Review

Review of cold storage materials for air conditioning application

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ABSTRACT

This paper reviews the recent development of available cold storage materials for air conditioning application. According to the type of storage media and the way a storage medium is used, water and ice, salt hydrates and eutectics, paraffin waxes and fatty acids, refrigerant hydrates, microencapsulated phase change materials/slurries and phase change emulsions are separately introduced as suitable energy storage or secondary loop media. Water storage and static ice storage, which are already well-established technologies, have little need for further study. Dynamic ice slurry application is discussed especially for its generation method, relating to the efficiency and reliability of converting water or aqueous solution to ice crystals or ice slurry. Thermal and physicochemical properties of different phase change materials have been summarized including latent heat, thermal conductivity, phase separation, supercooling, and corrosion. Moreover, corresponding solutions for issues of different materials are also discussed. Thermal and hydraulic characteristics of phase change slurries (mainly about clathrate slurries, microencapsulated phase change slurries, and phase change emulsions) are discussed and summarized. In addition, the principle of the sorption cold storage is described and different kinds of working pairs are introduced. Relevant perspectives for commercialization of storage materials are discussed.

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Matériaux à accumulation thermique pour les applications de conditionnement d'air : état de l'art

1. Introduction

Cold storage, which primarily involves adding cold energy to a storage medium, and removing it from that medium for use at a later time, has wide applications for air conditioning use in buildings, vehicles, and other conditioned spaces. By separating the maximum cooling and power demands in time, it can offer cooling while reducing or eliminating the peak

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electric power load of the buildings, and has benefits such as waste heat recovery and renewable energy utilization.

Cold storage technologies in air conditioning applications can be classified according to the type of a storage medium and the manner in which the storage medium is used. Previous research has provided summaries and reasonable analyses for most of the common storage media such as water and ice. Saito (2002) suggested that water storage and static-type ice, which are based on established technologies, have little need for further study. More topics have surfaced in recent years for promising phase change material (PCM) storage, in which the storage media options can include materials such as salt hydrates and eutectics, paraffin waxes and fatty acids, refrigerant hydrates including clathrate slurries, microencapsulated phase change materials (MPCMs) or slurries, and phase change emulsions. Moreover, utilizing sorption technologies for cold storage purpose has been developed recently. In this paper, a brief introduction is provided for water storage and ice storage technologies, while more detailed description is provided for more promising cold storage materials in air conditioning application.

2. Chilled water and ice slurries

Chilled water storage, which utilizes the sensible heat (4.184 kJ kg^{-1} K^{-1}) to store cooling, needs a relatively large storage tank as compared to other storage systems that have a larger latent heat of fusion. However, it has wide application because of its suitable cold storage temperature (4—6 °C). This characteristic enables it to be directly compatible with conventional water chillers and distribution systems, and provides good unit efficiency with a low investment. Ice storage uses the high fusion heat of water (335 kJ kg^{-1}), which can make storage tank much smaller. However, it stores cooling in the form of ice, which means that the refrigeration equipment must operate at temperatures well below its normal operating range for air conditioning application. Therefore, either special ice making equipment is used, or refrigeration chillers are selected for low temperature service.

2.1. Chilled water storage

Water is most dense at 4 °C and becomes less dense at both higher and lower temperatures. Because of this density—temperature relationship, this kind of storage system has the phenomenon of a stratified temperature distribution in a storage tank. Effective chilled water storage requires that some form of separation should be maintained between the stored cold water and the warmer return water. The mixing of two water streams at different temperatures, which is caused by the inlet diffuser during charge and discharge processes, significantly affects the temperature distribution in the tank. Here the two diffuser types most commonly used in today's commercial chilled water storage tanks are shown in Fig. 1 (Bahnfleth et al., 2003). Most studies related to this stratification tried to enhance the chilled water storage in terms of performance, simplicity, cost, and reliability. In a single stratified tank that stores both hot and cold water, diffusers are located at the top and bottom of the tank. Various physical methods, such as membranes, internal
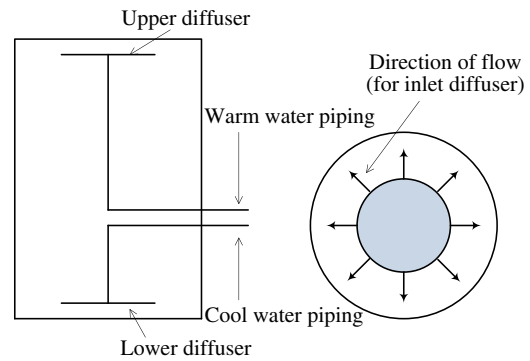
a With radial parallel plate diffusers
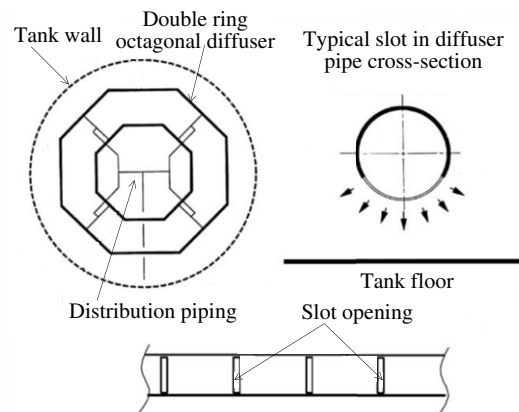
b With octagonal slotted-pipe diffusers

Fig. 1 — Stratified storage tank (Bahnfleth et al., 2003).

weirs, baffles, labyrinths, series tank, empty tanks, and thermally stratified systems, have been used to create the temperature stratification necessary for a high efficient storage (Mackie and Reeves, 1988; Dorgan and Elleson, 1993).

More attention has been paid to the numerical simulation for the transient behavior of the thermocline formation process in the thermal storage tank. Initially, one-dimensional simulation was developed. Cole and Bellinger (1982) developed a model based on tests performed in a scale model tank with a side inlet. Mixing was accounted for by a constant empirical mixing parameter, which is a function of the Fourier and Richardson numbers. They reported that their simulation results agreed with their experimental results both in the interior of the tank and at the tank outlet. The primary deficiency observed in this model was that it under-predicted the temperature below the thermocline. Truman and Wildin (1989) developed a model, which was found to be reasonable in predicting the tank storage performance. Other models such as an effective diffusivity model to quantify the inlet mixing effect caused by various inlet geometries were also developed (Zurigat et al., 1991; Ghajar and Zurigat, 1991; Caldwell and Bahnfleth, 1998). Later, many two-dimensional studies have attempted to simulate the thermocline formation process and were able to predict it reasonably. A steady state model was developed by Stewart et al. (1992) to study the effects of a submerged, downward-impinging flow from a slot in a chilled water storage tank. The flow was modeled

by a system of five nonlinear, coupled partial differential equations, and was solved using a successive substitution method. Another turbulent model was developed to simulate the mixing process of a cold flow into a two dimensional tank via a linear diffuser at a lower corner of the tank (Cai et al., 1993). Other related models are developed by Spall (1998), Musser and Bahnfleth (2001a, 2001b), and Bahnfleth et al. (2003).

2.2. Selection of depressant additives for ice slurry

As mentioned in the introduction, static ice storage will not be discussed in this paper, because it has been well established (Saito, 2002). In a dynamic ice storage system, ice slurry can be directly transported through pipes, due to its high fluidity, heat transfer ability, and heat capacity with minute ice particles. The ice particles are in the range of 0.1−1 mm in diameter. It is made from aqueous solutions to avoid adhesion of ice particles to a cold surface. A dynamic ice-making system allows the use of cool air distribution as a result of a large temperature difference. Its benefits include the ability to use smaller fans and ducts, as well as for the introduction of less humid air into occupied spaces. In order to realize the ice slurry, the freezing point depressant additives are added. The most common freezing point depressant materials for water are glycols (Hirata et al., 2000; Inaba et al., 1998), alcohols (Ohkubo et al., 1999) and salts. Ice slurry can be made from harmless aqueous solutions such as an ethanol solution, a propylene glycol solution, and an economical aqueous solution such as an ethylene glycol solution. The main purpose of using ice slurries is to take advantage of the latent heat of the ice crystals. Continuous ice slurry can usually be produced through buoyancy force (Hirata et al., 2000). Kumano et al. (2007) systemically studied the production of apparent latent heat from ice in aqueous solutions, which was defined as the effective latent heat, as shown in Fig. 2 (combined from original figures by Kumano et al. (2007)). It was found that the effective latent heat of fusion in an aqueous solution could be calculated by considering the effects of freezing point depression and dilution heat in each case. The relationship between the latent heat of fusion and the degree of freezing-point depression is also shown in Fig. 2. Amount of heat generated by dilution was large in propylene glycol and ethanol solutions, and latent heat decreased in conjunction with a lowered freezing point. Moreover, the effect of dilution in NaCl solution was small, although latent heat of fusion decreased with the freezing point. The decrease in latent heat was very small in $NaNO_3$ solution due to the effect of the endothermic reaction. Kumano et al. (2010) also studied the specific enthalpy of different aqueous solutions, and show the relationship between the specific enthalpy and initial temperature of the sample, as shown in Fig. 3 (combined from original figures by Kumano et al., 2010). For other materials, Lu et al. (2002) proposed using polyvinyl alcohol (PVOH) as an artificial additive in ice slurries. PVOH could be a substitute for antifreeze protein (AFP) type I, which is an effective additive for making ice slurries resistant to recrystallization. Grandum and Nakagomi (1997) and Grandum et al. (1999) measured the properties of ice slurry produced by using an antifreeze protein, and discussed types of crystals produced under various conditions. Inada et al. (1999, 2000) examined the microscopic structure of these additives on ice crystals and discussed the mechanism of the
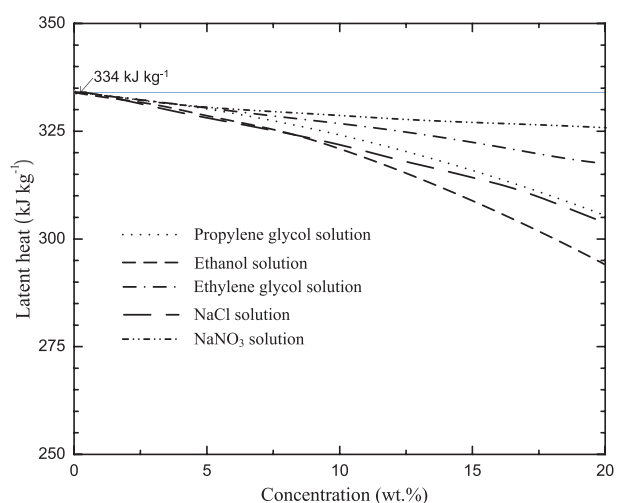
a Latent heat vs. concentration
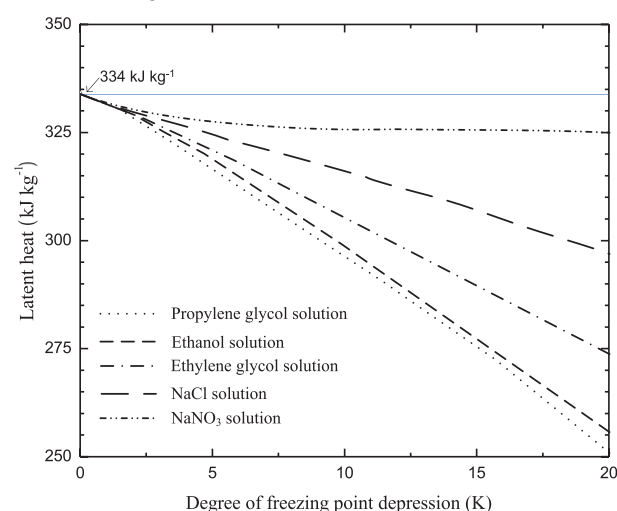
b Latent heat vs. degree of freezing point depression

Fig. 2 − **Latent heat of ice fusion in different aqueous solutions (Kumano et al., 2007).**

antifreeze effect. Silane coupling agents (SCAs) were used as substitutes for AFPs, and SCAs, which could form long-chain molecules in water, were effective for crystallization control. As seen with scanning tunneling microscopy (STM) observation, long-chain SCA molecules are adsorbed onto ice crystal surfaces, thus preventing crystal growth at the site where the long-chain SCA molecules are adsorbed.

2.3. Dynamic ice-making system

The most important issues of the ice slurry application are its efficiency and reliability in conversion of water or an aqueous solution to ice crystals or ice slurry. Usually, there are two ways of making ice: the dynamic ice making method using supercooled water, and the vacuum ice slurry method.

2.3.1. Dynamic ice making method using supercooled water
A liquid can be cooled below its normal freezing point without being crystallized if a seed nucleus does not exist. This is
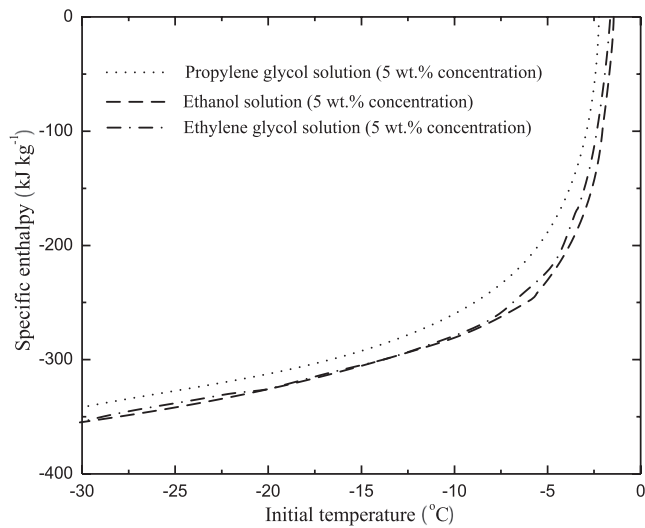
Fig. 3 – **Relation between specific enthalpy and initial temperature of the sample (Kumano et al., 2010).**

called as "supercooled liquid". Ice crystals can be produced in a special supercool release device to eliminate the super-cooled conditions from the water. A supercooler, which is a specially designed heat exchanger, is the core component necessary to realize dynamic freezing of supercooled water. A dynamic-type ice storage system using supercooled water is shown in Fig. 4 (Kozawa et al., 2005). Typically, the refrigeration system contains a supercooler, supercooler release device, and an ice-storage tank. Saito et al. (1992) studied the mechanical factors affecting the initiation of the freezing of supercooled water through experimenting the ice making methods using supercooled water. Okawa et al. (1997, 1999) and Okawa and Saito (1998) applied an electric charge on the freezing of supercooled water and reported its effects. They also studied the probability of ice-nucleation phenomena, and summarized possible solutions to control the initiation of crystallization. There are more scholars who have studied the fundamental issues related to ice making and heat transfer (Qu, 2000; Zhang et al., 2008; Li and Zhang, 2009). Usually the condition of supercooled water is unstable in dynamic-type ice storage systems. The water freezes easily with
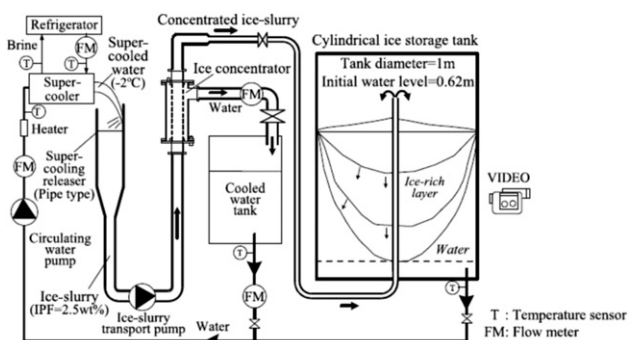
perturbation, and then can freeze inside the pipeline. In order to maintain a stable high-quality ice slurry, it is necessary to control the degree of supercooling. This has been a popular topic of research.

2.3.2. Vacuum ice slurry generation method

In this method, an aqueous solution used as the cold storage material is evaporated under a low-pressure condition, and the remaining solution is cooled and frozen as a consequence of the latent heat of evaporation. A circulating system to produce ice slurry is shown in Fig. 5 (Asaoka et al., 2009). The system consists of an evaporator, a vacuum pump, and a condenser. Aqueous solution in the evaporator evaporates so that ice forms within. The vapor produced in the evaporator is transported to the condenser via a vacuum pump. Condensed liquid is diluted and returned to the evaporator for re-use. Since the external surface of the evaporator is warmer than the ice slurry in this system, the issue of ice sticking to the cooling surface has been eliminated. This improves the system efficiency because ice slurry production is continuous without any interruption. Kim et al. (2001) studied the consistency between theory and experiment for the dissipation rate of a liquid droplet and the change of surface temperature when using an ethylene glycol solution with a water spray method, which was based on the dissipation-control evaporation model. Lugo (2004) and Lugo et al. (2006) studied equilibrium condition using an ammonia solution and an ethanol solution with this method. Asaoka et al. (2009) further studied the vapor–liquid equilibrium data to estimate the coefficient of performance (COP) of the system with an ethanol solution. Further related studies were developed by Shin et al. (2000), Ge et al. (2007) and others. At present, most of the research interests related to the vacuum method are focused on heat and mass transfer inside the liquid, as well as the optimizing equipment and its components. In addition to ice-making system researches, numerous studies have focused on the storage tank. Egolf et al. (2008) systemically summarized related research areas, such as ice particle fields, and showed a comparison of the usual method of storage with and without mixing in the tank, as shown in Fig. 6. This method of storage without mixing allows
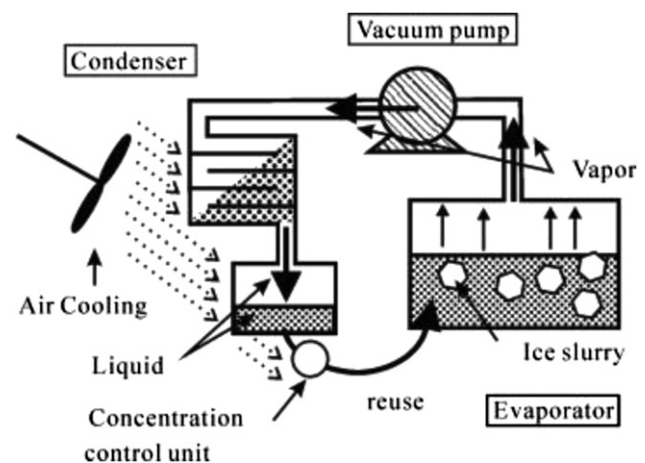

Fig. 4 – **Schematic diagram of a dynamic-type ice storage system using subcooled water (Kozawa et al., 2005).**

Fig. 5 – **Schematic diagram of a vacuum ice slurry generation system (Asaoka et al., 2009).**
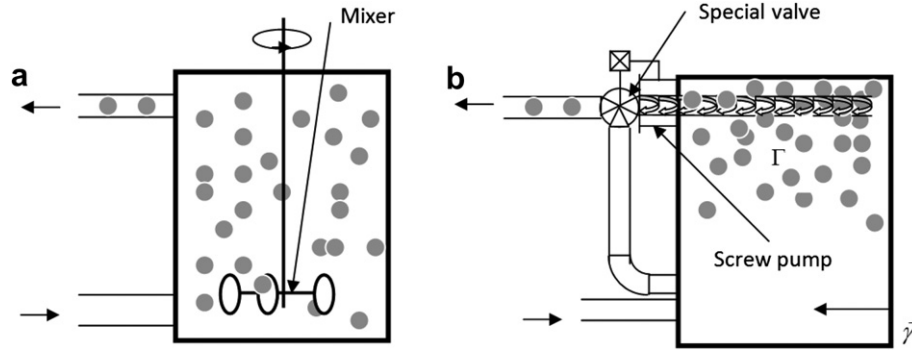
Fig. 6 − Schematic drawing of (a) usual method of storage with mixing and (b) a proposal for an alternative system without a mixer in the tank (Egolf et al., 2008).

saving the electrical energy. The inlets and outlets shown are parts of the secondary circuit.

3. Phase change materials (PCMs) and PCM slurries

PCMs, which can be produced in various chemical formulations, usually can be designed to melt and freeze at a suitable phase change temperature range for air conditioning systems. With the superiority of high latent heat, they have shown a promising ability to reduce the size of storage systems. PCMs have been used for various heat storage applications since the 1800s, but they have been used as a kind of cold storage media or a secondary loop fluid only recently.

In this section, materials with solid-to-liquid phase change with minor volume changes are the primary topic of discussion for practical applications. Early in 1983, Abhat (1983) suggested a useful classification of the substances used for thermal energy storage, as shown in Fig. 7. The melting temperature and fusion heat of existing PCMs are shown in Fig. 8 (Dieckmann, 2006). Obviously, the promising PCMs for air conditioning application are salt hydrates, eutectics, paraffin waxes, fatty acids, and refrigerant hydrates. Fig. 9 shows thermal properties of the PCMs studied in this section. In addition to PCM materials, PCM slurries as secondary loop fluids including clathrate slurries, micro-encapsulated phase change slurries, phase change emulsions are also discussed and summarized.
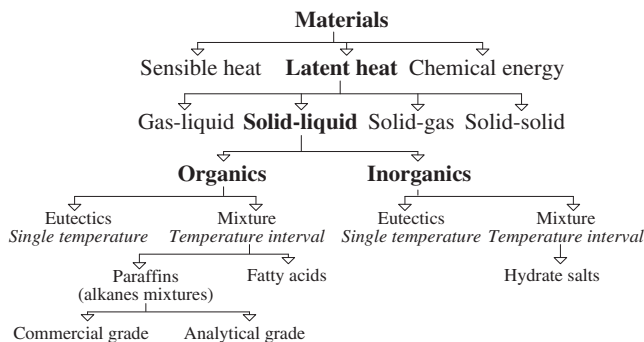
3.1. Selection criteria for PCMs or PCM slurries

Requirements for common solid−liquid PCMs or PCM slurries for cold storage in air conditioning applications are summarized as follows:

(1) Proper phase change temperature range (5−12 °C) and pressure (usually near atmospheric pressure), which involves the use of conventional air conditioning equipment and a storage tank for the chiller operation in buildings;
(2) Large fusion heat, which helps to achieve high cold storage density compared to sensible heat storage and allows for a more compact storage tank;
(3) Reproducible phase change, also called cycling stability, which can use the materials many times for storage and release of thermal energy with consistent performance. Usually the phase separation, which separates phases with different composition from each other macroscopically, is an important issue for cold storage. If phase has a composition different from the initial design composition optimized for cold storage, it will show a significantly reduced energy storage capacity.
(4) Good thermal conductivity to speed up phase change progress, and low supercooling.
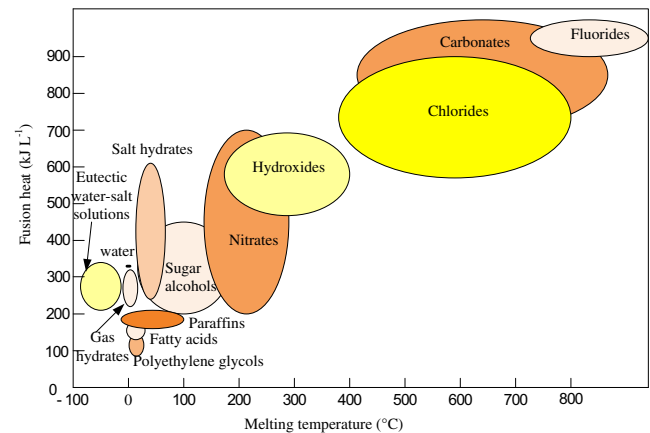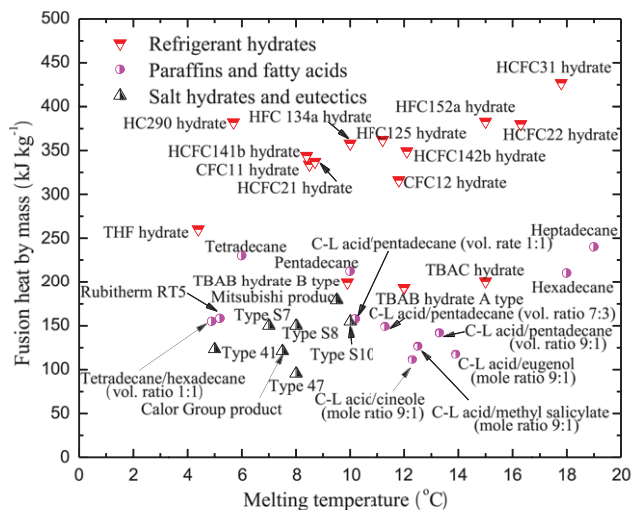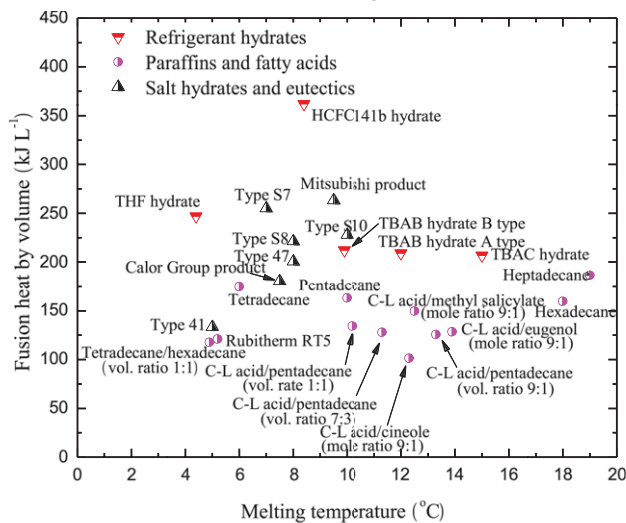(5) Stable chemical properties, low corrosivity, and low environmental impact factors, such as zero Ozone Depletion

Fig. 7 − Classification of PCMs (Abhat, 1983).

Fig. 8 − Melting temperature and fusion heat of existing PCMs (Dieckmann, 2006).

a Fusion heat by mass

b Fusion heat by volume

Fig. 9 – Thermal properties of PCMs.

a Salt hydrates and eutectics

b Paraffin waxes

c Fatty acids

d Refrigerant hydrates

Fig. 10 – Comparison of thermal properties of different PCMs.

a higher fusion heat. However, their major issues of phase separation, supercooling and corrosion, which are directly related to the cycle stability, are introduced later.

3.2.1. Material selection

Hydrated salts consist of a salt and water in a discrete mixing ratio. The word eutectic is derived from Greek and means "easy melting". It refers to a mixture of two or more components having the lowest melting point of any composition and combination of the same components. At this eutectic point, all of the components will crystallize simultaneously, like a pure substance. In this study for air conditioning application, the eutectics are mostly inorganic salts.

The most commonly used eutectic salt is Glauber salt ($Na_2SO_4 \cdot 10H_2O$), which contains 44 wt.% Na_2SO_4 and 56 wt.% H_2O (Telkes, 1952). With a melting temperature of about 32.4 °C and a high latent heat of 254 kJ kg^{-1} (377 MJ m^{-3}), it is one of the least expensive materials that can be used for thermal energy storage. To make the phase change temperature range appropriate for air conditioning applications, more proper $Na_2SO_4 \cdot 10H_2O$-related PCMs were developed, as summarized by Liu (2005), and shown in Table 2. The thermal properties of several commercial salt hydrates and eutectics, which could be used for air conditioning applications, are listed in Table 3 (Liu, 2005; PCM Products, 2011).

3.2.2. Phase separation minimization

As reported by Cantor (1978), phase separation, or incongruent melting, can cause a loss in enthalpy of solidification. Since phase separation can severely reduce the storage density, necessary solutions should be offered. Changing the
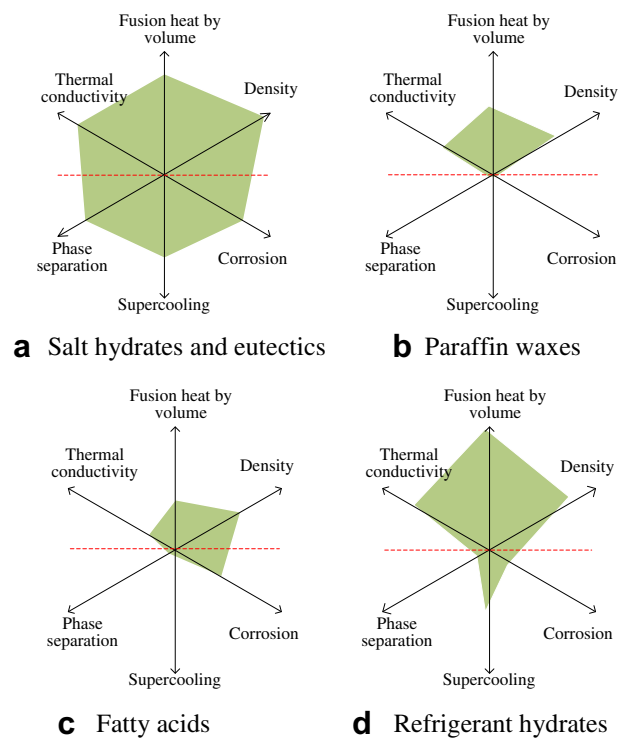
Potential (ODP) effect and low Global Warming Potential (GWP) effect.

(6) Low viscosity, good flow and heat transfer characteristics for PCM slurries.

(7) Easy manufacturing and low price.

Usually it is hard for a material to satisfy the entire requirements listed above so that here the primary four requirements are discussed here. A brief comparison of the thermal properties of the different types of PCMs is shown in Fig. 10.

3.2. Salt hydrates and eutectics

Much of the research on PCMs is focused on salt hydrates and eutectics due to their high fusion heat and suitable phase change temperature range. To provide a general understanding for different storage systems, Hasnain (1998) discussed the primary features of chilled water, ice, and eutectic salt cold storage systems, as shown in Table 1. In the following section, material selection is first introduced. Generally, salt hydrates have

Table 1 – Comparison of various thermal storage systems (Hasnain, 1998).			
Primary features	Chilled water storage	Ice storage	Eutectic salt storage
Specific heat (kJ kg^{-1} K^{-1})	4.19	2.04	–
Latent heat of fusion (kJ kg^{-1})	–	333	80–250
Maintenance	High	Medium	Medium
Warranty availability	Low	High	Medium
Tank interface	Open tank	Closed system	Closed tank
Discharge fluid	Water	Secondary coolant	Water
Charging temperature (°C)	4 to 6	−6 to −3	−20 to 4
Chiller	Standard water	Low temp. secondary coolant	Standard water
Packaged system	Medium	High	High
Heating capability	Low	High	Medium
Chiller charging efficiency	5.0–5.9 COP	2.9–4.1 COP	5.0–5.9 COP
Storage installed cost ($ kW^{-1} h^{-1})	8.5–28	14–20	28–43
Discharge temperature (°C)	Above 1–4	1–3	9–10

properties of the salt hydrate with the addition of another material such as water with a gelling or thickening agent can hinder the separation and sinking of heavier phases. A gelling agent is a cross-linked material (e.g. polymer) that is added to the salt in order to create a three-dimensional network that holds the salt hydrate together. A thickening agent is a material added to the salt hydrate to increase the viscosity and holds the salt hydrate together. In considering appropriate cross-linked materials for gelling, Ryu et al. (1992) studied the effects of two different polymeric hydrogels: a super absorbent polymer (SAP) made from acrylic acid copolymer and carboxymethyl cellulose (CMC). Thixotropic (attapulgite clay) and alginate have also been tested (Telkes, 1976). Thickening agents can be starch and various types of cellulose derivatives, such as silica gel (Ryu et al., 1992; Telkcs, 1974). Sodium acetate trihydrate (NaCH$_3$COO·3H$_2$O), used as a PCM, was studied by thickening it with each of four different thickening materials: starch, methyl cellulose, hydroxyethyl methyl cellulose, and bentonite (Cabeza et al., 2003). In addition, Biswas (1997) investigated the extra water to prevent the formation of heavy anhydrous salt. A comparison by Biswas (1997) using pure Glauber salt and a mixture of Na$_2$SO$_4$·10H$_2$O and H$_2$O (68.2 wt.%/31.8 wt.%) showed that the nucleation of the decahydrate occurred readily and even without the addition of borax. It should be noted that although the method of adding extra water makes the system stable with cycling, it may lead to a reduction of the storage density and the system should be operated with a large temperature swing. In addition, encapsulating the PCM and the mechanical stirring can also be good solutions to deal with the issue of phase separation. For all solutions, the issue of phase separation invites the meaningful perspectives for further study of salt hydrates and eutectics in air-conditioning applications.

3.2.3. Supercooling minimization

Supercooling is another serious issue. The use of nucleating agents, cold finger, and porous heat exchange surfaces has been utilized effectively to deal with this issue (Abhat, 1983). Many factors, such as crystal structure, solubility, and hydrate stability, were studied to determine whether a particular additive could promote nucleation. Good nucleating agents can be carbon nanofibers, copper, titanium oxide, potassium sulfate, and borax (Ryu et al., 1992; Elgafy and Lafdi, 2005). Studies show that 0.95 wt.% to 1.9 wt.% of pulverized borax in Glauber's salt was found to be the most effective in supercooling minimization (Lane, 1992; Onwubiko and Russell, 1984). Other promising nucleating agents to limit the degree of supercooling from 20 °C to 2 °C could be Na$_2$P$_2$O$_7$·10H$_2$0, BaCO$_3$, BaCl$_2$, BaI$_2$, Ba(OH)$_2$, CaC$_2$O4, K$_2$SO$_4$, MgSO$_4$, SrCl$_2$, SrCO$_3$, SrSO$_4$, Sr(OH)$_2$, and TiO$_2$.

3.2.4. Corrosion suppression

Corrosion is one more significant issue. It is also an important engineering design criterion for materials, which is subject to open to the atmosphere for a longer period of time. For salt hydrates and eutectics, the primary limiting factor to widespread use of these latent heat storage materials is the life of PCM container systems associated with the corrosion between the PCM and container. In an effort to address this issue, Kimura and Kai (1984) used NaCl to improve the stability of salt hydrates and eutectics. Porisini (1988) studied the corrosion rates on stainless steel, carbon steel, aluminum alloys and copper. Following thermal cycling tests, Porisini concluded that stainless steel was the most corrosion resistant among these metals for use with salt hydrates, though copper had a corrosion zone that did not increase even after long periods of time. Farid et al. (2004) summarized the stability of thermal properties under extended cycling. In addition, the corrosion

Table 2 – Components of eutectics salt with phase change temperature of 12.8 °C (Liu, 2005).					
Component	wt.% (salt)	Function	Component	wt.% (salt)	Function
Na$_2$SO$_4$	32.5	PCM	Na$_2$B$_4$O$_7$·10H$_2$O	2.6	Nucleating agent
H$_2$O	41.4	PCM	H$_3$BO$_3$	1.73	Equilibrium pH agent
NaCl	6.66	Temp. adjustment agent	Na$_5$P$_3$O10	0.25	Dispersing agent
NH$_4$Cl	6.16	Temp. adjustment agent	MinUGel200	8.7	Thickening agent

Table 3 – Thermal properties of eutectics slat and salt hydrates (Liu, 2005; PCM Products Ltd., 2011).

PCM component/PCM type	Phase change temperature (°C)	Fusion heat (kJ kg^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Density (kg m^{-3})	Specific heat capacity (kJ kg^{-1} K^{-1})	Company
Na$_2$SO$_4$, H$_2$O, NaCl, NH$_4$Cl	7.5	121	0.55 (liquid), 0.70 (solid)	1490	–	Calor group
Na$_2$SO$_4$·10H$_2$O, NaCl, NH$_4$Cl, Na$_2$B$_4$O$_7$·10H$_2$O, NH$_4$Br	9.5–10 (melting point) 8.0 (freezing point)	179, 122 (after 100 recycles)	0.75 (liquid), 0.93 (solid)	1470	–	Kyushu electric power, Mitsubishi
Type 41	5.0–5.5	123.3	–	–	–	Transphase
Type 47	8–9	95.4	–	–	–	Transphase
S7	7	150	0.40	1700	1.85	PCM products
S8	8	150	0.44	1475	1.90	PCM products
S10	10	155	0.43	1470	1.90	PCM products

rates of aluminum alloys and copper used in heat exchangers in the air conditioning industry were studied along with metallographic examinations after corrosion tests by Farrell et al. (2006), and ways of preventing corrosion of copper and aluminum by these PCM materials were discussed.

Salt hydrates and eutectics have a high latent heat per unit volume, high thermal conductivity, and are non-flammable and low in cost. However, they have not only phase separation and supercooling issues, but also corrosion issue to most metals. This leads to poor cyclic stability. Therefore, it is necessary to address such issues.

3.3. Paraffin waxes and fatty acids

Typical paraffin waxes are saturated hydrocarbon mixtures, and normally consist of a mixture of mostly straight chain n-alkanes such as CH$_3$–(CH$_2$)$_n$–CH$_3$. The crystallization of the (CH$_2$)$_n$ chain can release a large amount of latent heat. A fatty acid is characterized by the formula CH$_3$(CH$_2$)$_{2n}$COOH. Paraffin waxes and fatty acids are both organic and different from inorganic PCMs so that they are mostly chemically inert, stable and recyclable, exhibit little or no supercooling (i.e. they can be self-nucleating), and show no phase separation and a non-corrosive behavior (with the exception of fatty acids for the natural characters of acids). However, they have the disadvantages of low thermal conductivity and volumetric storage (less than 10^3 kg m^{-3}), and flammability that are opposite from those of inorganic PCMs.

3.3.1. Material selection

The various paraffin waxes, which are mainly products of petroleum refining process, are available with a range of melting points. This characteristic can lead to a good match between the melting temperature range and the air conditioning system operating temperature range. Examples of some single paraffin waxes that have been investigated as PCMs, are shown in Table 4 (Mehling and Cabeza, 2008). From the table, it can be easily determined that tetradecane and pentadecane have a great potential as a PCM in conventional cold storage systems for air conditioning application. Also, binary mixtures of tetradecane and hexadecane have also been tested well, and are excellent candidates (He et al., 1999). A binary mixture of laboratory-grade tetradecane and hexadecane, and the technical grade paraffin wax-Rubitherm RT5, were studied using differential scanning

calorimetry (DSC) (He and Setteerwall, 2002). Dimaano and Escoto (1998) and Dimaano and Watanabe (2002a, 2002b) systemically studied the capric–lauric (C–L) acid mixtures for PCM energy storage, from an initial assessment of thermal properties and investigation for lowest eutectic point with a suitable component compositions, to analysis for mixtures with pentadecane or proper additives in order to make the melting points in the range for cold storage, as shown in Table 4. With theoretical calculation and the experimental study of the liquid–solid equilibrium phase diagram on several kinds of fatty acid mixtures, the caprylic–lauric acid mixture (in the mass composition ratio of 80 and 20) was also suggested as a good cold storage material with a freezing point of 4.6 °C and a fusion heat of 152 kJ kg^{-1} (Cen et al., 1997). For other research related to fatty acids for air conditioning application, the literature by Li et al. (1996) can be referred.

3.3.2. Thermal conductivity improvement

For paraffin waxes and fatty acids, one of their serious issues is their low thermal conductivities. One possible solution is to add materials having a larger thermal conductivity. Mettawee and Assassa (2007) investigated a method of enhancing the thermal conductivity of paraffin wax by embedding aluminum powder in paraffin wax in a water base collector for solar energy storage unitization. It was found that the useful heat gain was increased by adding aluminum powder in the wax as compared to the case of pure paraffin wax. Another solution is embedding graphite matrix in PCMs to increase the thermal conductivity. Thermal conductivity of paraffin wax can be increased by two orders of magnitude through impregnating porous graphite matrices with the paraffin (RT-42, Rubitherm, Germany) (Mills et al., 2006). Also, a technical grade paraffin (melting point 48–50 °C) embedded with expanded graphite was studied and showed a good thermal conductivity (Zhang and Fang, 2006). For the two above solutions, they provide insight for thermal conductivity improvement for air conditioning application although the examples listed are for utilization other than the air conditioning application. Last, the use of finned tubes can also improve heat transfer performance for cold storage. All the previous studies for thermal conductivity improvement listed above can be used as guideline for enhancing PCM cold storage performance for air conditioning application. It should be noted that in order to prevent the liquid leakage during the solid–liquid phase change of the

Table 4 – Thermal properties of paraffin waxes and fatty acids (Mehling and Cabeza, 2008; He and Setteerwall, 2002; Dimaano and Escoto, 1998; Dimaano and Watanabe, 2002a, 2002b).

	PCM	Melting temperature ($^\circ$C)	Fusion heat (kJ kg^{-1})	Density (kg m^{-3})	Thermal conductivity (W m^{-1} K^{-1})	Specific heat (kJ kg^{-1} K^{-1})
Single paraffin wax	$C_{14}H_{30}$ (n-Tetradecane)	6	230	760 (liquid, 20 $^\circ$C)	0.21 (solid)	–
	$C_{15}H_{32}$ (n-Pentadecane)	10	212	770 (liquid, 20 $^\circ$C)	–	–
	$C_{16}H_{34}$ (n-Hexadecane)	18	210, 238	760 (liquid, 20 $^\circ$C)	0.21 (solid)	–
	$C_{17}H_{36}$ (n-Heptadecane)	19	240	776 (liquid, 20 $^\circ$C)	–	–
Paraffin wax mixture[a]	50:50 Tetradecane: Hexadecane (vol.%)	Sensor: 4–6 DSC: 4.9	154.839	–	–	–
	Rubitherm RT5	Sensor: 4–6 DSC: 5.2	158.332	–	–	–
Fatty acid[b] with pentadecane or additives	90:10 C-L Acid:P (vol.%)	13.3	142.2	883.2 (liquid) 891.3 (solid)	–	2.42 (liquid) 2.08 (solid)
	70:30 C-L Acid:P (vol.%)	11.3	149.2	858.0 (liquid) 872.7 (solid)	–	2.57 (liquid) 2.27 (solid)
	50:50 C-L Acid:P (vol.%)	10.2	157.8	827.8 (liquid) 850.4 (solid)	–	2.89 (liquid) 2.44 (solid)
	90:10 C-L Acid: Methyl Salicylate (mol. %)	12.5	126.7	1182.0 (liquid) 1272.9 (solid)	–	2.41 (liquid) 1.92 (solid)
	90:10 C-L Acid: Cineole (mol. %)	12.3	111.6	927.0 (liquid) – (solid)	–	2.37 (liquid) 1.71 (solid)
	90:10 C-L Acid: Eugenol (mol. %)	13.9	117.8	1091.0 (liquid) – (solid)	–	2.63 (liquid) 2.01 (solid)

a Carbon distribution of Rubitherm RT5 is 33.4 wt.% C14 (No. of carbon atoms), 47.3 wt.% C15, 16.3 wt.% C16, 2.6 wt.% C17 and 0.4 wt.% C18. Freezing temperature for paraffin wax mixture by test is 7.0 $^\circ$C.
b C–L Acid is composed with 65 mol % capric acid and 35 mol % lauric acid.

paraffin, a general solution is to encase the paraffin in spherical capsules or microcapsules, which is introduced in Section 3.5.
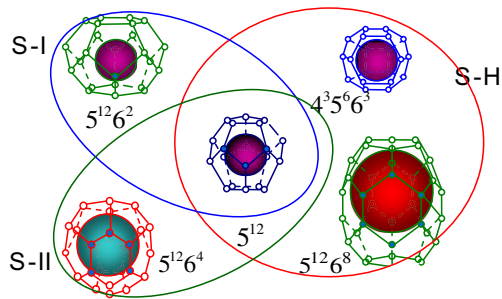
3.3.3. Flame retardancy improvement

For paraffin waxes and fatty acids, another serious issue is their high flammability. Usually the shape-stabilized PCM composites consist of the paraffin wax and a polymer material (such as high density polyethylene (HDPE)) acting as a dispersed PCM and supporting material, respectively. As long as the operating temperature is below the melting point of the supporting material, the shape-stabilized PCM can keep its shape even when the paraffin changes from solid to liquid. However, the high flammability property of paraffin waxes has severely restricted their wide applications. Usually improving flame retardant of polymer materials with the addition of some flame retardant to polymer materials can relieve this issue. There has been much concern worldwide over developing halogen free flame retardant (HFFR) polymeric materials. Intumescent flame retardant (IFR) material is used as an environmental, halogen-free additive (Cai et al., 2006). In order to improve the effective capacity to retard flames, synergistic agents have been used in IFR systems, such as some nanocomposites (Xia et al., 2007; Zhou et al., 2008). The influences of metal (iron, magnesium, aluminum, and zinc) on flame retardancy for paraffin/IFR as a PCM were studied by Zhang et al. (2010a). Microscale combustion calorimetry (MCC) and cone calorimetry (CONE) were used to characterize the sample. The results revealed that the flame retardant efficiency of IFR in the paraffin could be improved by adding metal. Also, the flame retardant mechanism for paraffin/IFR with metal was proposed. In another study (Song et al., 2010), PCMs based on ethylene–propylene–diene terpolymer (EPDM) (supporting material), paraffin (dispersed PCM), nano-structured magnesium hydroxide (nano-MH) and red phosphorus (RP) with various compositions were prepared. The thermogravimetric analysis (TGA) also indicates that the introduction of nano-MH into the form-stable PCMs (i.e. EPDM/paraffin blends) has significantly increased the fire resistance due to the formation of MgO during the combustion of nano-MH. MgO builds up char layers on the surface, insulates the underlying material, and delays the escape of the volatile products generated during decomposition. Therefore, it improves the fire resisting performance. In addition, expanded graphite can also be a good material to improve the flame retardancy of polymer materials. All these studies can be used as a guideline for enhancing PCM cold storage performance for air conditioning application.

3.4. Refrigerant hydrates

Gas hydrates, or clathrate hydrates, are ice-like crystals that are composed of host lattices (cavities) formed by water molecules linking with each other through hydrogen bonding, and other guest molecules. The guest molecules are firmly enclosed inside the host cavities under the weak van de Waals force. Usually there are three types (S-I, S-II and S-H) as shown in Fig. 11 (Khokhar et al., 1998). Different types of hydrates can be formed under different conditions. For this study, refrigerant hydrates, which are mainly the type S-II gas hydrates (i.e., M·nH$_2$O, where M is a molecule of guest material and n is hydrate number) are discussed. In addition, CO$_2$ hydrate (type S-I gas hydrate) and TBAB hydrate and TBAC hydrate (semi-clathrate hydrates) are also discussed in this section. Most refrigerant hydrates can be formed under low pressure (below 1 MPa) with suitable phase change temperature for air-

Fig. 11 – Types of hydrate structures and their cage arrangements (Khokhar et al., 1998).

Table 5 – Thermal properties of guest materials for refrigerant hydrate and hydrate.			
Guest materials of refrigerant hydrate	Hydrate melting point		Hydrate fusion heat (kJ kg^{-1})
	Temperature (°C)	Pressure (atm)	
HC-290	5.7	5.45	382
CFC-11	8.5	0.54	334
CFC-12	11.8	4.39	316
HCFC-22	16.3	8.15	380
HCFC-21	8.7	1.00	337
HCFC-31	17.8	2.82	427
HCFC-141b	8.4	0.42	344
HCFC-142b	12.1	2.25	349
HFC-152a	15.0	4.34	383
HFC-134a	10.0	4.10	358
HFC-125	11.2	9.44	362

conditioning and large fusion heat (270–430 kJ kg^{-1}). Unlike some liquid–solid PCMs discussed above, some refrigerants discussed here are in the gaseous state under atmospheric pressure, so pressure is noted for hydrate formation. Obviously, refrigerant hydrates have a larger fusion heat than eutectic salts, paraffin waxes and fatty acids. A hydrate storage system with the hydrate fusion heat near to that of ice shows the advantage of allowing use of chilled water as circulation medium rather than antifreeze coolant or brine, which are used in ice storage systems. Since this type of novel cold storage medium was first proposed by Tomlinson (1982), many research efforts have been conducted. A series of outstanding achievements were made in the research of hydrate cold storage technology (Ternes, 1983; Akiya et al., 1997; Mori and Mori, 1989; Fournaison et al., 2004; Guo et al., 1998).

3.4.1. Material selection

(1) HFC hydrate

In the 1990s, researchers first studied cold storage characteristics of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) hydrates, such as CFC-11, CFC-12, HCFC-21, HCFC-22 and HCFC-141b gas hydrates. With the phase out of CFCs and HCFCs for environmental protection, more attention should be paid for alternative substitutes for guest materials of refrigerant hydrates like hydrofluorocarbon (HFC) hydrate. Oowa et al. (1990) studied the phase equilibrium of HFC-134a hydrate. HFC-32 and HFC-125 hydrates were researched by Akiya et al. (1997). HFC-134a and HFC-152a hydrates were researched as cold storage media, and the energy charge and discharge processes were studied in a transparent apparatus (Guo et al., 1996). Thermal properties of some new HFC gas hydrates are presented in Table 5. It can be seen that the melting temperature of some refrigerant hydrates is a little higher. Through the addition of NaCl, CaCl$_2$, and ethylene glycol (Tanii et al., 1997), the melting temperature can be reduced to make hydrates more suitable for air conditioning applications. HFC-245fa, HFC-236ea, and HFC-365mfc are considered to be the primary alternative fluids for HCFC-141b, and they possibly form gas hydrates for air conditioning application.

(2) CO$_2$ hydrate slurry

CO$_2$ hydrate slurries, which are mixtures of solid CO$_2$ hydrate crystal and liquid aqueous solution, can also be used as secondary working fluids (Marinhas et al., 2006). They have the advantage of being produced by a non-mechanical generation process based on a simple CO$_2$ injection in a pre-cooled aqueous solution. Moreover, the heat of fusion of solid CO$_2$ hydrate crystal (500 kJ kg^{-1}) is higher than that of ice (334 kJ kg^{-1}). As a recently developed secondary refrigerant, CO$_2$ hydrate slurry should contain sufficient solid crystals in order to release plentiful latent heat in delayed time as a cold source. In addition, the solid hydrate crystal should not affect the flowing conditions of hydrate slurry. The melting point of CO$_2$ hydrate slurry is adjustable according to the production conditions and can be applied to positive temperature range (+5 °C or +7 °C or even higher) for air conditioning application.

(3) TBAB hydrate slurry, TBAC hydrate slurry, THF hydrate slurry

Since most refrigerants (HFCs, CO$_2$, etc) are not very immiscible with water, it is necessary to search for water-soluble materials for rapid hydrate formation such as tetra-n-butyl ammonium bromide (TBAB), tetra-n-butyl ammonium chloride (TBAC), tetrahydrofuran (THF), acetone, etc. In addition, unlike other clathrate hydrates, which are usually produced under high pressure and low temperature conditions, the materials listed here can form hydrate under 1 atm pressure and room temperature. It should be noted that the structures of TBAB hydrate and TBAC hydrate crystals are different from common type S-II hydrates, and they can form semi-clathrate hydrates, in which TBAB or TBAC molecules are both the host and guest in the structure. Also two types of hydrate crystals can be formed for TBAB hydrate and TBAC hydrate with different hydration numbers. Schematic structure of one type for TBAB hydrate crystal (type A with hydration number: 26) is shown in Fig. 12 (Shimada et al., 2003). It is a semi-clathrate hydrate. Tetra-n-butyl ammonium located at the center of three tetrakaidecahedrons and one pentakaidecahedron. Broken bonds are shown by dotted lines. The dotted lines represent bonds which have disappeared from the classical hydrate structure. The dodecahedral cages are empty as shown by the hatched areas.

Thermal properties of three hydrate crystals are listed in Table 6. Zhang et al. (2010b) gave a detailed introduction to determine thermal properties of clathrate hydrate slurries.
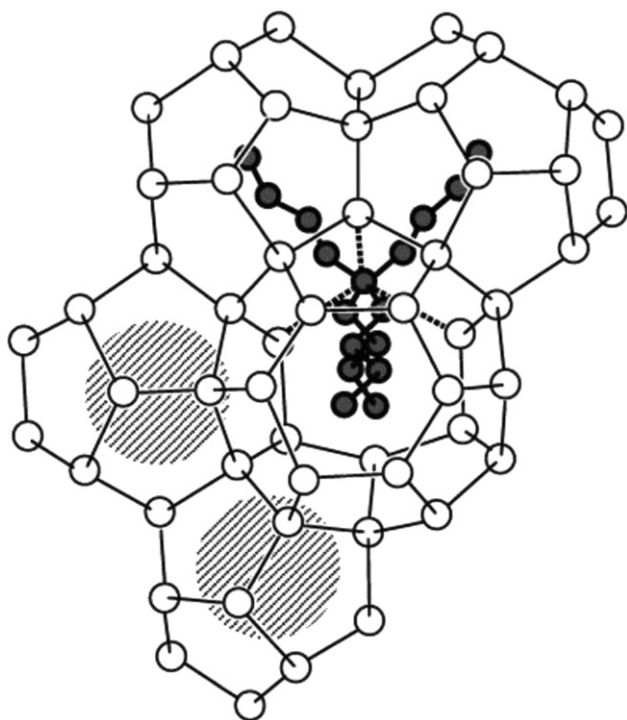
Fig. 12 – Schematic structure of type A TBAB hydrate crystal (Shimada et al., 2003).

Also hydrate mixtures, such as TBAB/THF mixtures, have been also studied for air conditioning application by Li et al. (2010). Since published literature on environment friendly clathrate hydrate mixture is limited, it is not discussed here in details.

3.4.2. Hydrate formation improvement and storage apparatus designation

Most refrigerants are insoluble in the water, leading to slow hydrate formation (also called crystallization) with a supercooling effect and a slightly longer induction time. To deal with these shortcomings, enhancement methods are very necessary, and are summarized as follows:

(1) One solution is to stir the reaction materials. A mechanical agitator inside the tank can stir the reaction materials directly, or the guest materials and the water can be mixed by continuously being pumping out separately from the tank (Shu et al., 1999), or mixed with the help of an injector (Tong et al., 2000).

(2) Another solution is the inclusion of additives to reduce induction time, the supercooling degree, or to change melting temperature more suitable in air conditioning application. Useful additives are sodium dodecyl sulfate (SDS) (Zhang et al., 2002), ethylene glycol, n-butyl alcohol (Zhang et al., 1999), metals or metaloxide compound powders such as copper, zinc, and iron (Isobe and Mori, 1992), inorganic salts, and organic fungi.

(3) The third solution is applying the outfields. A special magnetic field has remarkable influence on the refrigerant gas hydrate formation process, by reducing induction time and increasing the amount of formed hydrate (Liu et al., 2003a). Ultrasonic waves were also studied for hydrate formation (Liu et al., 2003b). The induction time was longer under the function of a staircase-like supersonic probe than with that of the index–cone-like probe. The range of the ultrasonic wave power that has a good effect on hydrate formation was 58–1000 W.

For a clear understanding of the heat transfer modes between the cold storage media and the refrigerant or the coolant, it is necessary to study the hydrate storage apparatus design. Xie et al. (2004) summarized this by studying both the direct contact heat transfer mode and the indirect contact heat transfer mode. In the indirect contact heat transfer mode, the cold storage medium and the refrigerant (or the coolant) exchange heat through the heat exchanger. In the

Table 6 – Thermal properties of TBAB/TBAC/THF hydrate crystals.							
Hydrate guest material	Hydration number	Melting temperature (°C)	Latent heat (kJ kg^{-1})	Density (kg m^{-3})	Specific heat (kJ kg^{-1} K^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Literature
TBAB	26/38	12.0/9.9	193.2/199.6		1.86–2.61/2.0–2.54[a]		Oyama et al. (2005)
	26/36	12.3/9.6		1082/1067			Darbouret et al. (2005)
	26/36	11.8/–	193/205	1082/1030	2.22/–	0.42/–	Hayashi et al. (2000)
							Ogoshi and Takao (2004)
TBAC	30	15.0	200.7				Nakayama (1987)
	29.7/32.1	15.0/14.7		1034/1029			Dyadin and Udachin (1984)
THF	17	4.4	~260	~950	1.930–2.020[b]	0.489–0.496[b]	Leaist et al. (1982)
							Waite et al. (2005)

a Between 20 and 0.2 °C.
b Between −25 and −7.5 °C. Hydration number for type A TBAB hydrate crystal is 26, while for type B TBAB hydrate crystal it is 36 or 38.

direct contact heat transfer mode, the cold storage medium and the refrigerant (or the coolant) exchange heat through direct contact. The hydrate storage apparatus types can be classified based on direct or indirect-contact charging and direct or indirect-contact discharging system, as shown in Fig. 13.

Several researchers (Mori and Mori, 1989; Carbajo, 1985; Najafi and Schaetzle, 1991) conducted detailed research on type (a) direct contact charge and direct contact discharge system. Researchers (McCormack, 1990; Dini and Saniei, 1992; Zhang et al., 1999) conducted detailed research on type (d) indirect contact charge and indirect contact discharge system. A comparison between direct-contact and indirect-contact systems is shown in Table 7.

From a more practical viewpoint, the hydrate storage apparatus is usually an indirect-contact system. Shu et al. (1999) developed a new hydrate cold storage system for this type of system, which had an internal heat exchanger and a small, external rotating crystallizer, which was the pump. This system could achieve a high-efficiency and high-density cold storage performance. Tong et al. (2000) proposed one type of cold storage system using an injector to spray the refrigerant liquid into the cavity where the liquid could be vaporized and completely mixed with the water to enhance heat mass transfer during hydrate formation.

3.4.3. Thermal and hydraulic characteristics of hydrate slurry
In the following introduction, TBAB slurry is mainly discussed as an example since it has been the topic of most intensive studies. Clathrate hydrate slurry is usually considered as non-Newtonian fluid for its solid–liquid two-phase mixture feature. Only when the solid fraction is very small it can be possibly be treated as Newtonian fluid. Darbouret et al. (2005) indicated that there was a critical volume fraction for TBAB hydrate slurry at which its flow behavior changed from Newtonian fluid flow to Bingham fluid flow. Hydrate slurry in higher volume fraction has higher yield stress and apparent viscosity. It was also found that the viscosity of type B TBAB hydrate slurry was a little larger than that of type A due to the different shapes of two types of hydrate crystals.

When compared to the chilled water, clathrate hydrate slurry exhibited a higher overall heat transfer coefficient due to the associated phase change. Results in literature (Ogoshi and Takao, 2004) show the cooling capacity of TBAB clathrate hydrate slurry is about 2.5–3.5 times larger than that of the chilled water at the flow rate of 1–5 kg min^{-1} Xiao et al. (2007) conducted experimental study on the heat transfer characteristics of TBAB slurry in a horizontal copper tube with 8 mm inner diameter. Results indicated that the influence of the volume fraction of solid phase on Nusselt number was small even with the change of Reynolds numbers. Ma et al. (2010) studied forced convective heat transfer characteristics of TBAB clathrate hydrate slurry with the volume fraction 0–20.0%. Heat transfer correlations of TBAB hydrate slurry flowing through straight circular tubes under constant heat flux were developed for the laminar, transition, and turbulent flow regimes. It was found that the volume fraction was the major factor which influenced the heat transfer in the laminar region while the flow velocity was more important in the transition and turbulent flow regions. Thermal and hydraulic characteristics of clathrate hydrate slurry in a plate heat exchanger were also studied by Ma and Zhang (2011). In another study, Xiao et al. (2006) tested the flow characteristics of TBAB slurry in a PVC pipe with 21 mm inner diameter. Power law fluid equation was applied, which

a Direct contact charge and direct contact discharge system

b Direct contact charge and indirect contact discharge system

c Indirect contact charge and direct contact system

d Indirect contact charge and indirect discharge contact discharge system
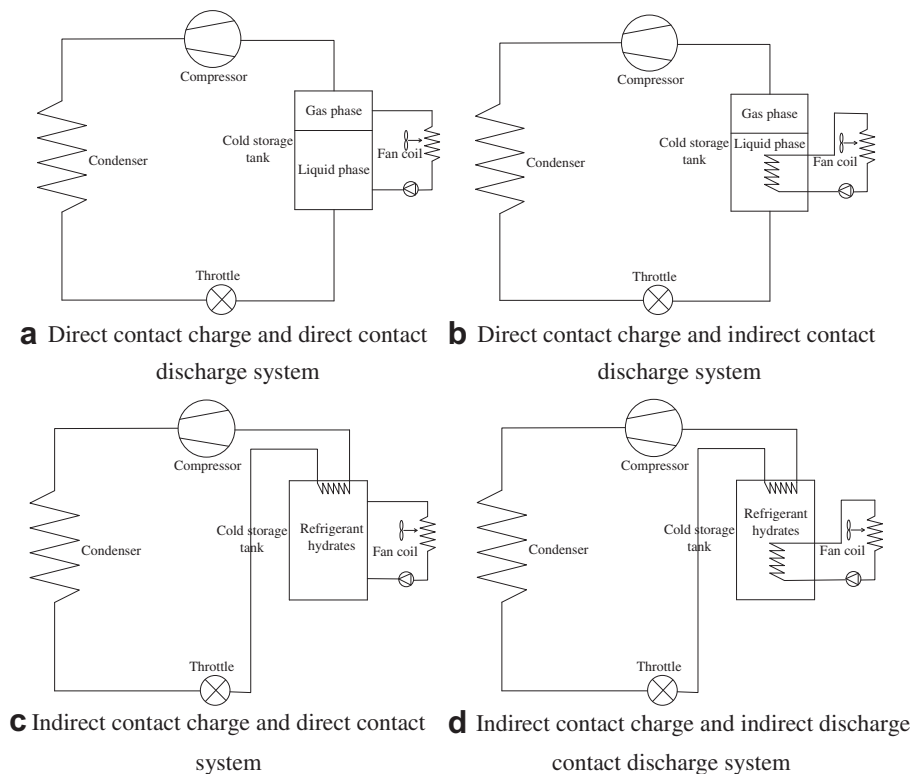
Fig. 13 – **Different types of hydrate charge and discharge system (Xie et al., 2004).**

Table 7 – Comparison of direct-contact and indirect-contact systems.		
System type	Advantage	Disadvantage
Charge process Direct contact	Evaporator heat exchanger not needed; high heat transfer performance; high temperature of refrigerants returning to compressor; defrosting equipment not needed; low energy consumption	Oil-free compressor and water separator needed; high investment
Charge process Indirect contact	Regular compressor used; regular refrigeration cycle; low investment	Evaporator heat exchanger needed; relatively poor heat transfer performance; low temperature in the evaporator and reduced compressor performance; defrosting equipment needed when ice exists; high energy consumption
Discharge process Direct contact	Heat exchanger not needed; low temperature difference between cold storage medium and coolant; low energy consumption	Sophisticated pump needed to make liquid refrigerant to be pumped without cavitations' problem or leaks at the seals
Discharge process Indirect contact	Regular pump	Heat exchanger needed; high temperature difference between cold storage medium and coolant; high energy consumption

showed that the apparent viscosity of 0–16 vol.% TBAB slurry was 3–8 times higher than that of water. Therefore, it is necessary to make reasonable considerations for hydrate application in air conditioning systems. In fact, thermal and hydraulic characteristics of clathrate hydrate slurry are usually be affected by many factors, such as volume fraction of hydrate crystal particles, the pipe shape and size, which make the flow characteristics very complicated and need further investigations.

3.5. Microencapsulated PCMs or PCM slurries and phase change emulsions

3.5.1. Microencapsulated PCMs or PCM slurries

Microencapsulated PCM (MPCM) is the encapsulation of PCM particles (the core) with a continuous film of polymeric material (the shell). The PCM core particles vary in size, ranging from 1 μm to 1000 μm in diameter. There are two processes used in microencapsulation: physical and chemical. The physical processes are spray drying, centrifugal and fluidized bed processes, or coating processes involving rolling cylinders. The chemical processes are in-situ encapsulations like complex coacervation with gelatin, interfacial polycondensation resulting in a polyamide or polyurethane shell, and precipitation due to polycondensation of amino resins. The in-situ processes have the ability to yield microcapsules with the best quality in terms of diffusion-tightness of the wall. The surface morphology of microcapsules, as observed using a scanning electron microscope (SEM), is shown in Fig. 14 (Hawlader et al., 2003). The advantages of MPCMs are: (1) reduction of the reactivity of the PCMs with the outside environment, (2) improvement of heat transfer to the surroundings due to the large surface to volume ratio of the capsules, (3) improvement in cycling stability since phase separation is restricted to microscopic distances, and (4) no leakage during its liquid phase for some PCMs. Thermal properties of two MPCM products are listed in Table 8 (Microtek Laboratories Inc., 2011). The appearance of the two products is white to slightly off-white color with good thermal cycling. The form of MPCM 6 is a wet cake (70% solids, 30% water), and MPCM 6D is a dry powder.

When the MPCM is dispersed into the carrier fluid, e.g. water, a suspension of MPCM slurry is formed. In the

a Spray-dried microparticles　　**b** Coacervated microparticles
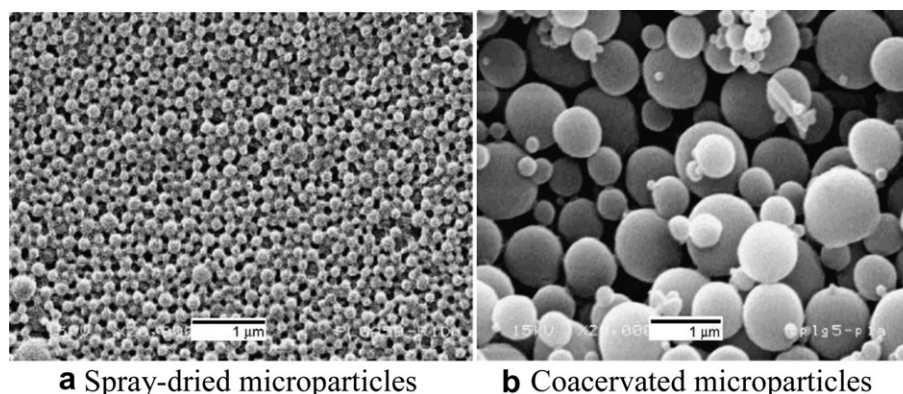
Fig. 14 – Surface morphology of microcapsules studied by a scanning electron microscope (SEM) (Hawlader et al., 2003).

Table 8 – Thermal properties of microencapsulated phase change materials (slurries) (Microtek Laboratories Inc., 2011; Diaconu et al., 2010).

MPCM type	Phase change temperature (°C)	Latent heat (kJ kg^{-1})	Comments
MPCM 6	6 (melting)	157–167 (melting)	Specific gravity: 0.9 Core material: Tetradecane
MPCM 6D	6 (melting)	157–167 (melting)	Mean particle size:17–20 micron Capsule composition: 85–90 wt.% PCM 10–15 wt.% polymer shell
Microencapsulated RT6 slurry	4.1–7.5 (melting) 2.2–5.8 (freezing)	53 (melting) 56 (crystallization)	DSC scanning rate: 0.1 °C min^{-1}
Microencapsulated RT6 slurry	4.0–6.8 (melting) 3.6–6.0 (freezing)	55 (melting) 49.4 (crystallization)	DSC scanning rate: 0.01 °C min^{-1}

fabrication process, the proper amount of surfactants is used for helping MPCM fully disperse into the carrier fluid, thus increasing the lifetime of the MPCM slurry. Because the phase change with latent heat is involved, the effective specific heat of the fluid is remarkably increased with results in the heat transfer enhancement. Obviously, MPCM slurries can be used as both thermal energy storage and heat transfer fluid. The thermal properties of MPCM slurries, like effective thermal conductivity, viscosity and effective specific heat, are different from those of the bulk PCM so that the influence of carrier fluids should be considered. The effective thermal conductivity with flowing condition is generally higher than that predicted by Maxwell's equation due to the interaction between the particle and fluid. A detailed introduction has been developed by Zhang et al. (2010b).

In one study (Alvarado et al., 2004), MPCM particles were made by microencapsulating 99% pure tetradecane with gelatin through the process of complex coacervation. The average microcapsules diameter is 145 μm. On average, the particles contained 2% by weight of an effective nucleating agent. Based on microscopic observations and DSC analysis, each capsule is made of about 88% PCM and 12% shell material. A characteristic micrograph of MPCM can be seen in Fig. 15. Thermal properties of an MPCM slurry with a different MPCM mass fraction is shown in Fig. 16, which shows that this kind of MPCM slurry has the potential to become a successful heat transfer fluid for cold storage in air conditioning applications.

Diaconu et al. (2010) also studied a kind of MPCM slurry for air conditioning applications. It consisted of an aqueous dispersion of PCM (Rubitherm RT6) encapsulated in a polycyclic cell, resulting in microcapsules with a volume mean diameter of 2.24 μm. RT6 is a commercial PCM, and the PCM mass fraction of the slurry was 45%. Thermal properties of the MPCM slurry by DSC study are shown in Table 8. From this table, the conclusion can be made that the narrower phase change temperature range is suitable for air conditioning application.

3.5.2. Phase change emulsions

Phase change emulsion, similar to the MPCM slurry, is a novel two-phase fluid composed of PCM particles as a dispersed phase and water as a continuous phase. Due to the large surface to volume ratio of the dispersed phase, it also has greater apparent specific heats and higher heat transfer abilities in the phase change temperature range than the conventional single-phase heat transfer fluids such as water. Also, phase change emulsion systems store energy not only by using the sensible heat capacity of the carrier fluid, but also by using the latent heat capacity of the media. Thus they are advantageous in the field of the convective heat transfer enhancement and energy transport for both a dynamic type cold storage system and a secondary loop. In addition, a nucleating agent is often used to prevent the effect of supercooling of the emulsion. Illustration of a phase change emulsion is shown in Fig. 17.

Rubitherm RT10 (Huang et al., 2009), which is paraffin mixture of tetradecane, pentadecane, and hexadecane, is presented as a PCM, as shown in Fig. 18. The total heat capacity of the paraffin/water emulsions and the ratio of heat capacity of the emulsions to that of water versus RT10-concentration in the temperature range of 5–11 °C are shown in Fig. 19. Obviously, the paraffin/water emulsion is an attractive candidate for air conditioning application.

The thermal properties of tetradecane-based phase change emulsions have been studied by many researchers (Inaba, 1996; Zhao et al., 2001, 2002.), and are considered attractive candidates for air conditioning application. The melting point
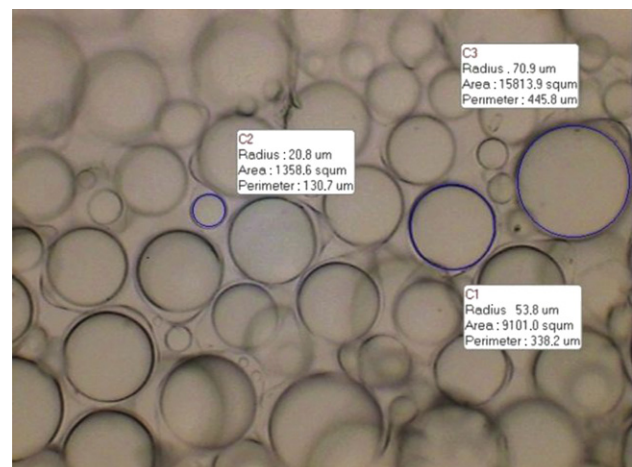
Fig. 15 – Micrograph of one kind of MPCM (n-Tetradecane with gelatin) (Alvarado et al., 2004).
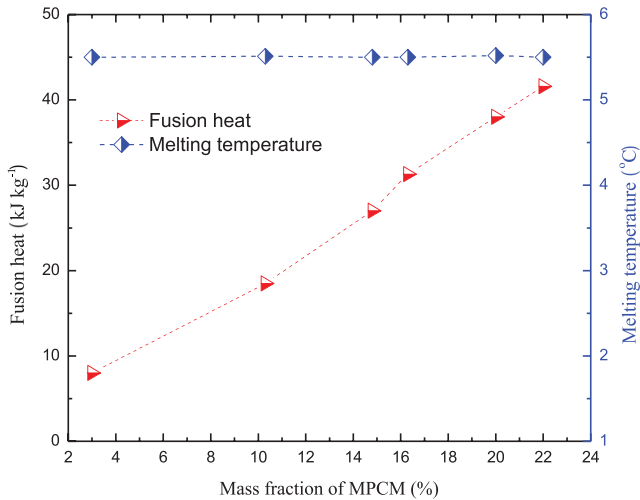
Fig. 16 – Thermal properties of one kind of MPCM slurry (Alvarado et al., 2004).

Fig. 18 – Micrograph of the emulsion containing 30 wt.% RT10 at 20 °C (Huang et al., 2009).

of tetradecane is 5.8 °C and the fusion heat is 229 kJ kg^{-1}. A study of tetradecane-based phase change emulsions is shown in Table 9 (Xu et al., 2005a).

3.5.3. Supercooling minimization

Though the core materials (PCMs) for microencapsulated PCM slurries and phase change emulsion are usually paraffin waxes, which are insoluble with water, supercooling is an important issue to deal with. Nucleation agents can be used to relieve this issue. In one study by Huang et al. (2009), a nucleation agent was added to the paraffin to prevent supercooling before the emulsifying process for the paraffin emulsion in cooling applications. The necessary surface can be offered by the agent to start nucleation in the interior of the paraffin droplets, therefore the agent works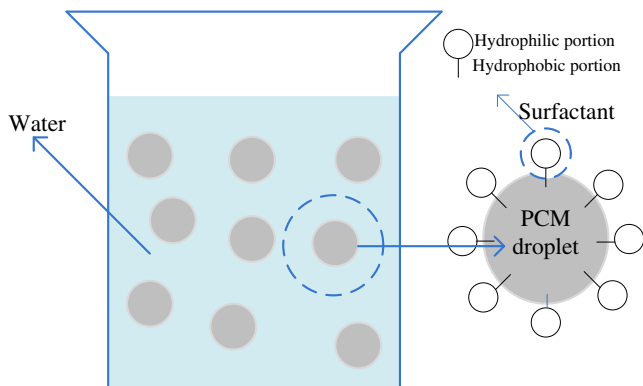 as the nucleation catalyzer. The supercooling was reduced to 0.1 °C with the nucleation agent, while it was 7 °C without that. In another study by Alvarado et al. (2006), a concentration of 2% tetradecanol resulted to be sufficient to suppress supercooling both in tetradecane and microencapsulated tetradecane, and the

heterogeneous nucleation was more favorable in the presence of tetradecanol. Also additional consideration should be given that the amount of nucleation agent for suppressing supercooling effect should be the smallest possible because adding excessive amount of nucleation agent will lead to a reduction of the latent heat of the PCM. l-tetradecanol was added as nucleation agent by Yamagishi et al. (1996) and good results were achieved for two n-tetradecane and n-dodecane microencapsulated slurries. In addition, cold finger and porous heat exchange surfaces have been utilized effectively to deal with this issue.

3.5.4. Thermal and hydraulic characteristics

Since the working fluids studied in this section are mainly used for the secondary loop systems in air conditioning application, it is necessary to study the thermal and hydraulic characteristics. It should be noted that MPCMs should be durable during its long term operation, because it might be broken by the circulating pump. The MPCM slurry is generally

Fig. 17 – Illustration of a phase change emulsion. Note: PCM-in-water emulsions, where fine PCM droplets are directly distributed in water and maintained in dispersion by a surfactant.

Fig. 19 – Total heat capacity of the phase change emulsions and ratio of heat capacity of the emulsions to that of water (Huang et al., 2009).

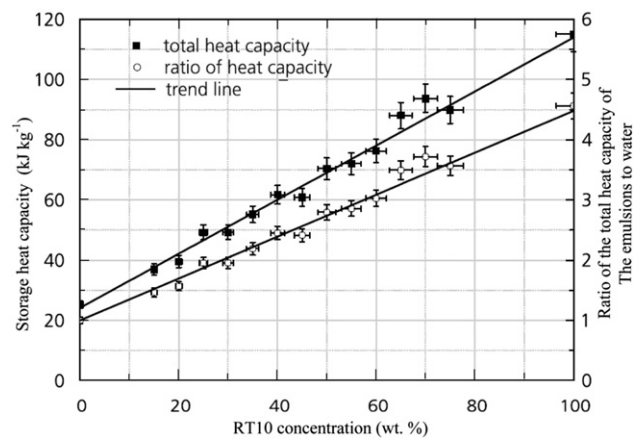| Table 9 – Thermal properties of tetradecane-based phase change emulsions (Xu et al., 2005a).				
Phase change emulsion (tetradecane/water)	Melting point (°C)	Fusion heat (kJ kg^{-1})	Average specific heat in the phase change region (kJ kg^{-1} K^{-1})	Average specific heat in non-phase change region (kJ kg^{-1} K^{-1})
10:9 0tetradecane: water (wt.%)	4.36	18.69	5.7	3.9
20:80 tetradecane: water (wt.%)	4.57	31.56	6.6	3.7
30:70 tetradecane: water (wt.%)	4.51	73.47	10.1	3.6

considered as the Newtonian fluid when the volume fraction of MPCM is less than 25%. The viscosity of the working fluid is a critical factor for cold energy transportation. Based on literature (Wang et al., 2008; Yamagishi et al., 1999), results indicated that the working fluid showed the Newtonian fluid behavior and the apparent viscosity was about 1.5–10 times of the water as the mass fraction of MPCM increased from about 5 to 30%. The MPCM slurry can be treated as the homogeneous fluid at low volume fraction.

Inaba et al. (2004) investigated the mixing effect of the large size PCM (n-docosane) particles under the condition without a phase change and the small size PCM (n-tetradecane) slurry with a phase change. Results showed that the flow drag reduction could be achieved in the turbulent flow regime, while the pressure drop was increased in the laminar flow regime in the case of higher mass fraction of large size particles. The ratio between the heat transported by MPCM slurry (including both latent heat and sensible heat) and the pumping power of the circulating pump was larger than that for water in the turbulent flow regime. In the laminar flow regime, the ratio decreased from larger than that for water to less than that for water as increasing the fraction of the larger MPCM particles. Therefore, reasonable consideration for both the energy transportation and pumping power should be paid in practical application.

In another study by Alvarado et al. (2007), MPCM (n-tetradecane as the core material) with the diameter of smaller than 10 mm was proven to be durable and impact-resistant in the durability test with a cavity pump. MPCM slurry with low mass fraction had much smaller pressure drop than that of water. Moreover, the difference was reduced with an increased mass fraction of MPCM. The drag reduction effect of slurry would be the possible reason. Around melting temperature of n-tetradecane, the heat transfer coefficient of slurry reached its peak.

Study by Diaconu (2009) revealed that the convective heat transfer coefficient between the MPCM particles and the carrier fluid (water) played a critical role during charging/discharging processes. In addition, MPCM mass fraction and particle diameter were studied for optimizing the thermal storage system. Study by Yamagishi et al. (1996) also investigated MPCM (core material: n-tetradecane and n-dodecane) slurries. From this study the tolerance against the shear force induced by pumping is quite essential in practical application. Large apparent viscosity can be achieved with high volume fraction, and this can increase the pressure drop and pumping power. Pressure drop can be effectively reduced by using the drag reduction additives in the case of high volume fraction of MPCM. Based on the discussion above, viscosity,

pressure drop, pumping power, convective heat transfer coefficient, laminar/tubular flow regime, are all important factors when investigating thermal and hydraulic characteristics, which still need further study.

4. Sorption cold storage

For sensible and latent cold storage in air conditioning application, the temperature of the cold storage tank is lower than the ambient temperature. Accordingly, the cold energy loss from the storage tank must be considered in such a system during the storage period. This may be disadvantageous for the system, especially when it is used for a long term storage period. In the following, the sorption cold storage is introduced as a solution for a long term storage period, especially for adsorption storage. Sorption cold storage uses sorption working pairs (sorbents/refrigerants) in air conditioning applications. The sorbents, which can induce physical or chemical attraction with an active refrigerant gas for a refrigeration effect, can either be in liquid phase (absorption technology) or in solid form (adsorption technology). The cooling capacity can be preserved for a long term with no pollution and no cooling energy losses. Also it can be readily discharged when needed only by connecting the generator (for absorption storage) or adsorbent bed (for adsorption storage) to the evaporator. This kind of cold storage system, which can be driven by electricity, industry waste heat, or solar energy, contributes significantly to the concept of sustainable system development. In addition, especially for an adsorption cold storage system, after energy charging, it can be moved to another place that cannot provide energy by itself to produce refrigeration power for short term air conditioning. Usually a sorption system uses alternative clean refrigerants, with no pollution other than the CFC or HCFC refrigerants in a conventional vapor compression system. Also, it can be operated without moving parts, other than some magnetic valves, is mechanically simple, and has high reliability, low vibration and a long lifetime. A general comparison of absorption and adsorption storage technologies is shown in Fig. 20.

4.1. Basic storage principle

4.1.1. Absorption cold storage
A schematic drawing of the basic principle for absorption storage is shown in Fig. 21(a). Using the working pair LiBr/H$_2$O as an example, with the shut-off valve after the poor solution opened, the poor solution (low concentration of absorbent) is

a Absorption   **b** Adsorption

Fig. 20 – Comparison of absorption and adsorption storage technologies.

a Absorption storage

b Adsorption storage

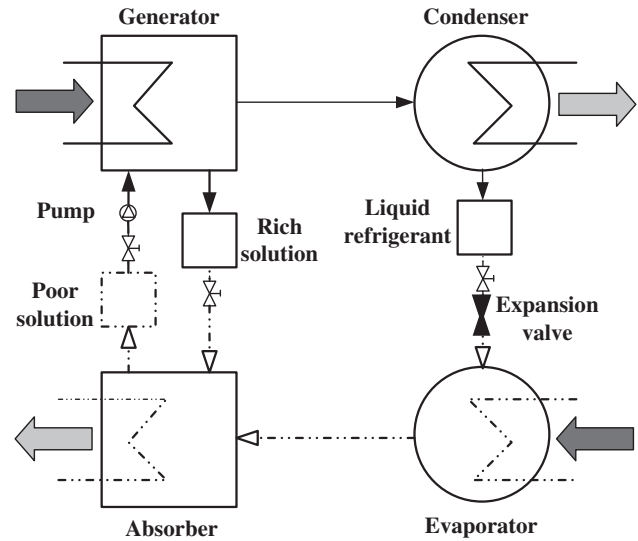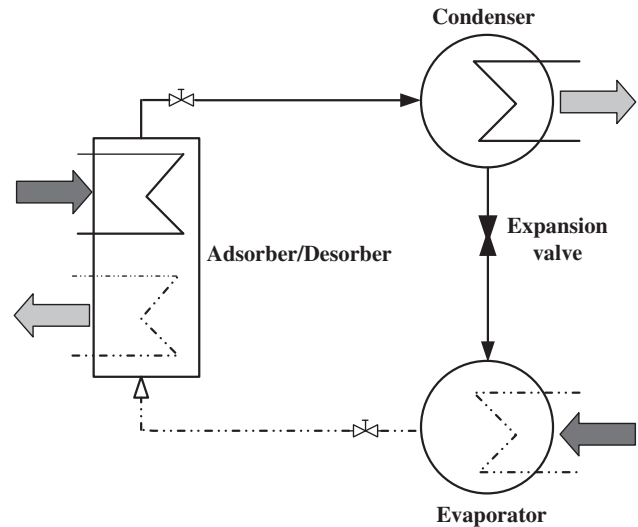**Fig. 21 – Schedule drawing of basic principle for sorption storage.**
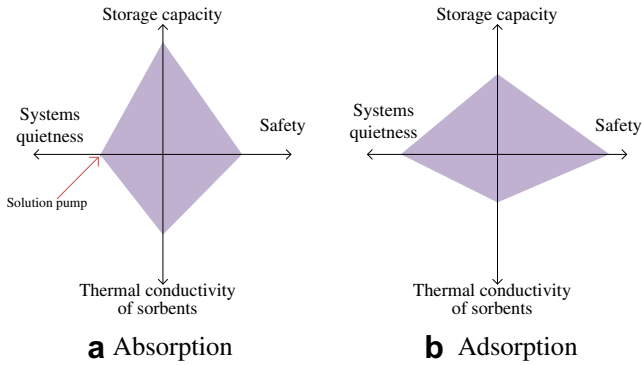
pumped towards the high-pressure zone, and then the mixture is heated in the generator during the charging process. The contribution of heat (driving heat) allows the separation of the refrigerant (H_2O) from the absorbent (LiBr solution). The refrigerant vapor is sent to the condenser, where it is condensed to liquid by a cooling fluid. The liquid refrigerant is stored in a container for cold storage, while the rich solution from the generator is also stored in a container. The liquid refrigerant in the container as the cold storage can be used to produce the cooling effect for air conditioning application. During the discharging process, the shut-off valve after the poor solution is closed, the liquid refrigerant is expanded with the shut-off valve on the liquid refrigerant side opened and sent to the evaporator, and rich solution flows to the absorber with the shut-off valve on the rich solution side opened. Thus, the water vapor in the evaporator is absorbed by the rich solution and the cooling effect is produced in the evaporator at low pressures. And the rich solution absorbs the water vapor and releases absorption heat, which can be used for heating purposes. Gradually, the poor solution from the absorber is stored in a container. Because the absorption refrigeration system has been well developed for the market, only a brief introduction is given in this paper.

4.1.2. Adsorption cold storage
A schematic drawing of the basic principle for adsorption storage is shown in Fig. 21(b). Adsorption is the general phenomenon resulting from the interaction between a solid (adsorbent) and a gas (refrigerant), based on a reversible physical or chemical reaction process. During the charging process, a desorber (can also be an adsorber during the discharging process) connected to a condenser is heated by a heat source with the shut-off valve after the desorber opened. Next, the refrigerant vapor flows from the desorber to the condenser and is cooled to a liquid state. It then passes through the expansion valve and is stored in an evaporator under low-pressure condition for cold storage. During the discharging process, the shut-off valve after the adsorber is closed. The adsorber is cooled by a heat transfer fluid and its pressure drops. When the pressure drops below that of the evaporator, the shut-off valve after the evaporator is opened and the refrigerant is evaporated and moves to the adsorber because of

the pressure difference. Cold temperatures are then produced in the evaporator for air conditioning application.

4.2. Working pair selection

During charge or discharge processes, important heat and mass flows are produced with frequent use of sorption working pairs. The thermal properties of these working pairs play a very important role for storage used in air conditioning applications. Here, the thermal property mainly refers to the storage capacity or the ratio of the amount of cold storage by evaporation of refrigerant to the mass or volume of the sorbent. It is one of the basic criteria required for designing an efficient storage process. To provide a general understanding on thermal properties of different working pairs, Mugnier and

a NH_3 as refrigerant

b H_2O as refrigerant

c Other materials as refrigerant
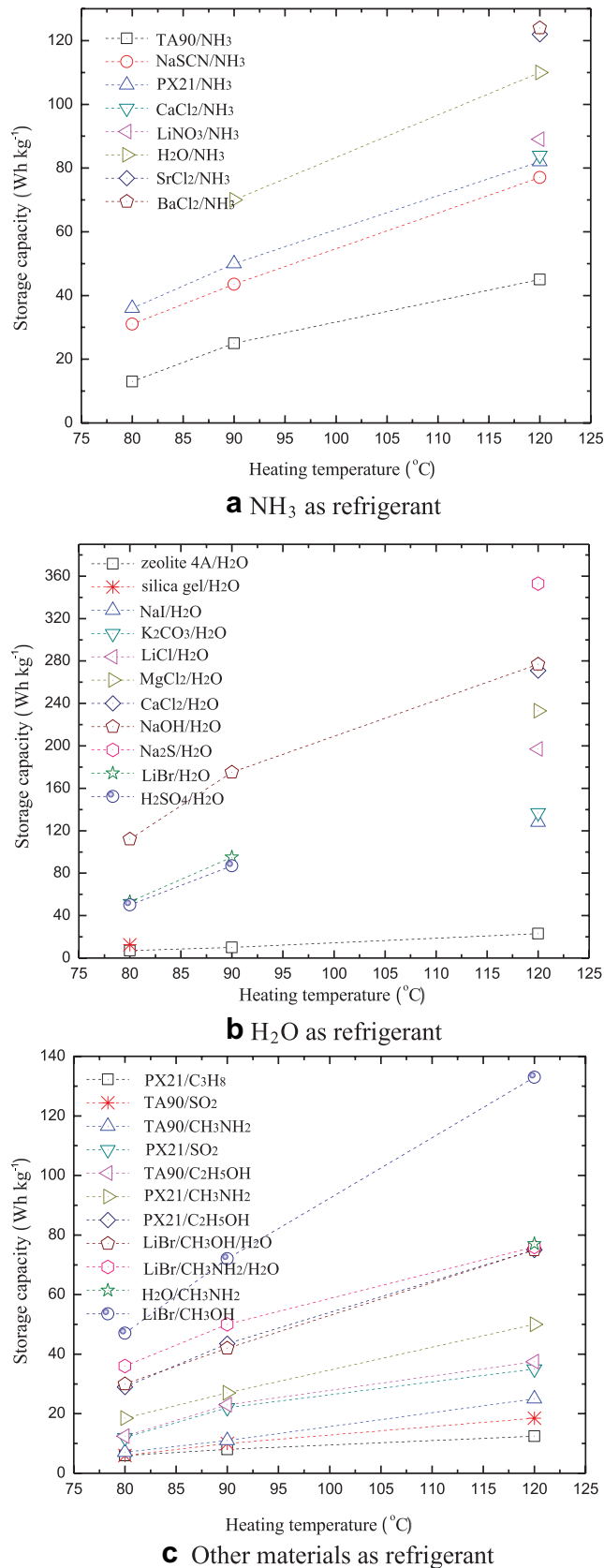
Fig. 22 − Storage capacity of different sorption working pairs with ambient temperature of 35 °C and evaporation temperature of 5 °C (Mugnier and Goetz, 2001).

Goetz (2001) summarized and compared their storage capacities. Based on the data, and with a rigorous calculation protocol obtained from the literature (Mugnier and Goetz, 2001), thermal properties of working pairs for air conditioning applications were extracted and summarized as shown in Fig. 22. The summary examines them under the same conditions of an ambient temperature of 35 °C and evaporation temperature of 5 °C. Storage capacity and minimum heating temperature of different sorption working pairs under same conditions is shown in Fig. 23. From the figures above, the most suitable and efficient working pair for the sorption storage system is water and solid/gas reaction used as the refrigerant and sorbent, respectively. For the requirements of a working pair, the refrigerant should have environment safety, large latent heat per volume, no toxicity, no flammability, no corruption, good thermal stability, low material cost, and better volatility of the solution in the absorption system. For the sorbent, especially for the adsorbent, it should have the large adsorption capacity, large change of adsorption capacity with temperature variation, a more flat desorption isotherm, and good compatibility with refrigerant. Generally speaking, there are no perfect working pairs meeting all of these requirements.
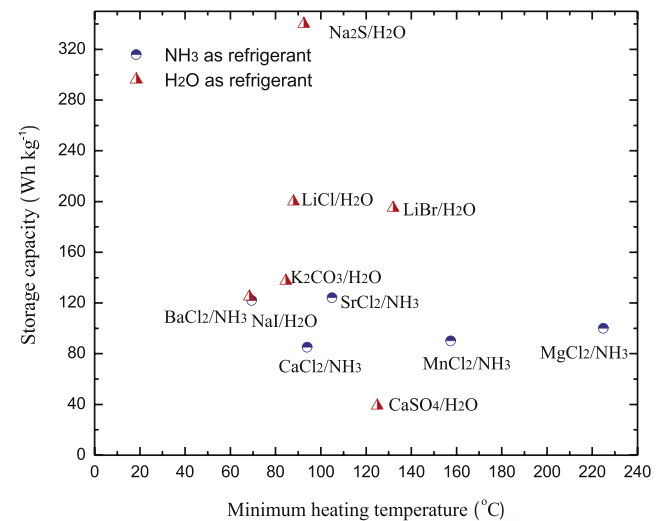
4.2.1. Absorption working pairs

Among the absorption absorbent/refrigerant pairs, $LiBr/H_2O$ and H_2O/NH_3 are the most common ones. The former is usually used for air conditioning application and the latter can be used for subzero applications, such as ice making, etc. In addition, H_2O/NH_3 has several disadvantages: (1) higher generator inlet temperature (about 90–180 °C, while it is about 70–90 °C for $LiBr/H_2O$), (2) higher pressures and hence higher pumping power needed, (3) a more complex system needed due to a rectifier to separate ammonia and water vapor at the generator outlet, and (4) hazards by the use of ammonia. Therefore, $LiBr/H_2O$ is more suitable for air conditioning application. In addition, the comparison of working pairs, $LiBr/H_2O$, NaOH/

Fig. 23 − Storage capacity and minimum heating temperature of different sorption working pairs with ambient temperature of 35 °C and evaporation temperature of 5 °C (Mugnier and Goetz, 2001).

Working pairs	Absorbent price (Euro ton^{-1})	Without crystallization			With crystallization		
		Concentration maximum (%) (kg absorbent kg^{-1} solution^{-1})	Capacity (kJ kg^{-1})	Temperature requirement for heat driving (°C)	Concentration maximum (%) (kg absorbent kg^{-1} solution^{-1})	Capacity (kJ kg^{-1})	Temperature requirement for heat driving (°C)
LiBr/H_2O	6000	60	1535	74	69	2068	93
LiCl/H_2O	3400	46	2922	68	70	5271	78
NaOH/H_2O	300	53	3442	84	69	5225	135
CaCl$_2$/H_2O	140	45	628	50	51	1103	56

Table 10 – Evaluation points of different absorption working pairs (Liu et al., 2009).

H_2O, LiCl/H_2O, and CaCl$_2$/H_2O, has also been studied. As shown in Table 10, different working pairs were compared under the same conditions of a temperature of absorption of 25 °C, a temperature of evaporation of 10 °C and a temperature of condensation of 30 °C (Liu et al., 2009). From this table, and based on the analysis from literature (Liu et al., 2009), the NaOH/H_2O and LiCl/H_2O pairs have excellent performance on storage capacity. The NaOH has the advantage of a low price, but has the disadvantage of a temperature requirement for solar energy utilization (84–135 °C). The CaCl$_2$ is the least expensive material, but its storage capacity is low so that the volume of storage tanks would be bigger than for the other pairs. The NaOH/H_2O could be the most economic material because of its low price and high storage capacity. However, due to its high temperature requirement for solar energy utilization, the system's solar collector would be operated at low efficiency. This solution is also highly corrosive.

4.2.2. Adsorption working pairs

The commonly used working pairs of silica gel/H_2O and zeolite/H_2O, which closely meet these requirements, are introduced here.

(1) Silica gel/H_2O

Based on Faninger (2004), the storage density of silica gel is up to four times that of water. From the literature by Yang (1991), the adsorption heat of silica gel/H_2O is about 2500 kJ kg^{-1} and the desorption temperature can be very low, but above 50 °C. Normally the desorption temperature should not be higher than 120 °C, and it is usually below 90 °C. Approximately 4–6 wt.% water is connected with a single hydroxyl group on the surface of a silica atom to maintain the adsorption capacity. If the desorption temperature is too high

(above 120 °C), adsorption performance will drop significantly, even to the point of losing its adsorption capacity. In addition, the adsorption quantity of this pair is low, about 0.2 kg kg^{-1} (Wang et al., 2009).

(2) Zeolites/H_2O

Zeolites are alumina silicates with high microporosity (Nielsen, 2003), and are considered to be reliable even in the harshest environmental conditions (Zeolith-Technologie GmbH, 2008). Since synthetic zeolites are expensive, Han et al. (1994) conducted a contrast study of natural zeolites to the synthetic zeolite 13X. They reported that natural zeolites could be used as a storage material instead of the 13X synthetic zeolite when the heating temperature is below 100 °C. For the zeolite/H_2O pair, the adsorption heat is about 3300–4200 kJ kg^{-1}, higher than that of silica gel/H_2O pair (Wang et al., 2009). Additionally, the temperature of desorption can reach high than 200 °C, at which point the zeolite/H_2O can be still stable. The zeolites are usually employed for air conditioning application with a heat source between 200 and 300 °C. Several kinds of crystal cell units of zeolite are shown in Fig. 24 (Yang, 1991). The volume of pores for type X and Y zeolites, whose void ratio can be as high as 50% when there is no water adsorbed, is larger than that of other types of pores. One crystal unit can have 235 molecules of water after adsorption, and most of the molecules would accumulate in the center pore.

The adsorption process of the working pairs discussed above is physical adsorption, which is caused by the van de Walls force between the molecules (Ponec et al., 1974) of the adsorbent containing mesopores or micropores, and the refrigerant. For details about chemical adsorption, please refer to literature (Wang et al., 2009).
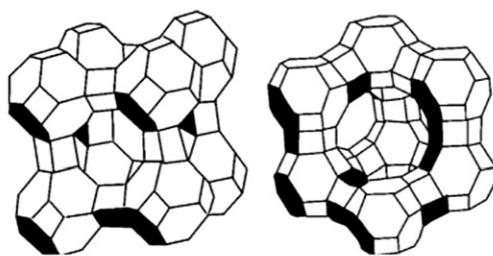
a Crystal cell unit of type A zeolite   **b** Crystal cell unit of type X, Y zeolite or faujasite

Fig. 24 – Crystal cell unit of zeolite (Yang, 1991).

Table 11 – Review of absorption thermal energy storage technologies for air conditioning application (Yang et al., 2011).

Absorption pair	Driving source	Thermal storage density (kW h m^{-3})	Standard for thermal storage volume
LiBr/H$_2$O	Compressor cycle	111.7 (full storage type) 109.4 (part storage type)	Mixed storage volume and water volume
LiBr/H$_2$O	Solar energy, single effect	58.2	Dilute solution volume, concentrated solution and water volume
LiBr/H$_2$O	Solar energy	116.7	Mixed storage volume and water volume
LiBr/H$_2$O	Heat pump	90	Optimized dilute solution volume, concentrated solution
LiBr/H$_2$O	Compressor cycle	32.78	Mixed storage volume and water volume

4.3. Heat transfer and system performance enhancement

The sorption cold storage is closely related to the sorption cooling technologies. The absorption storage was initially studied in conjunction with solar energy, and the system design was gradually improved based on the technologies of absorption refrigeration system. Components of absorption systems were studied for improving heat transfer. An example of such a study involves the optimization of liquid refrigerant tank with reasonable volume to make the system operate in an improved state for better storage capacity (Sheridan and Kaushik, 1981). Additionally, various recycle system configurations have been used to improve system performance (Li and Sumathy, 2000; Yang et al., 2011). Based on the literature review (Wan et al., 2006; Qiu et al., 2009; Xu et al., 2008, 2005b; Rizza, 2003), Yang et al. (2011) summarized related absorption cold storage technologies. The most commonly used working pair, LiBr/H$_2$O, was extracted and is shown in Table 11.

For the adsorption storage, the adsorption cold storage system with zeolite/H$_2$O working pair was studied by Lu et al. (2003). Results showed that the adsorption cold storage system could be successful used for the locomotive air conditioning system. This system is simple and can be handled easily compared with other multi-bed adsorption systems. Also, the operating process of the system is in conformity with the running time of the locomotive. An average refrigeration power of about 4.1 kW was obtained, which was enough to make the driver's cabin fairly comfortable. However, this study also mentioned that the heat and mass transfer of the adsorber needs to be improved to get better performance. Here the main issue of the poor heat and mass transfer of adsorbent beds, especially the low thermal conductivities and poor porosity characteristics of adsorbents, is discussed.

Li and Wang (2002) reached the conclusion that adding packing density to an adsorbent, adopting double glass covers, using selective coating material, and using heat transfer fins or plate heat exchangers could enhance the heat transfer and thermal conductivity of the adsorbent beds. Additionally, composite adsorbents, which are normally a combination of physical sorbents (silica gel or zeolite) and chemical sorbents (metal chlorides) can experience increases physical adsorption capacity through the addition of extra chemicals. For improving system performance of adsorption storage, there are two main parameters to with which to evaluate the performance for adsorption refrigeration: COP, which is the ratio of cold production from the evaporator to the heat supplied by driving energy, and SCP, which is the ratio of cooling power for the semi-cycle to the adsorbent mass in one adsorbent bed. To improve the COP, in addition to adapting advanced heat exchanger, adsorption storage with different advanced cycles has been studied extensively (Sumathy et al., 2003). To improve the SCP, more technologies are needed to improve heat and mass transfer of adsorbent beds, which are discussed above to some extent. Wang et al. (2009) summarized the performance of the COP and SCP with a fair comparison of different working pairs from the literature (Lai, 2000; Eun et al., 2000; Wang et al., 2005a, 2005b). The water-based working pairs for air conditioning applications are extracted from their study and shown in Table 12.

For the adsorption storage technologies, the main factors impeding the commercialization of this storage technology for air conditioning application are high equipment and maintenance cost, big size, and the need for an auxiliary energy system. There is still much more work to do for optimizing and reducing the cost of these systems with more advanced technologies.

Table 12 – Performance comparison of different adsorption working pairs (Wang et al., 2009).

Adsorption working pair	Evaporating temperature (°C)	COP	SCP (W kg^{-1})	Characteristics
Graphite/silica gel/water	3		70	Composite adsorbent to intensify the heat transfer
Silica gel/water	10	0.4	85	Split heat pipe type evaporator
Zeolite/water	5	0.9	250	Intermittent convective thermal wave cycle

5. Challenges and technology perspective

Different kinds of available cold storage materials that can be used for air conditioning applications are introduced in this paper. Technology perspectives, with regard to water storage, ice storage, PCM storage and sorption storage are summarized as follows:

(1) Water storage and static ice storage, which are already well-established technologies, have little need for further study. The important issue concerning the dynamic ice slurry application is its generation method, relating to the efficiency and reliability of a water or aqueous solution converting to ice crystals or ice slurry, which needs to be investigated further.

(2) Salt hydrates and eutectics, and refrigerant hydrates are material candidates for cold storage, and demonstrate high latent heat of fusion, high thermal conductivity, and low flammability. However, salt hydrates have more serious issues of phase separation, supercooling, and corrosion. Paraffin waxes and fatty acids are mostly chemically inert, stable and recyclable, exhibit little or no supercooling. They show no phase separation or non-corrosive behavior (with the exception of fatty acids for the natural characters of acids). However, they have the shortcomings of low thermal conductivity and high flammability. Some works have been done for such issues by past researchers, which were introduced and summarized in this paper.

(3) Thermal and hydraulic characteristics of phase change slurries (mainly about clathrate slurries, micro-encapsulated phase change slurries, and phase change emulsions) are discussed and summarized. Viscosity, pressure drop, pumping power, convective heat transfer coefficient, and laminar/tubular flow regime, are all important factors for thermal and hydraulic characteristics and reasonable consideration should be made for practical application.

(4) The suitable and efficient working pair that can be used for the sorption storage system is water and solid/gas reaction used as the refrigerant and sorbent, respectively. One of main issues is the poor heat and mass transfer of adsorbent beds, especially for the low thermal conductivities and poor porosity characteristics of adsorbents. Additionally, the main factors impeding the commercialization of this storage technology are high equipment and maintenance cost, big size, and the need of an auxiliary energy system. Therefore, there is still much further work to do with regards to optimizing and reducing the costs of these systems with more advanced technologies.

Acknowledgments

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