

Review

# Inorganic Salt Hydrate for Thermal Energy Storage

Ning Xie <sup>1</sup>, Zhaowen Huang <sup>1</sup>, Zigeng Luo <sup>1</sup>, Xuenong Gao <sup>1,2,\*</sup>, Yutang Fang <sup>1,2</sup> and Zhengguo Zhang <sup>1,2</sup> 

<sup>1</sup> Key Laboratory of Enhanced Heat Transfer and Energy Conservation, The Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China; clairening6628@outlook.com (N.X.); huang.linsay@gmail.com (Z.H.); zglo93@foxmail.com (Z.L.); ppytfang@scut.edu.cn (Y.F.); cezhang@scut.edu.cn (Z.Z.)

<sup>2</sup> Guangdong Engineering Technology Research Center of Efficient Heat Storage and Application, South China University of Technology, Guangzhou 510640, China

\* Correspondence: cexngao@scut.edu.cn; Tel.: +86-020-8711-4763

Received: 31 October 2017; Accepted: 14 December 2017; Published: 18 December 2017

**Abstract:** Using phase change materials (PCMs) for thermal energy storage has always been a hot topic within the research community due to their excellent performance on energy conservation such as energy efficiency in buildings, solar domestic hot water systems, textile industry, biomedical and food agroindustry. Several literatures have reported phase change materials concerning various aspects. Among these materials, salt hydrates are worthy of exploring due to their high-energy storage density, rational price, multiple sources and relatively good thermal conductivity. This paper reviews the present state of salt hydrates PCMs targeting classification, properties, defects, possible solutions as well as their idiographic features which are suitable for applications. In addition, new trends of future research are also indicated.

**Keywords:** inorganic salt hydrates; phase change materials; thermal energy storage; application

## 1. Introduction

With the growing consumption of fossil fuels and increasing emission of carbon dioxide, thermal energy storage (TES) has received a great deal of attention. Latent heat storage and sensible heat storage are two main forms of TES. Using phase change materials (PCMs) for latent heat storage, which can storage and release energy by melting and solidification, is becoming an effective way to solve the contradiction of supply and demand of energy, such as peak difference of power load and gap of solar energy [1,2]. High storage density, stable performance, wide phase change temperature range and reasonable price make PCMs play a significant role in energy conserving areas.

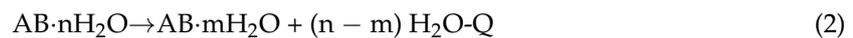
In the field of phase change energy storage technology, it is a fundamental step to develop high latent heat, stable, and cost-effective materials. Different types of PCMs have been studied after petroleum crisis in 1970s, including solid-solid PCMs (polyalcohols and other polymers), solid-gas PCMs and solid-liquid PCMs (salt and salt hydrates, clathrate hydrates, paraffins, fatty acids and their mixtures, alloys and ect) [3,4]. Among these, salt hydrates, which account for a large proportion in inorganic PCMs, have always been attracted attention owing to their reasonable price, wide sources, good thermal conductivity and high volumetric energy storage density. However, some defects, such as leakage, causticity, supercooling and phase separation impose restrictions on their practical applications [5–7]. In order to reduce such adverse effects, form-stable PCMs are studied recent years by incorporating PCMs into porous materials or through the method of microencapsulation to prevent leakage and phase separation [8–10]. Moreover, different kinds of nucleating agents have also been developed to reduce supercooling degree.

It is a promising direction to apply low-cost inorganic PCMs to energy conservation areas such as electric peak-shaving, industrial waste heat utilization, aerospace field, air conditioning cold storage

and so on. This paper reviews the research progress of salt hydrates for TES including properties, improvements as well as their specific characteristics, which are suitable for practical application in different fields in recent years. Research trends and potentials of these PCMs are also prospected.

## 2. Properties of Inorganic Salt Hydrated PCMs

Salt hydrates can be generally described as formula of  $AB \cdot nH_2O$ , where  $n$  represents number of water molecules and represents salt composition. During phase transformation dehydration of the salt happens, the process can be expressed as (1) and (2).



According to the phase transition performance, the salt hydrates can be divided into three categories: salt hydrates with congruent melting behavior, incongruent behavior and semi-congruent behavior. There is a good deal of salt hydrates that can be regarded as available candidates for PCMs. However, a large proportion of salt hydrates which process large transition latent heat and moderate phase change temperature cannot melt congruently. The most meritorious ones are salt hydrates with congruent melting behavior, low supercooling degree and competitive profitability. Thermophysical, kinetic and chemical properties of such salt hydrates, which can possibly meet the requirements, are presented in Table 1. The most representative salt hydrates are sodium sulfate decahydrate, calcium chloride hexahydrate, sodium phosphate, dodecahydrate and magnesium chloride hexahydrate [5,11]. However, the phase transition temperature range of single salt hydrate cannot always meet the requirements of practical application. Therefore, two or more salt hydrates can be mixed to adjust the melting point. Salt hydrate mixtures can be classified as eutectics with congruent behavior and non-eutectics with incongruent melting points. The eutectics do not tend to segregate during melting and freezing process because they freeze to a friendly blend of crystals [12–15]. Binary or multicomponent eutectics with a common melting point and large latent heat can reduce the melting point of single constituent salt hydrate and then they can be utilized in wider fields [16]. Besides, the eutectics can also make up for the deficiencies of single salt hydrates such as supercooling and phase separation. Liu [17,18] respectively added  $Na_2HPO_4 \cdot 10H_2O$  to  $Na_2SO_4 \cdot 10H_2O$  and  $Na_2CO_3 \cdot 10H_2O$  to prepare two novel eutectics. It demonstrated that  $Na_2HPO_4 \cdot 12H_2O$  can effectively inhibit phase separation of  $Na_2SO_4 \cdot 10H_2O$  and  $Na_2CO_3 \cdot 10H_2O$ . The melting point and supercooling degree of the prepared eutectics also decreased. Some of salt hydrate eutectics with potential use as PCMs are listed in Table 2.

**Table 1.** Thermo-physical properties of salt hydrates.

Salt Hydrates	Melting Temperature (°C)	Heat of Fusion (J/g)	Density (Solid) (10 <sup>3</sup> kg/m <sup>3</sup> )	Thermal Conductivity (Solid) (W/mK)	Specific Heat (Solid) (J/g·°C)	Reference
LiClO <sub>3</sub> ·3H <sub>2</sub> O	8	253				[13]
KF·4H <sub>2</sub> O	19	231	1.45		1.84	[5,11]
Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	25.8	125.9	1.60			[13]
CaCl <sub>2</sub> ·6H <sub>2</sub> O	28	174	1.80	1.088	1.42	[1,13]
LiNO <sub>3</sub> ·3H <sub>2</sub> O	30	256				[13]
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	32.4	248	1.49			[14]
Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	33	247			1.88	[14]
CaBr <sub>2</sub> ·4H <sub>2</sub> O	34	115.5	1.52			[19]
LiBr <sub>2</sub> ·2H <sub>2</sub> O	34	124				[19]
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	35–44	280		0.514	1.7	[5,11]
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	36	149.6	1.94		1.34	[19]
KF·2H <sub>2</sub> O	42	162				[14,19]
MgI <sub>2</sub> ·2H <sub>2</sub> O	42	133				[5,11]
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	42.4				1.46	[14]
Fe(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O	47	155				[14]
Na <sub>2</sub> SiO <sub>3</sub> ·4H <sub>2</sub> O	48	168				[14]
K <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O	48	99				[14]
MgSO <sub>4</sub> ·7H <sub>2</sub> O	48.5	202				[1]
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	49	220	1.75	1.46		[1]
Ca(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	51	104		1.46		[14]
FeCl <sub>3</sub> ·2H <sub>2</sub> O	56	90				[1]
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	57	169				[1]
CH <sub>3</sub> COONa·3H <sub>2</sub> O	58	226–264	1.45	1.97		[1,14]
MgCl <sub>2</sub> ·4H <sub>2</sub> O	58	178				[14]
Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	65–69	190				[14]
LiCH <sub>3</sub> COO·2H <sub>2</sub> O	70	150				[14]
Na <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·12H <sub>2</sub> O	70	184				[14]
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	78	266				[14]
Al(NO <sub>3</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	89			1.17		[1]
Al(NO <sub>3</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	89.3	150				[1]
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	89.9	163	1.636	1.81	0.669	[1]
NH <sub>4</sub> Al(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	95	269	1.65	1.71		[1]
Al <sub>2</sub> (SO <sub>3</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	112					[1]
MgCl <sub>2</sub> ·6H <sub>2</sub> O	117	167	1.56	1.59		[14]

**Table 2.** Melting temperatures and heat of fusion of some eutectic mixtures.

Eutectic Mixtures	Melting Temperature (°C)	Heat of Fusion (J/g)	Reference
55% CaCl <sub>2</sub> ·6H <sub>2</sub> O + 45% CaBr <sub>2</sub> ·6H <sub>2</sub> O	14.7	140	[1]
75% CaCl <sub>2</sub> ·6H <sub>2</sub> O + 25% MgCl <sub>2</sub> ·6H <sub>2</sub> O	21.4	102.3	[16]
66.6% CaCl <sub>2</sub> ·6H <sub>2</sub> O + 33.3% MgCl <sub>2</sub> ·6H <sub>2</sub> O	25	127	[1]
40% Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O + 60% Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	27.3	220.2	[17]
47% Ca(NO <sub>3</sub> ) <sub>2</sub> ·10H <sub>2</sub> O + 33% Mg(NO <sub>3</sub> ) <sub>2</sub> ·10H <sub>2</sub> O	30	136	[1]
25% Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O + 75% Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	31.2	262.3	[18]
58.7% Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + 41.3% MgCl <sub>2</sub> ·6H <sub>2</sub> O	59	132.2	[1,13]
50% Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + 50% MgCl <sub>2</sub> ·6H <sub>2</sub> O	58–59	132	[1]
80% Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + 20% MgCl <sub>2</sub> ·9H <sub>2</sub> O	60	150	[1]
53% Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O + 47% AL(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O	66	168	[13]
14% LiNO <sub>3</sub> ·3H <sub>2</sub> O + 86% Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	72	180	[1]

Generally speaking, it is difficult to determine the thermo-physical properties of PCMs due to the limitation of the conventional devices such as differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC) and differential thermal analysis (DTA). DSC method is common for measuring enthalpy, specific heat and phase change temperature for PCMs. However, only a small amount of samples can be measured once, which lead to possible errors of results. In addition to this, the measuring results are largely influenced by environmental factors. Consequently, the investigations on thermo-physical properties of salt hydrates are inadequate in literature. However, they are vital for heat flow transformation process, which is a decisive factor for effective heat storage system. In recent years, Temperature-history (T-history) method has been mentioned by Yin et al. [20]. As a simple, accurate, and economic way for determining the main thermophysical properties such as enthalpy, specific heat, supercooling degree as well as process of phase transition, T-history method represents an advance to obtain average properties of PCMs especially for sensitive salt hydrate PCMs which suffer supercooling.

### 3. Supercooling of Salt Hydrates

Supercooling is a common phenomenon among salt hydrates due to their poor nucleating ability [20]. Some salt hydrates without a nucleating agent do not crystallize even when supercooling temperature is decreased under tens of degrees. This always brings undesirable effects to practical application [21]. For instance, when we impregnated salt hydrates into building materials using as wall boards, the phenomenon of supercooling impedes the solidification process of PCMs and then the storing heat in PCMs cannot release even when the surrounding temperature has reached their freezing point. Consequently, the PCM with high supercooling degree will not have functions to regulate the indoor temperature fluctuation and this lead to the lost of the meaning of latent thermal energy storage. Supercooling degree depends on several kinds of parameters, such as nucleating agents, cooling rate, stirring rate, stirring time, solution composition. To overcome the supercooling problems, a number of methods have been suggested. One of the most effective and economical ways is adding nucleating agents. Theoretically, the choice of nucleating agents should be close to the lattice parameter of the target materials. For instance, Borax is always regarded as the most suitable nucleating agents for Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, which can reduce supercooling of Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O from 15 °C to about 2–3 °C [22]. Wu et al. [23] investigated the surface effects of interaction between salt hydrates and nano-particles. Three nano-particles of aerosol SiO<sub>2</sub>, RNS-A SiO<sub>2</sub> and liquid phase SiO<sub>2</sub> were compared by adding them to Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O. Results showed that aerosol SiO<sub>2</sub> can easily suppress the supercooling. CaCl<sub>2</sub>·6H<sub>2</sub>O is also mentioned frequently as a kind of fine PCMs. However, its supercooling degree is up to 20 °C. Sutjahja [24] used SrCl<sub>2</sub>·6H<sub>2</sub>O (1.0 wt %), Ba<sub>2</sub>CO<sub>3</sub> (0.5 wt %), and K<sub>2</sub>CO<sub>3</sub> (0.5 wt %) as additives to CaCl<sub>2</sub>·6H<sub>2</sub>O. It was found that SrCl<sub>2</sub>·6H<sub>2</sub>O exerted the best effect on CaCl<sub>2</sub>·6H<sub>2</sub>O, this result was consistence with paper [25]. Palittin [26] adopted sonocrystallization method which used ultrasound radiation for promoting CaCl<sub>2</sub>·6H<sub>2</sub>O to crystallize and results indicated this technique

made crystals have uniform distribution and dense arrangement. Analogously, Miyasaka et al. [27] observed that ultrasound irradiation excelled in controlling primary nucleation of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and suggested that nucleation induced by ultrasound was probably the main cause of temperature rise. Application of nanomaterials has recently put forward to give notable effect on reducing supercooling degree. Li et al. [28] focused on nanocomposite PCMs and found that the degree of supercooling is within the range of 0.3–1.1 °C when  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  composite contained with 1 wt % nanomaterials and the complete solidification times were reduced by 17.84%. Fine graphite powder less than 50  $\mu\text{m}$  [29], borax [30], disodium phosphate dodecahydrate [31] and nano silver particles [32] can reduce the supercooling degree of  $\text{C}_2\text{H}_3\text{NaO}_2 \cdot 3\text{H}_2\text{O}$  under 2 °C. Calcium oxalate monohydrate [33],  $\text{SrCO}_3$  [34],  $\text{Sr}(\text{OH})_2$  [34,35]  $\text{SrCO}_3$  [35] and  $\text{Na}_3\text{AlF}_6$  [36] are both good nucleating agents for bischofite ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). For decreasing supercooling degree of  $\text{Mg}(\text{NO}_3)_6$ , both  $\text{Mg}(\text{OH})_2$  and  $\text{BaO}$  are good choice to promote its crystallization [37]. Ushak et al. [38] reports that supercooling of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  was slightly reduced by adding 1 wt %  $\text{NaCl}$ . Another paper [39] demonstrated that black carbon was good for crystallization of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CaF}_2$  was beneficial for  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . In conclusion, graphite nanoparticles, metal nanoparticles, nano-silica molecules, borax are relatively effective nucleating agents, ultrasonic can also be regarded as good methods for reduce supercooling degree. Further research may pay attention on this.

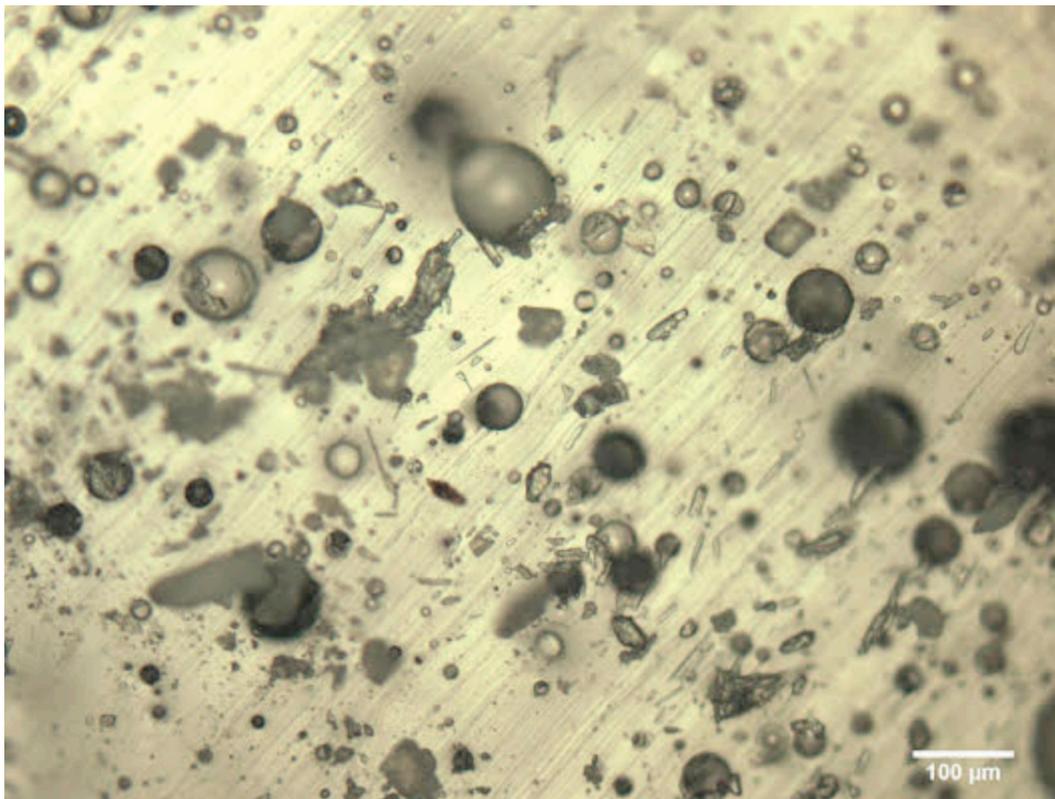
#### 4. Phase Separation of Salt Hydrates

A number of salt hydrates with large latent heat which can be regarded as PCMs cannot melt congruently [11]. As a result, the amount of water released by salt hydrates is no enough to dissolve the crystalline salt formed during the process of dehydration. Residual salts will deposit on the bottom due to a larger density and then lead to phase separation. With the continuous cold-thermal cycle, the sediments will continue to increase, resulting in gradually declining of thermal storage capacity. Thus, phase separation is another major problem of salt hydrate PCMs [40].

Adding thickener agents into salt hydrates is one of common methods to minimize or avoid phase separation. Many researchers used hydroxyethyl cellulose, nanocellulose, cellulose [41–44], super absorbent polymer [45], polyethylene glycol [46] and some silicone derivatives [47] as thickeners. Porous materials such as expanded graphite [29,48], diatomite [49–51] and nano-titanium dioxide [52,53] etc. were also reported as fine supporting materials for inorganic materials. They increase the viscosity of solution so that the solid particles can be evenly distributed. In addition to this, microencapsulation, macro encapsulation (hermetically packed in vessel) and impregnation with porous materials to prepare composite PCMs are effective methods. This cannot only solve problems of phase separation, but can also effectively prevent leakage problem attributing to the melting process of PCMs.

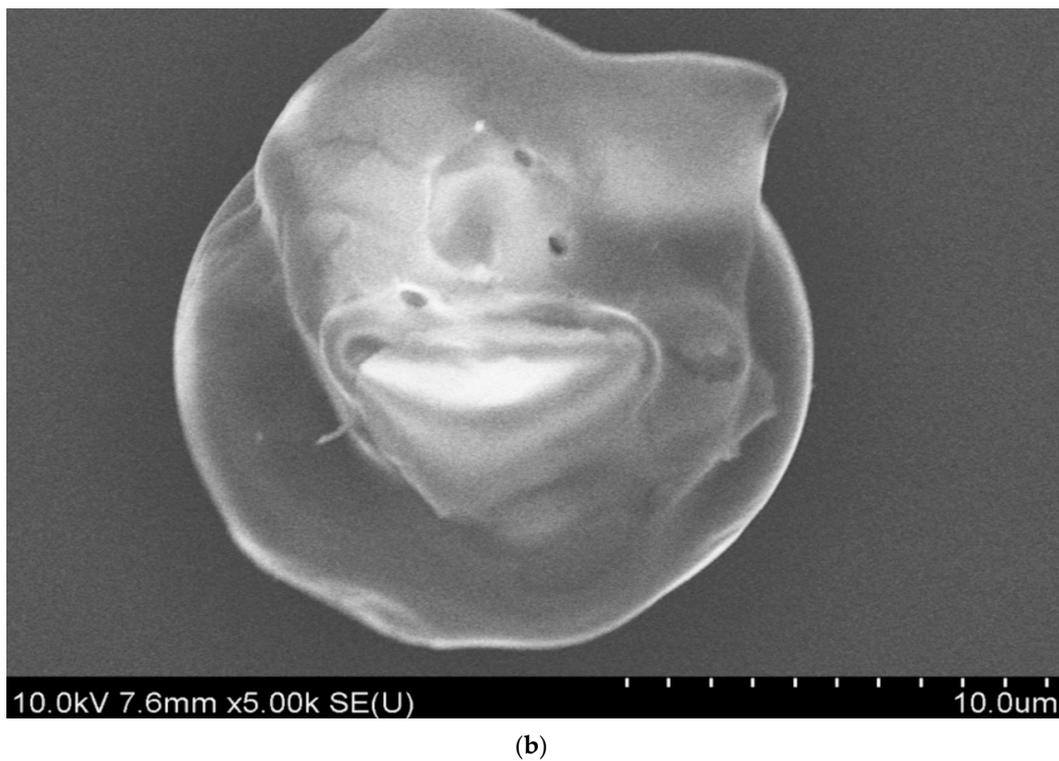
Microencapsulation phase change materials (MEPCMs) usually consist of a polymeric material as shell and a desired PCM as core [54]. Microencapsulated salt hydrates can reduce the reactivity with the outside surroundings, which can be utilized in powder form or dispersed into a carrier fluid, and then prevent PCMs from phase separation and leakage. Physical and chemical processes are two major methods to prepare MEPCMs. Physical methods typically consist of spray drying, fluidized bed and complex coacervation. Interfacial polymerization, in situ polymerization, suspension-like polymerization, and sol-gel methods make up chemical method [55,56]. Hitherto, vast researches have accomplished to formulate MEPCMs, whereas most of them focused on organic materials as cores because it is more troublesome to formulate water-solubility salt hydrate MEPCMs. Consequently, only a few literatures have reported hydrated salt microencapsulation. Streufert [57] outlined a novel microencapsulated PCM which used sodium acetate trihydrate as core materials. Its ability of dispersions into a matrix and variation of mechanical properties were investigated. The study performed two different emulsions: emulsion by using microfluidic device with acrylate as shell material and emulsions preparing by mechanically creating with poly(trimethylene carbonate) (PLA) as shell. Figures 1 and 2 shows SEM image and optical microscope image of the PLA microcapsules and

microfluidic device as microcapsules, respectively. From the results we can clearly see more stable and less dispersive microcapsules by microfluidic device. The microcapsules showed outstanding performance without leakage and phase separation. Fully loaded microencapsulated PCM with  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  as core and methyl methacrylate as shell was prepared by Huang et al. [58], which was exploited suspension copolymerization-solvent volatile method. During the procedure of polymerization reaction, the original salt hydrate  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  lost 5 crystal waters through heating process and the remainder was successfully scattered into organic solvent. It was worthy noted that the thermal conductivity did not seem to change after microencapsulated  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  formed. This excellent PMMA/ $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  MEPCM can be deemed as a potential material for solar space heating.

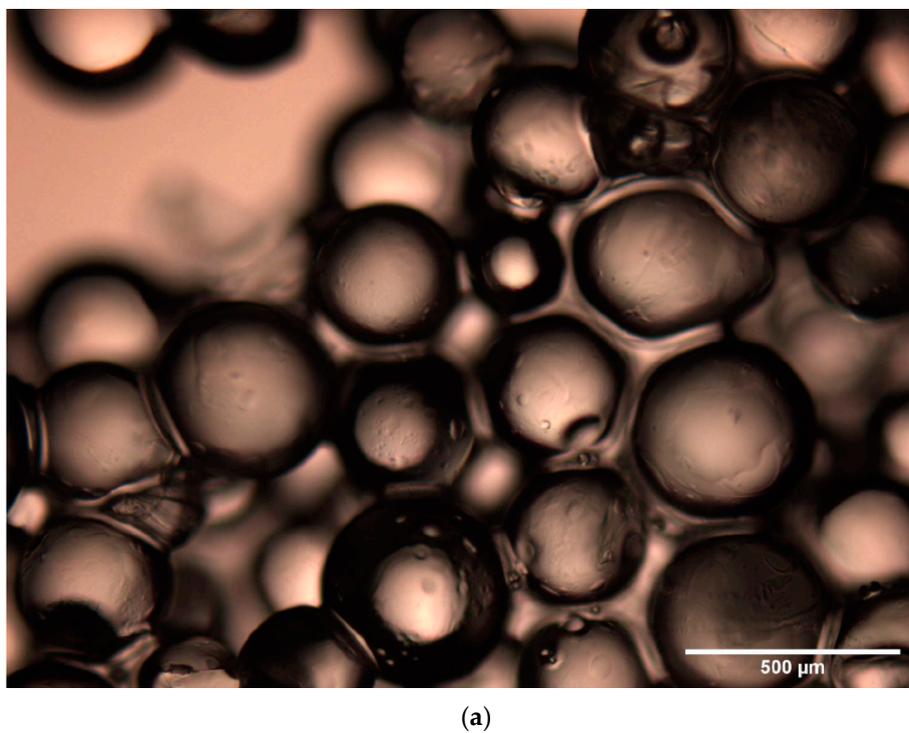


(a)

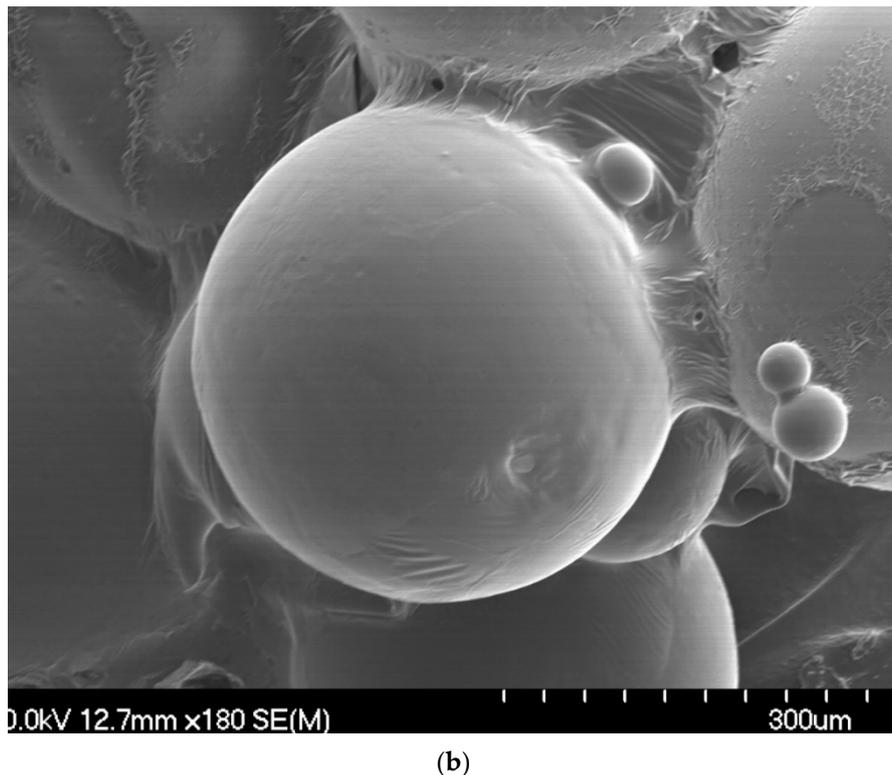
**Figure 1.** *Cont.*



**Figure 1.** (a) Optical microscope images and (b) SEM (Scanning Electron Microscope) image of the PLA (polytrimethylene carbonate) microcapsules in vacuum. Reproduced with permission from [57], IDEALS, copyright 2015.



**Figure 2.** *Cont.*



**Figure 2.** (a) Optical microscope images and (b) SEM image of microcapsules synthesized in a microfluidic device. Reproduced with permission from [57], IDEALS, copyright 2015.

Porous materials like carbon foam, diatomite, expanded graphite and expanded perlite used as supporting materials can also effectively overcome leakage, phase separation and corrosion problems of PCMs. Such composite materials are often synthesized by blending or impregnating PCMs with porous matrix [59]. The supporting materials with large specific surface area make liquid materials be adsorbed by their internal pores and then shortcomings of phase separation and leakage of PCMs can be overcome. EG (expanded graphite) is a sort of carbon materials by heating graphite at high temperature through microwave irradiation. EG/PCM composites have good performance with high thermal conductivity, light weight, no phase separation leakage phenomenon and slight supercooling degree owing to the capillary and surface tension of EG [60–63]. Duan et al. [48] prepared  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /EG composites by adsorbing liquid salt hydrate into EG. The shape-stable composite was obtained by putting EG into fused  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . Alkylphenols polyoxyethylene-10 (Op-10) as emulsifier was also added to enhance binding force between EG and salt hydrate. Thermal conductivity also improved by 82% compared with neat  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . Another composite salt hydrate/EG composite was prepared by Wu et al. [64].  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  mixture was impregnated into air voids by vacuum impregnation methods and then coated by paraffin. In addition, the wax additive did not affect the thermal conductive at all. Phase segregation and supercooling of salt hydrates mixtures were also almost inhibited. Li [28] investigated the influence of oxidation expandable graphite (OEG) on thermal behaviors of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , and results showed that OEG can be served as nucleation to promote crystallization process thanks to their uniform distribution in salt hydrates. Similar research was carried out by Mao [31]. Latent storage, supercooling degree and other properties of sodium acetate trihydrate-disodium-dodecahydrate-carboxyl methyl cellulose/expanded graphite composite PCMs were investigated. With the increasing mass proportion of EG, lower enthalpy and higher transfer efficient emerged. The maximum heating temperature was determined not higher than  $78^\circ\text{C}$ , which is beneficial for refraining from undercooling. Ultimately, the system with 3 wt % EG was known as the most suitable selection. Liu [65] combined graphene oxide-modified hydrate salt with

poly copolymer hydrogel. The results indicated that the obtained composite was a promising material for achieving further phase transition behavior targets, which can be used for thermal storage under a wide scope of ambient temperatures. Except for EG, other composite salt hydrate PCMs were studied as well. Cui [66] used vacuum impregnation method to prepare  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and sepiolite compound. Sepiolite, as a fibrous clay mineral with superior capability, possesses a good flare retardance property, can be widely applied to buildings. The obtained composite with 70 wt %  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  resulted in good phase change energy storage properties. However, sepiolite leads to a decrease in enthalpy and thermal stability. Extensive studies have been developed with respect to porous silica, which owns large surface area and porosity. Wu et al. [67] adopted sol-gel method by impregnating mixture of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  into porous silica matrix. Polymethylene was furthermore coated on the surface of silica for preventing the water vapor from evaporating through the pores during phase transition. No leakage and phase separation was observed. Meanwhile, depressing melting pointing was observed by DSC, which was attributed to the difference of wettability between coated and uncoated composite.

In a word, in spite of some disadvantages, salt hydrates are generally considered as suitable materials for thermal energy storage applications due to more and more effective methods are developing to overcome the problems [68,69]. Except for nucleating agents and thickening agents, preparing composite salt hydrate PCMs are also worthy noting due to their excellent abilities for solving phase separation and eliminating supercooling degree. Future trends of salt hydrates materials will most likely be related to the area of microencapsulated PCMs and shape-stabilized materials prepared by PCMs and supporting materials. Nanomaterials which can improve thermal conductivity of PCMs are also supposed to be paid attention.

## 5. Application

Application of salt hydrate PCMs emerged among various areas such as energy-effective construction industry, smart electronics, concentrated solar domestic hot water systems, functional textile industry and food industry in recent years [14,70]. Limited by temperature range for most salt hydrates, using salt hydrates for thermal storage in buildings have always attracted interests of researchers due to their abilities for changing the increasingly indifferent energy generation [71]. It can be deduced the trends in decreasing the energy demand of buildings is necessary [72]. Salt hydrates combining with active and passive systems can minimize variations between energy consumption and demanding in extremely cold and hot areas. There are two main methods to combine salt hydrates with building materials: integrating salt hydrates into light weight construction materials and using packaging materials for encapsulating. However, corrosion with mild metal containers is also a universal behavior of salt hydrates. This phenomenon causes severe effects related to safety and economic in actual applications. As a result, the compatibility between PCMs and metal containers has been widely studied and valuable suggestions have been proposed. Sole [68] focused on immersion corrosion test of metal vessel (Cu, Al, stainless steel, carbon steel) with solid salt hydrates, aiming to searching for optimized container. Metal specimens immersed in salt hydrates were weighted after experiments. Results demonstrated that stainless steel can be considered as the most corrosion-resistant for all experimental salt hydrates.

### 5.1. Salt Hydrates for Hot Water Tanks

Presently, the most widely used heat storage systems for solar thermal energy are hot water tanks, which process an energy storage density of  $69.4 \text{ kW} \cdot \text{h} \cdot \text{m}^{-3}$  ( $\Delta T = 60 \text{ K}$ ) but a finite storage time [73]. Salt hydrates with melting temperature of  $50 \sim 60 \text{ }^\circ\text{C}$  can be incorporated into hot water tanks of solar domestic to reinforce stratification. Salt hydrate PCMs put off the time of reaching thermal equilibrium between top layer with higher temperature and bottom layer with low temperature. An experimental solar stand was constructed by Cabeza [74] with two identical thermal solar collectors. The picture of the installation is shown in Figure 3. One of them was inserted by

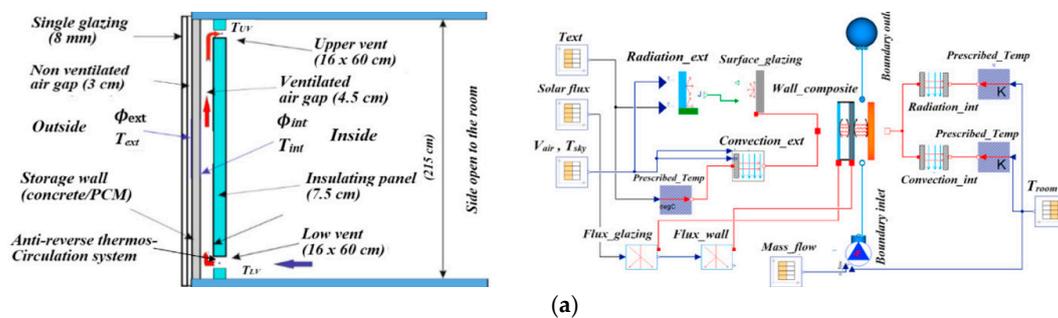
sodium acetate trihydrate. It was found that the inclusion of a PCM module in water tanks for domestic hot-water supply is a very promising technology. It would allow to have hot-water for longer periods of time even without exterior energy supply, or to use smaller tanks for the same purpose. Three types of encapsulated commercial salt hydrates (DC58, PT58 and HD60) are tested inside tanks through continuous temperature measurements with four sensors installing at various heights [75]. The percentage of liquid state of PCMs remaining after tests was obtained by energetic analysis, from which the solidification processes could be clearly knew.



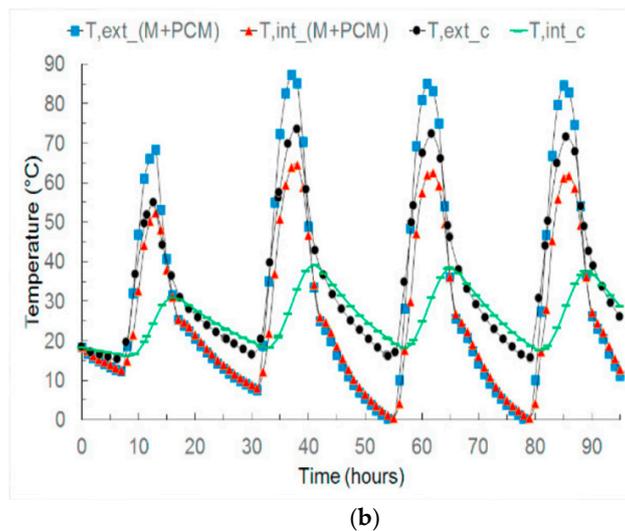
**Figure 3.** (a) Solar thermal collectors (b) Hot-water tanks with PCM modules. Reproduced with permission from [74]. Elsevier: Solar Energy Materials and Solar Cells, copyright 2006.

### 5.2. Salt Hydrates for Wallboards

With the increasing emission of carbon dioxide, blending PCMs in building materials or directly using PCMs as wall boards, is able to store considerable energy during the daytime at high temperature and release energy at night when temperature is low by melting and solidifying processing. The combination of PCMs with building materials has showed superior performance which can contribute to energy saving, electricity shifting and human comfort [70,76–79]. Figure 4a showed a schematic of a kind of full-scale room with PCM concrete wallboards. As seen in Figure 4b, the effects of alleviating temperature fluctuation of a kind of PCM wall room compared with ordinary room are apparent [80]. However, PCMs used in construction field has certain requirements in terms of phase change temperature, stability, strength and price. Consequently, it is a significant step to choose suitable materials and methods of building envelope enclosures, as it is a major parameter to decide by what extent the thermal mass is activated. High fusion heat, odorless and nontoxic properties make salt hydrates be good candidates for construction energy saving.

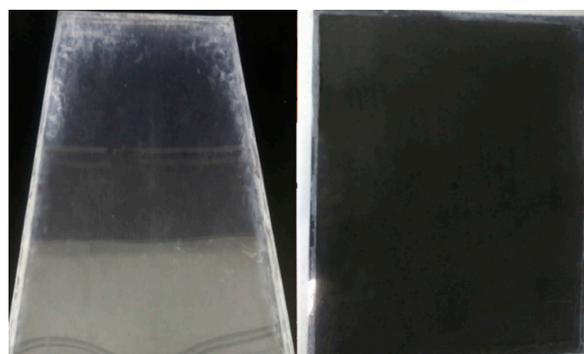


**Figure 4.** Cont.



**Figure 4.** (a) The schematic of a full-scale experimental room with PCM; (b) Temperature comparison of ordinary wall room and PCM room. Reproduced with permission from [80]. Elsevier: Energy Procedia, copyright 2017.

In early years, Hadjieva [81] mixed  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  with porous concrete. Due to the formation of strong hydrogen bond, composite PCMs concrete system showed high stability and it could be further applied to floor construction. Large absorption area of autoclaved porous concrete was also observed. Ye et al. [82] carried out a detailed study on thermal properties of artificial climatic chamber with  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded graphite composite panels at different position. Figure 5 showed the PCM panel packed by polyvinyl chloride (PVC) panel followed by compacting. Four pieces of the PCM panels were fabricated by the same process to use as wallboards. The thermal performance of the test room equipped with the PCM panels at each position was evaluated by placing the room in an artificial climatic chamber. It was revealed that both elements of position and quantity could influence thermal performance of the testing rooms. Moreover, numerical modeling verified the experimental investigations, and better performance of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  was found comparing with organic (RT27/EG composite PCM) panel. This success model showed that radiative effects of salt hydrate wallboards could evidently enhance thermal comfort of residents. Recently, Fu et al. [83] developed a novel nonflammable  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded perlite composite and then fabricated into a board for replacing the foam board to be employed as the core in a foam insulating brick to obtain a PCM board. It is found that when applied PCM brick as the roof of a test room, the indoor peak temperature decreased more apparently compared with foam brick.



**Figure 5.** Photographs of the panels without (left) and with the  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  /EG composite PCM (right). Reproduced with permission from [82]. Elsevier, Applied Energy, copyright 2017.

### 5.3. Salt Hydrates for Refrigeration System

Table 3 presented a variety of salt solutions with large enthalpy values that can apply to low temperature fields.  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{NH}_4\text{Br}$  etc are mainly additional salt that can add to other PCMs to decrease melting point according to their abilities to weaken the hydrogen bond among water molecule [84,85]. An investigation of PCM panels with  $\text{NH}_4\text{Cl}$  and water placing against internal wall in a refrigeration during 24 h for 2 weeks was carried out by Gin [86]. Performance of this system was evaluated by drip loss and ice crystal sizes of beef muscle and ice cream in the commercial freezer. Results showed that PCM panels can assist to lessen the rate of temperature fluctuations within the freezer. Little drip loss has been found in meat and minimal crystal sizes were observed on the surface of ice cream by microscopy and image analysis tool. Analogously, another experiment of improving thermal performance of freezer containing with sodium nitrate and water was conducted in [87]. The commercial salt hydrate PCM with melting point of minus 18 °C was placed in 10 mm thick stainless panels at diverse position of refrigerated trucks. Test packages with chemical components were used to simulate frozen food. The result of door opening tests demonstrated that the salt evidently maintained interior temperature constantly for more than 3 h of power loss. This paper also stated that it is significantly to choose appropriate phase change temperature which is supposed to be near the storage temperature of freezer.

**Table 3.** Melting temperatures and heat of fusion of salt solutions for refrigeration systems.

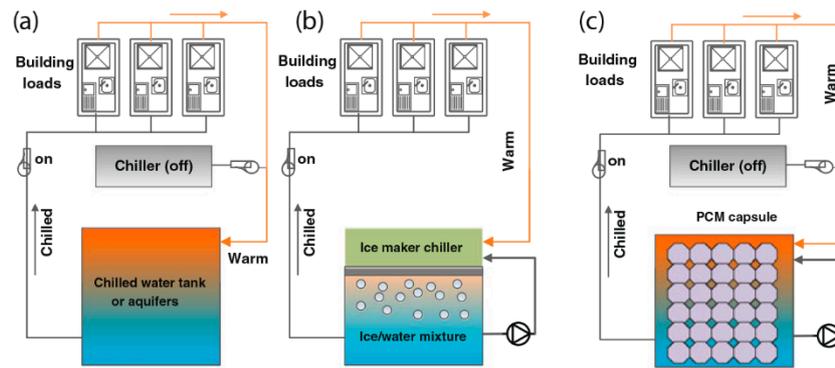
Salt Solution	Melting Temperature (°C)	Heat of Fusion (J/g)	Reference
30.5% $\text{Al}(\text{NO}_3)_3/\text{H}_2\text{O}$	−30.6	131.5	[88,89]
32.3% $\text{NH}_4\text{F}/\text{H}_2\text{O}$	−28.1	199.1	[88]
21.5% $\text{KF}/\text{H}_2\text{O}$	−21.6	225.2	[88]
22.4% $\text{NaCl}/\text{H}_2\text{O}$	−21.2	222	[89]
21.5% $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$	−16	289	[89]
39.7% $(\text{NH}_4)\text{SO}_4/\text{H}_2\text{O}$	−18.5	269	[88]
36.8% $\text{K}_2\text{HPO}_4/\text{H}_2\text{O}$	−13.5	189	[88]
22.1% $\text{BaCl}_2/\text{H}_2\text{O}$	−7.7	102	[89]
27.2% $\text{ZnSO}_4/\text{H}_2\text{O}$	−6.5	208	[89]
18.63% $\text{MgSO}_4/\text{H}_2\text{O}$	−4.8	84.96	[89]
3.9% $\text{NaF}/\text{H}_2\text{O}$	−3.5	309.2	[89]
5.9% $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$	−2.1	281	[88]
6.49% $\text{K}_2\text{SO}_4/\text{H}_2\text{O}$	−1.55	268.8	[89]

### 5.4. Salt Hydrates for Air Conditioning System

Apart from applications in freezers, eutectic salt hydrates are also popularly applied to air condition system due to their similar temperature with the evaporation of the mainly refrigeration host and high density compared with water. There are following characteristics of air conditioning cold energy storage technologies with eutectic salts.

- (1) Transfer the electricity peak and time of power consumption
- (2) Capacity and power of refrigeration equipment can be reduced by 30~50%
- (3) Improve efficiency of operation and utilization

Figure 6 [90] showed several air conditioning system by various media with chilled water, ice and PCMs. Nanoparticles like  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  [88–91] are often added into PCMs to increase melting rate and reduce problems of refrigerating mediums such as environmental pollution, low thermal conductivity, large size and high installing and running cost. Hui et al. [92] found that  $\text{LiCl}/\text{H}_2\text{O}$  and  $\text{NH}_3/\text{H}_2\text{O}$  pairs have good performance among several absorbent/refrigerant pairs, which can be used for air conditioning application and subzero applications, respectively.



**Figure 6.** (a) Chilled water tank for air conditioning; (b) Ice storage tank for air conditioning (c) PCM storage tank for air conditioning. Reproduced with permission from [90]. Springer: Energy Solutions to Combat Global Warming, copyright 2016.

## 6. Conclusions

The available information of salt hydrate PCMs has been concluded on the basis of thermal-physical classification, properties, problems, possible solutions and applications in this paper. It is generally agreed that salt hydrates have significant merits among phase change materials for latent heat storage. In spite of some disadvantages may limit their application in certain aspects, corresponding solutions are developed continuously. It is worthy noting that the excellent performance of combination PCMs with porous materials to prepare shape-stabilized PCMs can successfully solve phase separation and leakage problems when phase transition happens. Nanoparticles are also predominant additions which can ameliorate thermal conductivity and reduce supercooling degree of most hydrates. Highly stable PCMs are being increasingly applied to different sectors. The low phase change temperature range and rational cost of salt hydrates makes them be paid high attention in constructions, air condition, and solar heating systems. However, careful designation should be taking into account of temperature and enthalpy decreasing caused by operational thermal cycling and technical performance of salt hydrates.

For the prospect, surface properties of pore materials which can be regarded as inorganic supporting materials are needed to be regulated furthermore, low cost and anti-corrosion microencapsulation or encapsulation techniques should be studied as well. Any critical testing standards for PCMs should try to be confirmed at international level, this will contribute to directly measure properties of different kinds of PCMs.

**Acknowledgments:** This work was supported by the National Natural Science Foundation of China (No. U1507201).

**Author Contributions:** Ning Xie wrote the paper; Zhaowen Huang, Zigeng Luo, Xuenong Gao, Yutang Fang and Zhengguo Zhang substantially revised the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Cabeza, L.F.; Castell, A.; Barreneche, C.D.; De Gracia, A.; Fernández, A. Materials used as PCM in thermal energy storage in buildings: A review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1675–1695. [[CrossRef](#)]
2. Li, T.X.; Wu, D.L.; He, F.; Wang, R.Z. Experimental investigation on copper foam/hydrated salt composite phase change material for thermal energy storage. *Int. J. Heat Mass Transf.* **2017**, *115*, 148–157. [[CrossRef](#)]
3. Da Cunha, J.P.; Eames, P. Thermal energy storage for low and medium temperature applications using phase change materials—A review. *Appl. Energy* **2016**, *177*, 227–238. [[CrossRef](#)]
4. Castellani, B.; Morini, E.; Filippini, M.; Nicolini, A.; Palombo, M.; Cotana, F.; Rossi, F. Clathrate hydrates for thermal energy storage in buildings: Overview of proper hydrate-forming compounds. *Sustainability* **2014**, *6*, 6815–6829. [[CrossRef](#)]

5. Kenisarin, M.; Mahkamov, K. Salt hydrates as latent heat storage materials: Thermophysical properties and costs. *Sol. Energy Mater. Sol. Cells* **2016**, *145*, 255–286. [[CrossRef](#)]
6. Zhang, P.; Xiao, X.; Ma, Z. A review of the composite phase change materials: Fabrication, characterization, mathematical modeling and application to performance enhancement. *Appl. Energy* **2016**, *165*, 472–510. [[CrossRef](#)]
7. Pielichowska, K.; Pielichowski, K. Phase change nanomaterials for thermal energy storage. In *Nanotechnology for Energy Sustainability*; Wiley: Hoboken, NJ, USA, 2017; pp. 459–484.
8. Wang, T.; Wang, S.; Luo, R.; Zhu, C.; Akiyama, T.; Zhang, Z. Microencapsulation of phase change materials with binary cores and calcium carbonate shell for thermal energy storage. *Appl. Energy* **2016**, *171*, 113–119. [[CrossRef](#)]
9. Giro-Paloma, J.; Martínez, M.; Cabeza, L.F.; Fernández, A.I. Types, methods, techniques, and applications for microencapsulated phase change materials (MPCM): A review. *Renew. Sustain. Energy Rev.* **2016**, *53*, 1059–1075. [[CrossRef](#)]
10. Aguayo, M.; Das, S.; Maroli, A.; Kabay, N.; Mertens, J.C.; Rajan, S.D.; Sant, G.; Chawla, N.; Neithalath, N. The influence of microencapsulated phase change material (PCM) characteristics on the microstructure and strength of cementitious composites: Experiments and finite element simulations. *Cem. Concr. Compos.* **2016**, *73*, 29–41. [[CrossRef](#)]
11. Mohamed, S.A.; Al-Sulaiman, F.A.; Ibrahim, N.I.; Zahir, M.H.; Al-Ahmed, A.; Saidur, R.; Yılbaş, B.S.; Sahin, A.Z. A review on current status and challenges of inorganic phase change materials for thermal energy storage systems. *Renew. Sustain. Energy Rev.* **2017**, *70*, 1072–1089. [[CrossRef](#)]
12. Hussain, S.I.; Dinesh, R. Roseline, A. Enhanced thermal performance and study the influence of sub cooling on activated carbon dispersed eutectic PCM for cold storage applications. *Energy Build.* **2017**, *143*, 17–24. [[CrossRef](#)]
13. Pielichowska, K.; Pielichowski, K. Phase change materials for thermal energy storage. *Prog. Mater. Sci.* **2014**, *65*, 67–123. [[CrossRef](#)]
14. Khan, Z.; Khan, Z.; Ghafoor, A. A review of performance enhancement of PCM based latent heat storage system within the context of materials, thermal stability and compatibility. *Energy Convers. Manag.* **2016**, *115*, 132–158. [[CrossRef](#)]
15. Lorente, S.; Bejan, A.; Niu, J.L. Construal design of latent thermal energy storage with vertical spiral heaters. *Int. J. Heat Mass Transf.* **2015**, *81*, 283–288. [[CrossRef](#)]
16. Li, G.; Zhang, B.; Li, X.; Zhou, Y.; Sun, Q.; Yun, Q. The preparation, characterization and modification of a new phase change material:  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} - \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  eutectic hydrate salt. *Sol. Energy Mater. Sol. Cells* **2014**, *126*, 51–55. [[CrossRef](#)]
17. Liu, Y.; Yang, Y. Preparation and thermal properties of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  eutectic hydrate salt as a novel phase change material for energy storage. *Appl. Therm. Eng.* **2017**, *112*, 606–609. [[CrossRef](#)]
18. Liu, Y.; Yang, Y. Use of nano- $\alpha\text{-Al}_2\text{O}_3$  to improve binary eutectic hydrated salt as phase change material. *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 18–25. [[CrossRef](#)]
19. Zalba, B.; Marín, J.M.; Cabeza, L.F.; Mehling, H. Review on thermal energy storage with phase change: Materials, heat transfer analysis and applications. *Appl. Therm. Eng.* **2003**, *23*, 251–283. [[CrossRef](#)]
20. Yinping, Z.; Yi, J. A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Meas. Sci. Technol.* **1999**, *10*, 201–205. [[CrossRef](#)]
21. Safari, A.; Saidur, R.; Sulaiman, F.; Xu, Y.; Dong, J. A review on supercooling of phase change materials in thermal energy storage systems. *Renew. Sustain. Energy Rev.* **2016**, *70*, 905–919. [[CrossRef](#)]
22. Feng, G.; Xu, X.; He, N.; Li, H.; Huang, K. Testing research of energy storage system during  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  phase change. *Mater. Res. Innov.* **2015**, *19*, 972–977. [[CrossRef](#)]
23. Wu, X.; Wang, Y.; Sun, R.; Lai, M.; Du, R.; Zhang, Z. In the anti-supercooling effect of surface-modified nano-scaled  $\text{SiO}_2$  in hydrated salts phase transition system. *J. Phys. Conf. Ser.* **2009**, *188*. [[CrossRef](#)]
24. Sutjahja, I.M.; Rahayu, S.; Kurniati, N.; Pallitine, I.D.; Kurnia, D. The role of chemical additives to the phase change process of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to optimize its performance as latent heat energy storage system. *J. Phys. Conf. Ser.* **2016**, *739*. [[CrossRef](#)]
25. Li, X.; Zhou, Y.; Nian, H.; Ren, X.; Dong, O.; Hai, C.; Shen, Y.; Zeng, J. Phase change behavior of latent heat storage media based on calcium chloride hexahydrate composites containing strontium chloride hexahydrate and oxidation expandable graphite. *Appl. Therm. Eng.* **2016**, *102*, 38–44. [[CrossRef](#)]

26. Palittin, I.D.; Kurniati, N.; Sutjahja, I.; Kurnia, D. Sonocrystallization technique to optimizing the crystallization process of PCM  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . *Adv. Mater. Res.* **2015**, *1112*, 559–562. [[CrossRef](#)]
27. Miyasaka, E.; Takai, M.; Hidaka, H.; Kakimoto, Y.; Hirasawa, I. Effect of ultrasonic irradiation on nucleation phenomena in a  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  melt being used as a heat storage material. *Ultrason. Sonochem.* **2006**, *13*, 308–312. [[CrossRef](#)] [[PubMed](#)]
28. Li, X.; Zhou, Y.; Nian, H.; Zhang, X.; Dong, O.; Ren, X.; Zeng, J.; Hai, C.; Shen, Y. Advanced nanocomposite phase change material based on calcium chloride hexahydrate with aluminum oxide nanoparticles for thermal energy storage. *Energy Fuels* **2017**, *31*, 6560–6567. [[CrossRef](#)]
29. Mao, J.; Hou, P.; Liu, R.; Chen, F.; Dong, X. Preparation and thermal properties of SAT-CMC-DSP/EG composite as phase change material. *Appl. Therm. Eng.* **2017**, *119*, 585–592. [[CrossRef](#)]
30. Mao, J.; Li, J.; Peng, G.; Li, J. A selection and optimization experimental study of additives to thermal energy storage material sodium acetate trihydrate. In Proceedings of the International Conference on Energy and Environment Technology, Guilin, China, 16–18 October 2009.
31. Mao, J.; Dong, X.; Hou, P.; Lian, H. Preparation research of novel composite phase change materials based on sodium acetate trihydrate. *Appl. Therm. Eng.* **2017**, *118*, 817–825. [[CrossRef](#)]
32. Ramirez, B.M.L.G.; Glorieux, C.; Martinez, E.S.M.; Cuautle, J.J.A.F. Tuning of thermal properties of sodium acetate trihydrate by blending with polymer and silver nanoparticles. *Appl. Therm. Eng.* **2014**, *62*, 838–844. [[CrossRef](#)]
33. Choi, J.C.; Sang, D.K. Heat-transfer characteristics of a latent heat storage system using  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . *Energy* **1992**, *17*, 1153–1164. [[CrossRef](#)]
34. Pilar, R.; Svoboda, L.; Honcova, P.; Oravova, L. Study of magnesium chloride hexahydrate as heat storage material. *Thermochim. Acta* **2012**, *546*, 81–86. [[CrossRef](#)]
35. Ushak, S.; Gutierrez, A.; Barreneche, C.; Fernandez, A.I.; Grágeda, M.; Cabeza, L.F. Reduction of the subcooling of bischofite with the use of nucleating agents. *Sol. Energy Mater. Sol. Cells* **2016**, *157*, 1011–1018. [[CrossRef](#)]
36. Sun, D.; Sung, W.P.; Chen, R. Studies on magnesium chloride hexahydrate as phase change materials. *Appl. Mech. Mater.* **2011**, *71*, 2598–2601.
37. Honcova, P.; Pilar, R.; Danielik, V.; Soska, P.; Sadvovska, G.; Honc, D. Suppressing supercooling in magnesium nitrate hexahydrate and evaluating corrosion of aluminium alloy container for latent heat storage application. *J. Therm. Anal. Calorim.* **2017**, *129*, 1573–1581. [[CrossRef](#)]
38. Ushak, S.; Suárez, M.; Véliz, S.; Fernández, A.G.; Flores, E.; Galleguillos, H.R. Characterization of calcium chloride tetrahydrate as a phase change material and thermodynamic analysis of the results. *Renew. Energy* **2016**, *95*, 213–224. [[CrossRef](#)]
39. Tang, Y.R.; Gao, D.L.; Guo, Y.F.; Wang, S.Q.; Deng, T.L. In Supercooling and phase separation of inorganic salt hydrates as PCMs. *Appl. Mech. Mater.* **2011**, *71*, 2602–2605. [[CrossRef](#)]
40. Dannemand, M.; Johansen, J.B.; Furbo, S. Solidification behavior and thermal conductivity of bulk sodium acetate trihydrate composites with thickening agents and graphite. *Sol. Energy Mater. Sol. Cells* **2016**, *145*, 287–295. [[CrossRef](#)]
41. Shin, H.K.; Park, M.; Kim, H.-Y.; Park, S.-J. Thermal property and latent heat energy storage behavior of sodium acetate trihydrate composites containing expanded graphite and carboxymethyl cellulose for phase change materials. *Appl. Therm. Eng.* **2015**, *75*, 978–983. [[CrossRef](#)]
42. Li, Y.; Yu, S.; Chen, P.; Rojas, R.; Hajian, A.; Berglund, L. Cellulose nanofibers enable paraffin encapsulation and the formation of stable thermal regulation nanocomposites. *Nano Energy* **2017**, *34*, 541–548. [[CrossRef](#)]
43. Hu, X.; Huang, Z.; Yu, X.; Li, B. Preparation and thermal energy storage of carboxymethyl cellulose-modified nanocapsules. *BioEnergy Res.* **2013**, *6*, 1135–1141. [[CrossRef](#)]
44. Jin, X.; Medina, M.A.; Zhang, X.; Zhang, S. Phase-change characteristic analysis of partially melted sodium acetate trihydrate using DSC. *Int. J. Thermophys.* **2014**, *35*, 45–52. [[CrossRef](#)]
45. Ryu, H.W.; Woo, S.W.; Shin, D.K. Prevention of supercooling and stabilization of inorganic salt hydrates as latent heat storage materials. *Sol. Energy Mater. Sol. Cells* **1992**, *27*, 161–172.
46. Gutierrez, A.; Ushak, S.; Galleguillos, H.; Fernandez, A.; Cabeza, L.F.; Grágeda, M. Use of polyethylene glycol for the improvement of the cycling stability of bischofite as thermal energy storage material. *Appl. Energy* **2015**, *154*, 616–621. [[CrossRef](#)]

47. Kazemi, Z.; Mortazavi, S.M. A new method of application of hydrated salts on textiles to achieve thermoregulating properties. *Thermochim. Acta* **2014**, *589*, 56–62. [[CrossRef](#)]
48. Duan, Z.-J.; Zhang, H.-Z.; Sun, L.-X.; Cao, Z.; Xu, F.; Zou, Y.-J.; Chu, H.-L.; Qiu, S.-J.; Xiang, C.-L.; Zhou, H.-Y. CaCl<sub>2</sub>·6H<sub>2</sub>O/expanded graphite composite as form-stable phase change materials for thermal energy storage. *J. Therm. Anal. Calorim.* **2013**, *115*, 111–117. [[CrossRef](#)]
49. Xu, B.; Li, Z. Paraffin/diatomite composite phase change material incorporated cement-based composite for thermal energy storage. *Appl. Energy* **2013**, *105*, 229–237. [[CrossRef](#)]
50. Liu, Z.; Hu, D.; Lv, H.; Zhang, Y.; Wu, F.; Shen, D.; Fu, P. Mixed mill-heating fabrication and thermal energy storage of diatomite/paraffin phase change composite incorporated gypsum-based materials. *Appl. Therm. Eng.* **2017**, *118*, 703–713. [[CrossRef](#)]
51. Wi, S.; Jeong, S.-G.; Chang, S.J.; Lee, J.; Kim, S. Energy-efficient heat storage using gypsum board with fatty acid ester as layered phase change material. *Energy Technol.* **2017**, *5*, 1392–1398. [[CrossRef](#)]
52. Lasfargues, M.; Bell, A.; Ding, Y. In Situ production of titanium dioxide nanoparticles in molten salt phase for thermal energy storage and heat-transfer fluid applications. *J. Nanopart. Res.* **2016**, *18*, 1–11. [[CrossRef](#)] [[PubMed](#)]
53. Li, Y.; Li, J.; Deng, Y.; Guan, W.; Wang, X.; Qian, T. Preparation of paraffin/porous TiO<sub>2</sub> foams with enhanced thermal conductivity as PCM, by covering the TiO<sub>2</sub> surface with a carbon layer. *Appl. Energy* **2016**, *171*, 37–45. [[CrossRef](#)]
54. Tiagi, V.; Kaushik, S.C. Development of phase change materials based microencapsulated technology for buildings: A review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 1373–1391.
55. Liu, F.; Wang, J.; Qian, X. Integrating phase change materials into concrete through microencapsulation using cenospheres. *Cem. Concr. Compos.* **2017**, *80*, 317–325. [[CrossRef](#)]
56. Ram, M.K.; Myers, P.D.; Jotshi, C.; Goswami, D.Y.; Stefanakos, E.K.; Arvanitis, K.D.; Papanicolaou, E.; Belessiotis, V. Microencapsulated dimethyl terephthalate phase change material for heat transfer fluid performance enhancement. *Int. J. Energy Res.* **2017**, *41*, 252–262. [[CrossRef](#)]
57. Streufert, J.R. Encapsulation of Shock-Sensitive Materials and Their Implementation into Matrices. Master's Thesis, University of Illinois at Urbana-Champaign, Champaign, IL, USA, 30 April 2015.
58. Huang, J.; Wang, T.; Zhu, P.; Xiao, J. Preparation, characterization, and thermal properties of the microencapsulation of a hydrated salt as phase change energy storage materials. *Thermochim. Acta* **2013**, *557*, 1–6. [[CrossRef](#)]
59. Korhammer, K.; Druske, M.-M.; Fopah-Lele, A.; Rammelberg, H.U.; Wegscheider, N.; Opel, O.; Osterland, T.; Ruck, W. Sorption and thermal characterization of composite materials based on chlorides for thermal energy storage. *Appl. Energy* **2016**, *162*, 1462–1472. [[CrossRef](#)]
60. Huang, Z.; Luo, Z.; Gao, X.; Fang, X.; Fang, Y.; Zhang, Z. Investigations on the thermal stability, long-term reliability of LiNO<sub>3</sub>/KCl—Expanded graphite composite as industrial waste heat storage material and its corrosion properties with metals. *Appl. Energy* **2017**, *188*, 521–528. [[CrossRef](#)]
61. Cheng, F.; Wen, R.; Huang, Z.; Fang, M.; Liu, Y.G.; Wu, X.; Min, X. Preparation and analysis of lightweight wall material with expanded graphite (EG)/paraffin composites for solar energy storage. *Appl. Therm. Eng.* **2017**, *120*, 107–114. [[CrossRef](#)]
62. Xu, T.; Li, Y.; Chen, J.; Liu, J. Preparation and thermal energy storage properties of lino 3-kcl-nano 3/expanded graphite composite phase change material. *Sol. Energy Mater. Sol. Cells* **2017**, *169*, 215–221. [[CrossRef](#)]
63. Huang, X.; Alva, G.; Liu, L.; Fang, G. Preparation, characterization and thermal properties of fatty acid eutectics/bentonite/expanded graphite composites as novel form-stable thermal energy storage materials. *Sol. Energy Mater. Sol. Cells* **2017**, *166*, 157–166. [[CrossRef](#)]
64. Wu, Y.; Wang, T. Hydrated salts/expanded graphite composite with high thermal conductivity as a shape-stabilized phase change material for thermal energy storage. *Energy Convers. Manag.* **2015**, *101*, 164–171. [[CrossRef](#)]
65. Liu, Y.; Yang, Y.; Li, S. Graphene oxide modified hydrate salt hydrogels: Form-stable phase change materials for smart thermal management. *J. Mater. Chem. A* **2016**, *4*, 18134–18143. [[CrossRef](#)]
66. Cui, W.; Zhang, H.; Xia, Y.; Zou, Y.; Xiang, C.; Chu, H.; Qiu, S.; Xu, F.; Sun, L. Preparation and thermophysical properties of a novel form-stable CaCl<sub>2</sub>·6H<sub>2</sub>O/sepiolite composite phase change material for latent heat storage. *J. Therm. Anal. Calorim.* **2017**, *20*, 1–7. [[CrossRef](#)]

67. Wu, Y.; Wang, T. Preparation and characterization of hydrated salts/silica composite as shape-stabilized phase change material via sol–gel process. *Thermochim. Acta* **2014**, *591*, 10–15. [[CrossRef](#)]
68. Solé, A.; Miró, L.; Barreneche, C.; Martorell, I.; Cabeza, L.F. Corrosion of metals and salt hydrates used for thermochemical energy storage. *Renew. Energy* **2015**, *75*, 519–523. [[CrossRef](#)]
69. Padovan, R.; Manzan, M. Genetic optimization of a PCM enhanced storage tank for Solar Domestic Hot Water Systems. *Sol. Energy* **2014**, *103*, 563–573.
70. Kara, Y.A. Diurnal performance analysis of phase change material walls. *Appl. Therm. Eng.* **2016**, *102*, 1–8. [[CrossRef](#)]
71. Kleiner, F.; Posern, K.; Osburg, A. Thermal conductivity of selected salt hydrates for thermochemical solar heat storage applications measured by the light flash method. *Appl. Therm. Eng.* **2017**, *113*, 1189–1193. [[CrossRef](#)]
72. Zhou, D.; Zhao, C.Y.; Tian, Y. Review on thermal energy storage with phase change materials (PCMs) in building applications. *Appl Energy* **2012**, *92*, 593–605. [[CrossRef](#)]
73. Mahdi, J.M.; Nsofor, E.C. Solidification enhancement of PCM in a triplex-tube thermal energy storage system with nanoparticles and fins. *Appl. Energy* **2018**, *211*, 975–986. [[CrossRef](#)]
74. Cabeza, L.F.; Ibáñez, M.; Solé, C.; Roca, J.; Nogués, M. Experimentation with a water tank including a PCM module. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 1273–1282. [[CrossRef](#)]
75. Porteiro, J.; Míguez, J.L.; Crespo, B.; de Lara, J.; Pousada, J.M. On the behavior of different PCMs in a hot water storage tank against thermal demands. *Materials* **2016**, *9*, 213. [[CrossRef](#)] [[PubMed](#)]
76. Akeiber, H.; Nejat, P.; Majid, M.Z.A.; Wahid, M.A.; Jomehzadeh, F.; Famileh, I.Z.; Calautit, J.K.; Hughes, B.R.; Zaki, S.A. A review on phase change material (PCM) for sustainable passive cooling in building envelopes. *Renew. Sustain. Energy Rev.* **2016**, *60*, 1470–1497. [[CrossRef](#)]
77. Copiello, S. Building energy efficiency: A research branch made of paradoxes. *Renew. Sustain. Energy Rev.* **2017**, *69*, 1064–1076. [[CrossRef](#)]
78. Navarro, L.; de Gracia, A.; Niall, D.; Castell, A.; Browne, M.; McCormack, S.J.; Griffiths, P.; Cabeza, L.F. Thermal energy storage in building integrated thermal systems: A review. Part 2. Integration as passive system. *Renew. Energy* **2016**, *85*, 1334–1356. [[CrossRef](#)]
79. Brancato, V.; Frazzica, A.; Sapienza, A.; Freni, A. Identification and characterization of promising phase change materials for solar cooling applications. *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 225–232. [[CrossRef](#)]
80. Leang, E.; Tittlein, P.; Zalewski, L.; Lassue, S. Numerical study of a composite Trombe solar wall integrating microencapsulated PCM. *Energy Procedia* **2017**, *122*, 1009–1014. [[CrossRef](#)]
81. Hadjieva, M.; Stoykov, R.; Filipova, T. Composite salt-hydrate concrete system for building energy storage. *Renew. Energy* **2000**, *19*, 111–115. [[CrossRef](#)]
82. Ye, R.; Lin, W.; Yuan, K.; Fang, X.; Zhang, Z. Experimental and numerical investigations on the thermal performance of building plane containing  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded graphite composite phase change material. *Appl. Energy* **2017**, *193*, 325–335. [[CrossRef](#)]
83. Fu, L.; Wang, Q.; Ye, R.; Fang, X.; Zhang, Z. A calcium chloride hexahydrate/expanded perlite composite with good heat storage and insulation properties for building energy conservation. *Renew. Energy* **2017**, *114*, 733–743. [[CrossRef](#)]
84. Shportko, K.; Kremers, S.; Woda, M.; Lencer, D.; Robertson, J.; Wuttig, M. Resonant bonding in crystalline phase-change materials. *Nat. Mater.* **2008**, *7*, 653–658. [[CrossRef](#)] [[PubMed](#)]
85. Bauer, T.; Laing, D.; Tamme, R. Characterization of sodium nitrate as phase change material. *Int. J. Thermophys.* **2012**, *33*, 91–104. [[CrossRef](#)]
86. Gin, B.; Farid, M.M. The use of PCM panels to improve storage condition of frozen food. *J. Food Eng.* **2010**, *100*, 372–376. [[CrossRef](#)]
87. Oró, E.; Miró, L.; Farid, M.M.; Cabeza, L.F. Improving thermal performance of freezers using phase change materials. *Int. J. Refrig.* **2012**, *35*, 984–991.
88. Mo, S.; Chen, Y.; Jia, L.; Luo, X. Reduction of supercooling of water by  $\text{TiO}_2$  nanoparticles as observed using differential scanning calorimeter. *J. Exp. Nanosci.* **2013**, *8*, 533–539. [[CrossRef](#)]
89. Lee, J.-H.; Hwang, K.S.; Jang, S.P.; Lee, B.H.; Kim, J.H.; Choi, S.U.; Choi, C.J. Effective viscosities and thermal conductivities of aqueous nanofluids containing low volume concentrations of  $\text{Al}_2\text{O}_3$  nanoparticles. *Int. J. Heat Mass Transf.* **2008**, *51*, 2651–2656. [[CrossRef](#)]

90. Mehling, H.; Cabeza, L.F. *Heat and Cold Storage with PCM*; Springer: Berlin/Heidelberg, Germany, 2008; pp. 1107–1111.
91. Altohamy, A.A.; Abd Rabbo, M.F.; Sakr, R.Y.; Attia, A.A.A. Effect of water based Al<sub>2</sub>O<sub>3</sub> nanoparticle PCM on cool storage performance. *Appl. Therm. Eng.* **2015**, *84*, 331–338. [[CrossRef](#)]
92. Hui, L.; Edem, N.K.; Nolwenn, L.P. Evaluation of a seasonal storage system of solar energy for house heating using different absorption couples. *Energy Convers. Manag.* **2011**, *52*, 2427–2436. [[CrossRef](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).