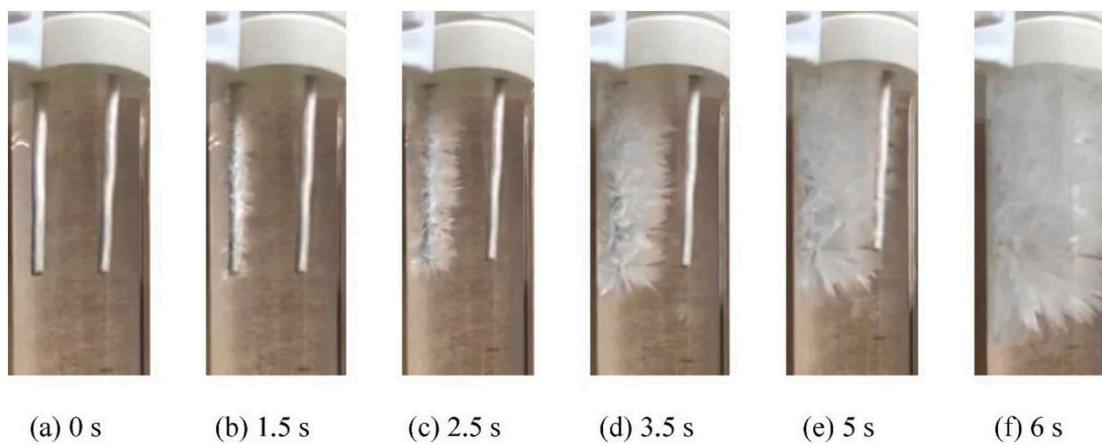
**4.1.2.2. Mechanical vibrations.** Mechanical excitation, as an alternative triggering method, has an excitation rate 2.75 times faster than the addition of crystalline species. The principle can be explained by reducing the nucleation-free energy barrier [138]. Ling et al. successfully triggered nucleation of supercooled  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in a short time with a vibrating device, in which about 126 kJ/kg of latent heat was released [14]. Zhou et al. conducted an experimental study on the effect of impact vibration triggering the solidification of a supercooled sodium acetate salt solution in a rounded rectangular thermal storage container using steel balls falling freely on the surface of a rounded rectangular thermal storage container. The experimental study showed that the activation of the solidification of the supercooled sodium acetate solution was favored by higher impact momentum (larger ball diameter and higher drop height) and when the impact was close to the lid cover and the edge of the container. But there was no mention of how much latent heat was released. In addition, the concept of impact effect was proposed to evaluate the impact effect on solidification activation [139]. Wang

et al. found that low impact energy of 0.007 J could reduce the supercooling degree by 80 %. In addition, they modified an existing model based on experimental data to create a revised model that estimates the impact energy required to trigger nucleation at the desired supercooling [138].

**4.1.2.3. Application of electric field.** Triggering crystallization can also be achieved by applying an electric field, and Fig. 20 shows the use of an electric field to trigger the nucleation of sodium acetate trihydrate. The method of applying electricity to a supercooled solution has advantages over other approaches, such as allowing small devices, requiring only a small amount of electricity that can be supplied by a 1.5 V dry cell, a simple switching system, and the reliable and high reproducibility of 100 % nucleation [140]. The basic principle is that reactive particles in solution, such as metal hydration ions, migrate towards the surface of the electrode in the presence of an electric field. The reactive particles that migrate near the electrode surface undergo a chemical conversion reaction (the hydration of the metal hydride ions is reduced and rearranged, and the coordination number of the metal ions is reduced). The reactive particles gain electrons and these are reduced to adsorbed metal atoms. The newly adsorbed metal atoms diffuse along the electrode surface to appropriate locations (growth sites) and enter the metal lattice to grow or aggregate with other new atoms to form nuclei and grow, thus forming crystals [141]. The magnitude of the voltage, the electric field's frequency, and the electrode's diameter are all important factors that affect the crystallization efficiency. In addition, Kumano et al. indicated in their study that the nucleation of supercooled PCMs is related to the electrode material [142]. Currently, the most common



**Fig. 19.** Controlled crystallization process: (a) intentional injection of bubbles during cooling, (b) intentional injection of bubbles during supercooling, (c) trigger moment at  $\Delta T_{\text{sup}} = 38$  °C recorded by digital thermocouple [88].

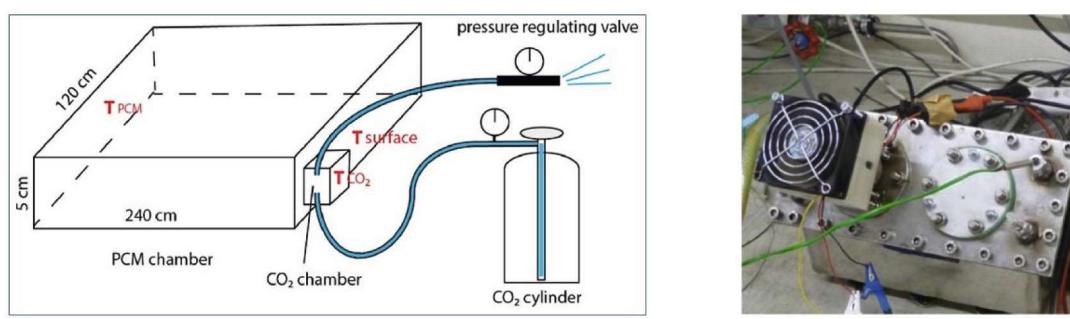


**Fig. 20.** Crystallization of supercooled sodium acetate trihydrate solution after electrical triggering [143].

electrodes are copper and silver electrodes. Relevant studies have shown that the performance of supercooled PCMs, copper electrodes, and silver-plated iron electrodes is rather unstable. In contrast, Ag electrodes show reliable long-term triggering performance. The reason for this is that the electrode potential of Ag is much higher than that of Cu; therefore, it is easier to develop a high transient electric field after the formation of the nucleus [143]. Munakata et al. showed that by varying the electric field's waveform, frequency and amplitude of the electric field it was possible to not only trigger crystallization but also achieve stable supercooling of the solution. A  $-1.5$  V DC electric field applied to a copper electrode can maintain the supercooled state of the solution. Solidification can always be initiated within 90 s by applying a rectangular wave electric field of 0.2 Hz and 1.5–3 Vp-p amplitude to the SAT solution [144]. Kurniawati et al. indicated that DC voltage provides favorable conditions for the nucleation process by reducing the randomness of the nucleation process. It was shown that the degree of supercooling varies with the interval between applied electric fields, the longer the time of the applied field, the smaller the degree of supercooling [145]. Dong et al. used a small DC voltage to trigger the crystallization of a supercooled SAT solution in their experiments. Ag electrodes with diameters  $>1.0$  mm were found to exhibit the best-triggering performance at DC voltages between 1.0 V and 1.8 V. Furthermore, an analysis of the effect of supercooling on the crystallization process showed that increasing the supercooling reduced the effective heat release from SAT solutions [143]. Sakurai et al. used Ag anodes with surface-embedded SAT crystals as latent heat storage devices to study electrogenic nucleation in supercooled aqueous SA solutions (45–54 wt%). It was shown that Ag anodes with SAT crystals embedded on the surface were more effective than standard Ag anodes.

Fast electrical nucleation is achieved when the DC voltage is  $>1.4$  V. When the voltage is set to  $>1.8$  V, the induction time for electro-nucleation increases with the number of operations. The Ag anode life increases when the voltage is  $<1.8$  V. At a voltage of 2.0 V, the anode resistance increases as the number of operations increases, the anode surface deteriorates and silver oxide is formed. In addition, the electroporation's repeatability and the supercooled solution's stability depend on the surface roughness [140].

**4.1.2.4. Cooling crystallization.** In addition, controlling the initialization of crystallization by cooling has also been shown to be feasible. Englmair et al. indicated that localized rapid cooling of a small portion of the PCMs storage cell could potentially be used as a way to initiate supercooled SAT crystallization. This could be used for a variety of SAT composite applications as long as the temperature reached is low enough. Their experiments successfully initialized crystallization by evaporating carbon dioxide through a chamber adjacent to the PCMs chamber containing the supercooled SAT composites (Fig. 21(a)). In addition, when the SAT was supercooled to below 30 °C, local cooling was also able to be generated through the Peltier elements mounted on the PCMs chamber at a low enough level to initiate the crystallization of the SAT composite (Fig. 21(b)). Using both methods, PCMs can all start to crystallize within 2–5 min [130]. Wang et al. experimentally investigated the effect of local cooling of semiconductor coolers on triggering the crystallization of supercooled SAT, STP, and their binary mixtures with different mass ratios. It was found that SAT has a higher discharge temperature and longer discharge time than STP, and the induction time and exothermic time of SAT are 39 s and 3 h respectively; however, after several melting-freezing cycles, STP has less phase separation, better



(a) Schematic diagram of the nucleation method using  $\text{CO}_2$  cooling.

(b) Peltier device installed on a thermal storage prototype.

**Fig. 21.** Trigger by lowering the temperature to the crystallization temperature [130].

cycle stability, and a shorter crystallization induction period than SAT. In addition, supercooled SAT-TP mixtures are more difficult to trigger than single-component hydrates but can effectively alleviate the phase separation problem of SAT. The crystallization induction period showed a trend of increasing and then decreasing with the increase of SAT content in SAT-TP blends. It was shown that the discharge time of eutectic mixtures above 30 °C was also longer compared to that of single-component hydrates [146].

#### 4.1.3. Thermal insulation

Theoretically, insulating the PCMs thermal storage container in the supercooled seasonal thermal energy storage is no need. However, in the current experimental study, to reduce sensible heat loss, still choose to insulate the heat source, piping, PCMs heat storage container, water tank and other components. The supercooled storage module can be insulated and placed in the basement, the heat loss from supercooling can also be reduced [42]. The ambient temperature, the material of the heat storage container and the thermal conductivity of the PCMs are all important factors affecting the thermal insulation. Insulation performance depends on the insulation method and the choice of insulation material. Two common insulation methods include (a) insulation applied to the exterior walls of storage chambers (e.g., using organic foam or vacuum insulation panels); (b) double-walled vacuum envelopes packed with powder pellets (also known as evacuated powders) [147]. The first method is more common in seasonal thermal energy storage.

The principle of action of insulation materials can be explained as a very good slow conductivity of heat through the air or inert gas in the very many small closed pores of the material itself, which makes the material itself change very slowly with the external temperature change and finally achieve insulation. Generally, insulation materials can be divided into organic foam materials (EPS, XPS and PUR-PIR) and inorganic fiber materials (rock wool, glass wool). When selecting insulation materials for seasonal thermal energy storage applications, thermal conductivity, moisture absorption, corrosion resistance, fire resistance, cost, flexibility, etc., need to be considered. Also, the degree of influence of the material on the environment needs to be taken into account. In 2022, Zhao et al. analyzed the environmental impact of some currently used insulation materials. In their article, they state that among the insulation materials used, PS, XPS, PU, and phenolic foam are four typical plastic insulation materials, but their adoption poses environmental severe impacts and fire risks. Silicone aerogel, dynamic insulation, PCMs, closed cell foam, gas-filled panels, vacuum insulation panels (VIP), reflective porous panels and nanoscale insulation are the more advanced insulation materials available. However, the weaknesses of these advanced insulation materials, such as high cost, inflexibility, thermal instability, poor mechanical strength, or uncertain service life, still limit their widespread use in the current building market [148]. The selection of insulation materials for seasonal thermal energy storage in more detail by Villasmil [147] and Bott [149] in their review. Mycelium-based composites and biocomposite materials are also an advanced areas of current research in insulation materials [150].

The materials mentioned below also include those used for the other two seasonal thermal energy storage methods. Consider all factors together. Polyurethane, polyurethane/polyisocyanurate (PUR/PIR), foam glass, glass wool, and extruded polystyrene (EPS) board are commonly used insulation materials in seasonal thermal energy storage. Zhou et al. used two layers of 50 mm thick polyurethane and 15 mm thick rubber/plastic insulation board for the heat source tank and heat storage tank in their experiments to reduce heat loss [151]. Englmaier et al. used 0.15 m of foam insulation to insulate the tank in their system to minimize sensible heat loss [152]. Gao et al. used 50 mm plastic insulation (thermal conductivity of 0.034 W/(K·m)) to insulate the hot water storage tank [20].

#### 4.2. Researches of STES systems

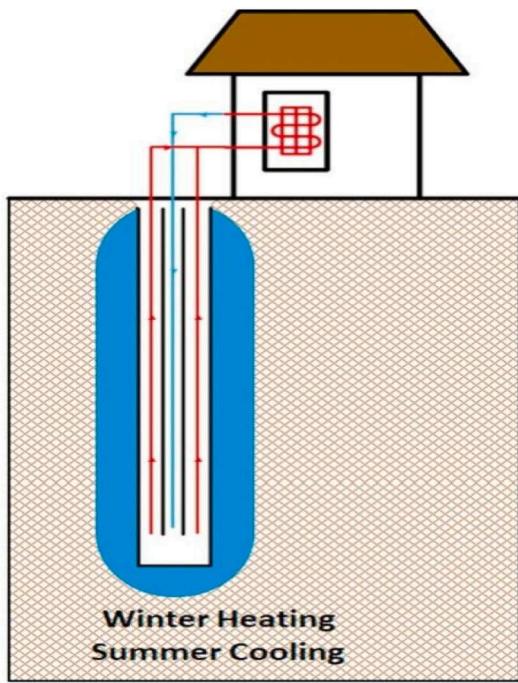
At present, there are few seasonal thermal energy storage systems with PCMs as the main storage medium, and those that exist are mostly at the experimental stage, and the PCMs that can be applied are relatively single. In most seasonal thermal energy storage systems, the PCMs mainly play an auxiliary role and do not act as the main thermal storage medium. There are two ways to use PCMs as seasonal thermal energy storage media, one is the direct-type, which directly uses the performance of PCMs, and the other we can call the supercooling-type, that is, using its supercooling capacity for thermal storage, the latter way is also the main way to use PCMs for seasonal thermal energy storage. The inherent defects of PCMs limit their large-scale application, especially in seasonal thermal energy storage. In the case that the stable supercooling and triggered crystallization technologies are not very mature, the difficulty of stable supercooling and triggered crystallization increases greatly with the increase of scale. In general, such systems mainly consist of solar collectors, heat exchangers, PCMs storage containers, water tanks, etc. This subsection focuses on the currently available seasonal systems that utilize phase change capacity storage.

##### 4.2.1. Cases of direct-type system

In 2008, Qi et al. designed a solar heat pump heating system with seasonal latent heat storage (SHPH-SLHTS system). They developed a mathematical model of the system to study its system performance. The system mainly consists of solar collector, thermal storage tank, heat pump unit, circuit pump and valve, etc. The storage medium used is  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . In summer, the heat transfer fluid (HTF), which gets energy from the solar collector, flows to the storage tank and injects energy into the PCMs in the storage tank. After that, it goes back to the solar collector. During winter operation, the storage tank extracts the energy from the PCMs stored in the storage tank and then flows to the evaporator of the heat pump unit to provide a heat source for space heating. Studies have shown that SHPH-SLHTS systems are smaller in size than central solar heating systems that use water for seasonal storage. But SHPH-SLHTS systems also have some disadvantages: (1) higher cost (2) more complex storage tanks due to more units inside the storage tanks [40]. In 2019, Fong et al. proposed a novel seasonal energy storage system that primarily utilizes the phase change capacity of groundwater as a storage medium. The system can utilize relatively stable ground temperatures to create a thermal gradient that allows for heating in winter and cooling in summer. The basic principle can be explained as follows: in winter, cold air passes through the exchanger, absorbing heat from the ground and forcing the water in the soil pores to undergo a phase change; in summer, hot air passes through the exchanger, melting the ice and cooling the air, the basic principle of which can be seen in Fig. 22. The results of the study show that the system is best suited as a preheating or pre-cooling phase, using low-grade heat/cooling to reduce the use of high-grade energy (electricity or natural gas) [153].

##### 4.2.2. Cases of supercooling-type system

In 2014, Hirano et al. evaluated the thermal characteristics of reheating operation using a supercooled latent heat storage device by experimentally encapsulating sugars in a thin, long cylindrical copper container. The energy storage device allowed 12.7 MJ of sensible heat to be extracted from the storage tank after the melting process. During the solidification process, 34.8 MJ is released from the storage tank. And after 56 h of supercooled storage, 27.1 MJ of heat was extracted. The study shows that the reheating method can effectively maintain the supercooled state in thermal equilibrium [128]. In 2017, Zhou et al. developed and applied a multiphase model to perform 3D transient CFD simulations of supercooled PCMs discharge characteristics. Three typical processes of stable supercooling triggered crystallization and regular solidification cycles were identified and analyzed. The simulation results show that during the stable supercooling period, the PCMs are finally in thermal equilibrium with the surrounding environment.



**Fig. 22.** Schematic diagram of the proposed full-size system [153].

The energy will be stored in this supercooled liquid state for a long time without external disturbance. During the trigger crystallization, the PCMs temperature rises rapidly to the melting point in a very short period of time. During regular solidification, the change starts at the upper and sidewall surfaces and then extends to the inner planes. Of the three processes, the regular solidification period accounts for a larger share of the exothermic heat [148].

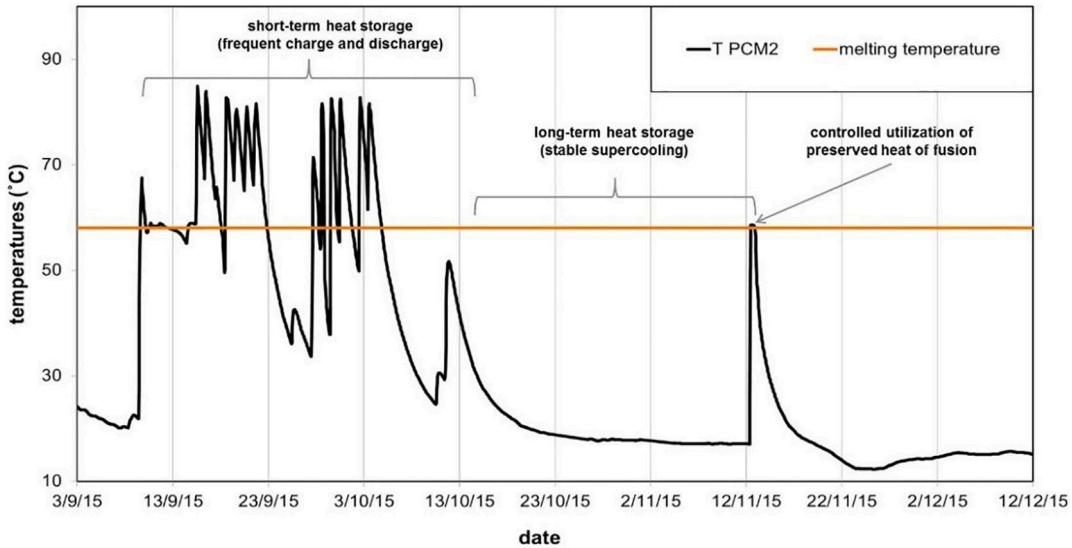
In 2018, Englmair et al. designed a prototype segmented thermal storage system with a  $22.4 \text{ m}^2$  solar collector, four 200 kg PCMs storage units, and a 735 L water tank. The system utilizes stable supercooling of the sodium acetate trihydrate composite to preserve latent heat of melting for long-term heat storage. Fig. 23 shows how a combined short- and long-term heat storage sequence with PCMs storage is achieved. The system does this by directing heat from the solar collector array to PCMs storage or water buffer storage. For solar charging, the temperature of

the heat transfer fluid within the operating range is controlled by an automatic sequence operating through a combination of a water tank and a variable number of PCMs units. The fluctuating heat transfer rate of the  $22.4 \text{ m}^2$  vacuum-tube collector array in the system reaches a peak of 16 kW, allowing for rapid charging of individual PCMs units (250 min). The single unit was charged with 27.4 kWh of heat in 4 h on a sunny day, and the PCMs temperature increased from  $20^\circ\text{C}$  to  $80^\circ\text{C}$ . In addition, fast unit charging in the supercooled state does not cause spontaneous crystallization. This allows the melted PCMs to be used as short-term sensible heat storage without compromising its long-term storage potential. At the same time, reliable supercooling is achieved for three PCMs cells out of the four cells in storage. The system uses mechanical crystal seed injection to initialize the crystallization. The peak discharge per unit during solidification is 8 kW. approximately 80 % of the latent heat of melting is transferred from the PCMs container to the tank within 5 h after solidification of the supercooled sodium acetate trihydrate. The thermal power and flow temperature of this PCMs unit discharged without and during solidification are high enough to meet the space heating demand of a domestic building. However, to ensure supply temperatures above  $45^\circ\text{C}$ , a backup heater must also be used to achieve a hot water supply [49].

In 2019, Englmair et al. developed a new combined solar energy system with short- and long-term thermal storage based on previous research (Fig. 24). Also, a numerical model was developed to investigate the performance potential of a combined utilization system of a water tank and PCMs unit, including on-demand crystallization of supercooled sodium acetate trihydrate. The prototype system consists of a  $22.4 \text{ m}^2$  (aperture) evacuated tubular collector, a 735 L water tank, and four PCMs cells, each containing 150 L of sodium acetate trihydrate composite. Studies have shown that a 200-l PCMs unit allows more efficient use of a  $0.6 \text{ m}^3$  water tank. The optimal solar collector array tilt is  $70^\circ$ . The study shows that the heat storage capacity of the PCMs can be utilized at least 5.5 times per year, and the storage capacity of the water tank will be utilized 116 times per year. With the optimized strategy, the solar fraction for heating is 71 % per year [154].

In 2020, Englmair et al. conducted a systematic test of evacuated tube collector arrays, space heating, and domestic hot water modes for a standard-scale passive house study under Danish climatic conditions and determined some practical operating parameters through the test. Fig. 25 shows the control strategy for this system [152].

In 2022, Wang et al. designed flexible thermal energy storage with short- and long-term heat storage using 137.8 kg of PCMs and 75 L of water as the heat storage material and investigated the thermal



**Fig. 23.** Operation sequence of charging and discharging PCMs units [49].

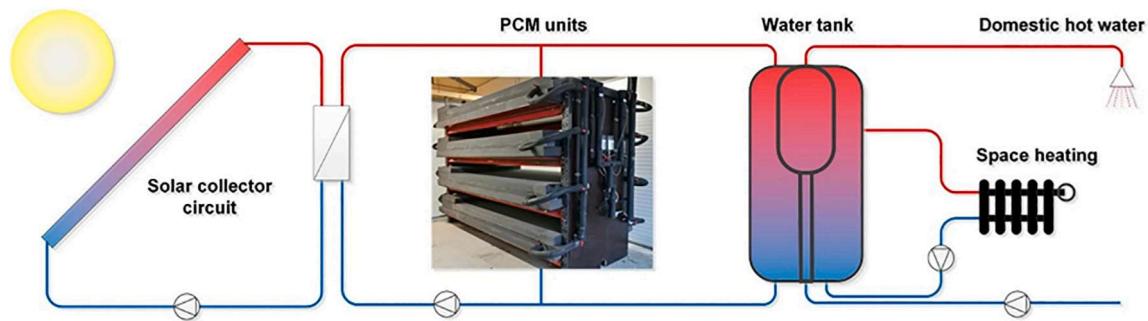


Fig. 24. Schematic diagram of the new solar combination system [154].

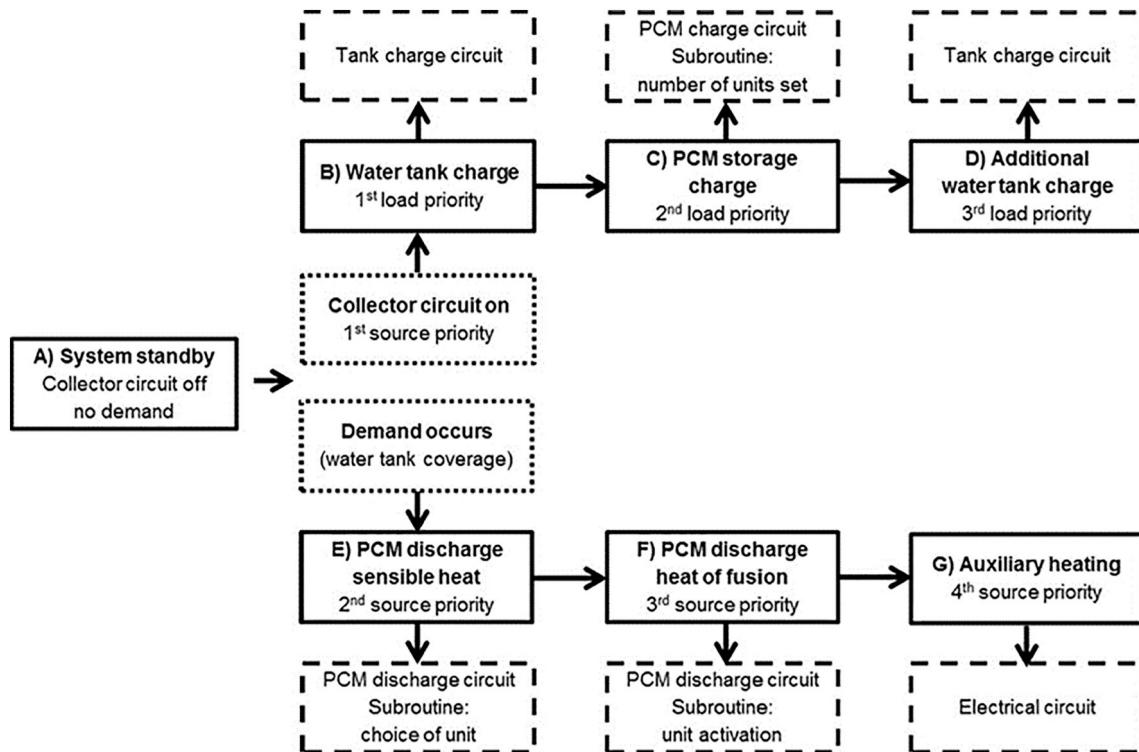


Fig. 25. Actual operation control during strategy [152].

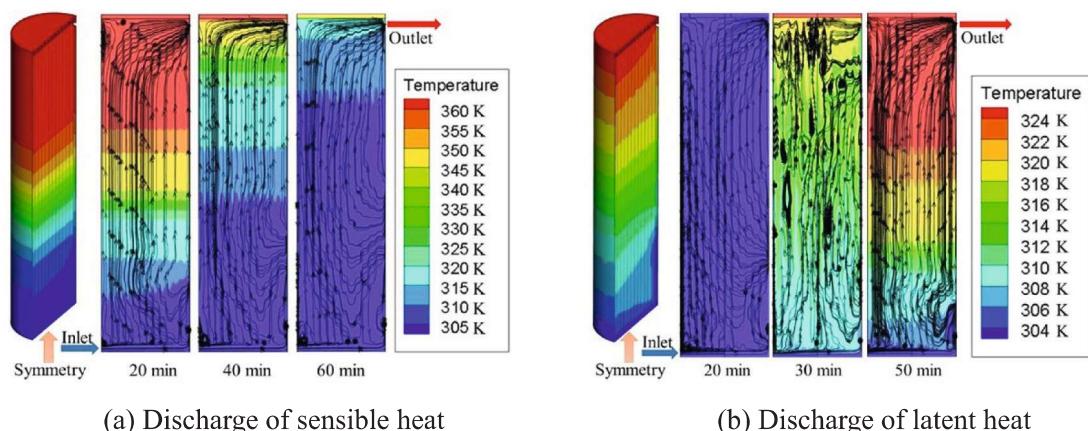


Fig. 26. Temperature distribution of the water flow pattern in the accumulator for different discharge processes [155].

performance and flowed characteristics of the storage heater through experiments and CFD simulations. After fully charging to 92 °C, the heat storage device can release heat flexibly in two steps. In the first step, 13.7 kWh of sensible heat can be released for short-term use; in the second step, 7.8 kWh of latent heat can be removed for long-term use. When releasing heat, there is a high degree of thermal stratification in the tank. In releasing sensible heat, the accumulator can provide 294 L of hot water with an average temperature of 68.2 °C. During latent heat release, 334 L of hot water with an average temperature of 46.7 °C is withdrawn from the accumulator. Fig. 26 (a) and (b) show the water flow pattern inside the accumulator during the sensible and latent heat release, respectively. The reduction rate of melting time in the heat storage system decreases with the increase of the flow rate, and the heat transfer effect of heat storage can be improved by increasing the flow rate. However, the effect decreases as the flow rate increases [155].

In the same year, Zhou et al. built a space heating system using supercooled PCMs. They conducted experiments on capillary mat floor water heating and direct heat release to room air using a thermal storage unit filled with supercooled liquid sodium acetate trihydrate (SAT). The system consists of a heat source, a heat storage tank, a test chamber, a heating terminal, a pump, connecting pipes, and a measuring instrument. The experimental study showed that using the capillary mat radiant floor end, the maximum water supply temperature reached 35 °C in 0.3 h. The room temperature increased from an initial 20.3 °C to a maximum of 25.8 °C in 2.8 h. After 12 h of system operation, the room temperature could be maintained above 24.8 °C. Although the direct heat release to indoor air is higher, the room temperature drops quickly. Compared with the direct discharge of heat to the indoor air, the capillary mat floor water heating temperature fluctuation is smaller and the vertical temperature gradient is lower, which can meet the room temperature requirements and has better thermal comfort [151]. Kutlu et al. designed a solar-assisted heat pump system for building heating and simulated a solar-assisted heat pump with a supercooled PCMs thermal storage unit in conjunction with the heating demand profile of an eco-house in Nottingham, UK. Fig. 27 shows the method of investigation of their overall system performance. The system consists of solar collectors, buffer tanks, heat pump units and supercooled SAT storage tanks, and each unit has a separate electrical trigger to trigger the SAT crystallization to activate according to the building's heating demand. The system can be energized during high solar radiation days and the stored heat is released according to the heating demand on the following days. Experimental studies have shown that the PCMs temperature can

increase from 20 °C to 56.4 °C in 20 s after triggering the crystallization. When an 8 cm diameter PCMs tube was used, the PCMs tank was found to have a charge time of 6.5 h [156].

## 5. Conclusion and future works

Seasonal thermal energy storage is of great significance in achieving low and zero-carbon goals. PCMs have received a lot of research due to their excellent properties. Seasonal thermal energy storage using the supercooling of PCMs can significantly save insulation costs. However, seasonal thermal energy storage using PCMs as the thermal storage medium is still in the development stage, and many problems are still to be solved. Stable supercooling and trigger crystallization are the two main problems. This paper reviews a brief introduction of the three existing seasonal thermal energy storage methods and a detailed review of seasonal thermal energy storage with supercooled PCMs as the storage medium. Supercooled seasonal thermal energy storage has excellent development prospects. The outlook of future key research directions is as follows:

- (1) Research on supercooled PCMs for seasonal thermal energy storage. The PCMs that can achieve stable supercooling are very few, and the research is dominated by inorganic hydrated salts SAT. In recent years, erythritol, xylitol, calcium chloride hexahydrate, and STP have also received some research and application. Generally speaking, PCMs used in seasonal thermal energy storage need to have several properties in addition to a suitable phase change temperature: ① Suitable supercooling. Firstly, using PCMs in seasonal thermal energy storage requires a certain degree of supercooling in the first place. Usually, the actual crystallization temperature is preferably lower than the ambient temperature, which is more conducive to preservation. Too much supercooling will make it more difficult to trigger crystallization, resulting in the latent heat being unable to be fully released. ② High latent heat. High latent heat of phase change reduces the cost of the heat storage container and the risk of spontaneous crystallization of the supercooled PCMs. ③ Others. In addition, the phase separation of PCMs, low thermal conductivity, corrosion, leakage, etc. still need further research.
- (2) More research on thermal storage containers with different geometries. At present, few thermal storage containers have been proven to be used for stable supercooling storage. There is a need

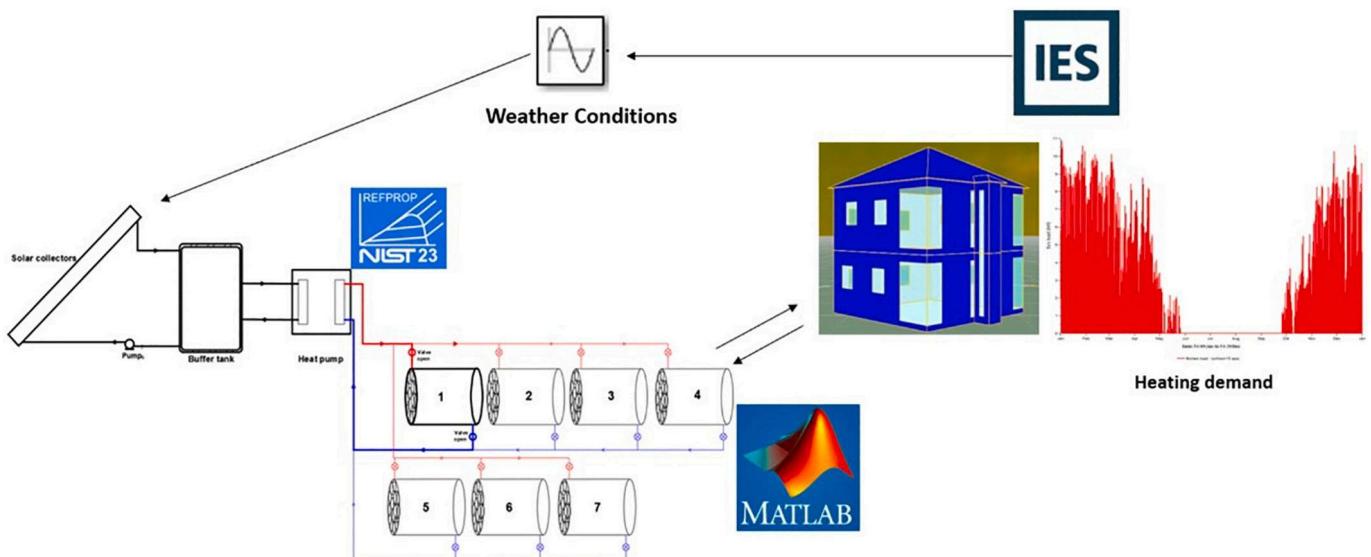


Fig. 27. Performance investigation methodology of the system [156].

- to study more thermal storage containers that can be used for stable supercooling of PCMs. Typically, these containers require good hermeticity, smooth inner surfaces, and small volumes, which are beneficial for achieving stable supercooling. Other relevant factors need to be further investigated. In addition, the internal structure of the cylindrical heat storage containers, which are mostly used in applications, needs further study. Coupling with the fins needs to be considered to enhance thermal conductivity and avoid incomplete melting in the container.
- (3) Research on the triggering method and triggering device. The triggering effect is different for different supercooled PCMs, and the common triggering methods are adding crystal seeds and mechanical shock. Among them, adding crystal seeds is the simplest and the highest success rate. Other triggering methods are difficult to guarantee the triggering effect in practical applications. In addition, in existing studies, little attention has been paid to the release of latent heat after triggering. Most of the attention is focused on the success rate and the time of triggering crystallization. The influence of triggering mode on the release of latent heat is also an important aspect. Therefore, further targeted research is needed on the triggering crystallization method. After the research of triggering devices, there are still few specific triggering devices with practical applications. In the study of the trigger device, it is necessary to consider the cyclic performance of the device, the trigger effect, whether it impacts the stability of supercooling, economics, and other factors.
- (4) Establishment and economic analysis of seasonal thermal energy storage system. At present, there are few systems for seasonal thermal energy storage, and the main application scenarios are relatively limited. The seasonal thermal energy storage system currently exists and has both short-term and long-term thermal storage functions. The main focus is on hot water supply and heating. In addition to this, more application scenarios need to be developed. Generally speaking, as the scale of the system increases, the unit investment process shows a gradually decreasing trend, and the price of PCMs greatly increases the initial investment of the system. Most of the current articles do not cover the economics of supercooled seasonal thermal energy storage. The economics can be analyzed in terms of payback period, traditional heating and hot water supply, and CO<sub>2</sub> emissions compared with the other two thermal storage methods.

In conclusion, although seasonal thermal energy storage with PCMs as the thermal storage medium has excellent application prospects, there are still many problems to be solved by researchers because it is just starting.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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