Carbon dioxide semi-clathrate hydrate for cold storage based air conditioning systems: materials and applications

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This work is an account of research undertaken between March 2013 and September 2016 through the College of Engineering and Computer Science at the Australian National University.

Except where otherwise indicated, this thesis is my own original work. No material in this thesis has been previously submitted for the purpose of obtaining a degree in any university or other tertiary education institution.

Xiaolin Wang

27 September 2016
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Abstract

The increasing use of household air conditioning has been claimed to be one of the main drivers for peak electricity grid load over the past decade. Cold thermal energy storage (CTES) allows excess cooling capacity to be collected and conserved for later use; thus it is proposed to alleviate peak diurnal electricity demand problems.

This thesis investigates the potential for CTES equipped air conditioning systems to time shift demand on electricity grids. In particular, CTES allows air conditioners to be operated overnight using off-peak electricity. It also provides backup for solar cooling systems.

A major component of this thesis is the development, modification and application of a phase change material (PCM) based on CO\textsubscript{2} hydrate.

The first part of this work demonstrates the feasibility of CTES for residential space cooling. A TRNSYS model is composed, in which a CO\textsubscript{2} hydrate cold store is integrated into a photovoltaic (PV) cooling system as a backup. This configuration is compared to a PV cooling system with an electrical energy store. The inclusion of CTES in the system strongly contributes to electricity savings. Electricity savings of the system with cold store is slightly lower than that of the system with battery. Moreover, the CO\textsubscript{2} hydrate cold storage provides superior electricity savings compared to conventional ice storage or fatty acid cold storage.

The second part of this work involves the development of a CO\textsubscript{2} hydrate based cold storage medium. In order to operate within the practical working pressure range of conventional cooling systems, the pressure adopted in this study is moderate (<8 bar). Tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium fluoride (TBAF) and tetra-n-butyolphosphonium bromide (TBPB) are employed to reduce the equilibrium pressure of the hydrate.

Instead of using complex calorimeters, the formation enthalpy of CO\textsubscript{2} hydrate is measured using a modified T-history method in a self-fabricated pressure tube. The T-history is applied for the first time to determine the enthalpy of gas hydrate under pressure. Through this test, the enthalpy of CO\textsubscript{2} hydrate is found to be high compared to other PCMs. However, the hydrate suffers a large supercooling degree and a long induction delay before the hydrate formation really takes place. Besides, there is a non-negligible difference between the freezing and thawing temperature, which would result in a temperature loss in the cold store. These are the main challenges to overcome in this study.
By using secondary promoters, such as sodium dodecyl sulfate (SDS) and titanium dioxide nanoparticles, formation behaviour of CO₂ hydrate is optimised. As a result, a composition is composed which has suitable formation temperature, acceptable supercooling degree and induction time. This composition consists of CO₂ + TBAB (20 wt%) + TBAF (0.25 wt%) + SDS (0.15 wt%).

The last part is the application of the developed composition in an emulated cold storage system. The aim is to evaluate the cyclic charging-discharging performance of the CO₂ hydrate based cold store. The 17.5 L cold store is equipped with a heat exchange coil and external ultrasonic vibrator. The working pressure of the hydrate is around 5 bar, which enables moderate cost storage vessels to be used in real cold storage systems. In this configuration, the cold storage medium showed further reduced supercooling degree, rapid formation and small difference between the freezing and thawing temperature.

It would be reasonable to claim that solutions to the serious impediments to trialling CO₂ hydrate cold storage technology are presented in this thesis. Further investigations are required to determine the heat transfer properties and longer term cyclic longevity of the material. Based on small scale costs and some assumptions, the cost of such a hydrate cold storage is in the order of $250 per kWh of electricity. This compares favourably to the contemporary battery electric storage cost of $1500 per kWh of electricity. Additionally, through instantaneous pressure control, the charging and discharging temperature can be adjusted for requirements of different chillers and air conditioning terminals.
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<tr>
<td>CTES</td>
<td>Cold thermal energy storage</td>
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<tr>
<td>PCM</td>
<td>Phase change material</td>
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<tr>
<td>PESR</td>
<td>Primary energy saving ratio</td>
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<tr>
<td>HTF</td>
<td>Heat transfer fluid</td>
</tr>
<tr>
<td>TBAB</td>
<td>Tetra-n-butylammonium bromide</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetra-n-butylammonium fluoride</td>
</tr>
<tr>
<td>TBPB</td>
<td>Tetra-n-butylphosphonium bromide</td>
</tr>
<tr>
<td>TRNSYS</td>
<td>Transient systems simulation program</td>
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<tr>
<td>NTU</td>
<td>Number of transfer units</td>
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**Indices**

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</tr>
<tr>
<td>l</td>
<td>Liquid phase of PCM</td>
</tr>
<tr>
<td>f</td>
<td>Heat transfer fluid</td>
</tr>
<tr>
<td>w</td>
<td>Water</td>
</tr>
<tr>
<td>s</td>
<td>Supercooling</td>
</tr>
<tr>
<td>r</td>
<td>Reference</td>
</tr>
<tr>
<td>*</td>
<td>Saturation state</td>
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**Variables**

<table>
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<th>Variable</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \varphi )</td>
<td>Phase change fraction</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Heat exchanger effectiveness</td>
</tr>
<tr>
<td>( \phi_{CO_2} )</td>
<td>Fugacity coefficient of CO$_2$</td>
</tr>
<tr>
<td>( \eta_{CS} )</td>
<td>Storage energy efficiency</td>
</tr>
<tr>
<td>( \gamma_c )</td>
<td>Self-consumption ratio</td>
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<tr>
<td>( \gamma_s )</td>
<td>Self-sufficiency ratio</td>
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<tr>
<td>( \alpha )</td>
<td>Convective coefficient of HTF</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density of PCM</td>
</tr>
</tbody>
</table>
\( \rho_{H2O} \) Density of water \([\text{kg} \cdot \text{m}^{-3}]\)  
\( \sigma \) Thermal diffusivity of PCM \([\text{m}^2 \cdot \text{s}^{-1}]\)  
\( \delta \) Radius of phase boundary \([\text{m}]\)  
\( A \) Heat transfer area \([\text{m}^2]\)  
\( A_c \) Convective heat-transfer area of the tube \([\text{m}^2]\)  
\( a \) Number of CO\(_2\) in the hydrate formula  
\( Bi \) Biot number  
\( c_p \) Specific heat \([\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]\)  
\( c_{p,t} \) Specific heat of T-history tube \([\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]\)  
\( c_{p,l} \) Specific heat of liquid PCM \([\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]\)  
\( c_{p,s} \) Specific heat of solid PCM \([\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]\)  
\( c_{p,w} \) Specific heat of water \([\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]\)  
\( c_{p,HTF} \) Specific heat of HTF \([\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]\)  
\( E_o \) Exergy output during discharge \([\text{kW}]\)  
\( E_i \) Exergy input during charge \([\text{kW}]\)  
\( h \) Phase change enthalpy of PCM \([\text{kJ} \cdot \text{kg}^{-1}]\)  
\( K_H \) Henry’s constant  
\( k \) Thermal conductivity \([\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]\)  
\( k_s \) Thermal conductivity of solid PCM \([\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]\)  
\( k_l \) Thermal conductivity of liquid PCM \([\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]\)  
\( k_w \) Thermal conductivity of tube wall \([\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]\)  
\( k_{PCM} \) Thermal conductivity of PCM \([\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]\)  
\( L \) Tube length \([\text{m}]\)  
\( m \) Mass \([\text{g}]\)  
\( m_p \) Mass of PCM \([\text{g}]\)  
\( m_t \) Mass of tube \([\text{g}]\)  
\( m_{H2O, i} \) Initial mass of water \([\text{g}]\)  
\( m_{\text{solution}} \) Mass of solution \([\text{g}]\)  
\( \dot{m} \) Mass flow rate of HTF \([\text{kg} \cdot \text{s}^{-1}]\)  
\( M_{CO2} \) Molar mass of CO\(_2\) \([\text{g} \cdot \text{mol}^{-1}]\)  
\( M_{H2O} \) Molar mass of water \([\text{g} \cdot \text{mol}^{-1}]\)  
\( M_{\text{salt}} \) Molar mass of salt \([\text{g} \cdot \text{mol}^{-1}]\)  
\( n_{CO2,l} \) Mole of dissolved CO\(_2\) in water \([\text{mol}]\)
\( n_{CO_2,g} \) Mole of gaseous \( CO_2 \) [mol]
\( n_{hyd} \) Mole of formed hydrate [mol]
\( n_{salt,hyd} \) Mole of salt in hydrate phase [mol]
\( n_{H2O,hyd} \) Mole of water in hydrate phase [mol]
\( n_{CO_2,hyd} \) Mole of \( CO_2 \) in hydrate phase [mol]
\( n_{salt,solution} \) Mole of salt in solution [mol]
\( n_{H2O,solution} \) Mole of water in solution [mol]
\( n_{CO_2,initial} \) Initial mole of \( CO_2 \) [mol]
\( P \) Pressure of reaction tube [Pa]
\( Q \) Power consumption [kW]
\( Q_i \) Cooling input during charge [kW]
\( Q_o \) Cooling output during discharge [kW]
\( Q_r \) Heat rejection to the surroundings [kW]
\( Q_{BC} \) Charged power in the battery [kW]
\( Q_{PV} \) Total generated power from PV [kW]
\( Q_{BD} \) Discharged power from the battery [kW]
\( Q_{LP} \) Load power [kW]
\( Q_C \) Charging rate [kW]
\( Q_D \) Discharging rate [kW]
\( Q_L \) Cooling capacity lose rate [kW]
\( \Delta Q \) Cooling capacity storing rate [kW]
\( r \) Radius [m]
\( r_i \) Inner radius of tube [m]
\( r_o \) Outer radius of tube [m]
\( r_{max} \) Maximum radius of frozen PCM between adjacent tubes [m]
\( R \) Thermal resistance [K·W\(^{-1}\)]
\( R_T \) Total thermal resistance [K·W\(^{-1}\)]
\( R_{PCM} \) Thermal resistance of PCM [K·W\(^{-1}\)]
\( R_{HTF} \) Thermal resistance of HTF [K·W\(^{-1}\)]
\( R_w \) Thermal resistance of tube wall [K·W\(^{-1}\)]
\( R_{gas\ constant} \) Gas constant (8.314 J·K\(^{-1}\)·mol\(^{-1}\))
\( T \) Temperature [°C]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_i$</td>
<td>Inlet HTF temperature of cold store</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_o$</td>
<td>Outlet HTF temperature of cold store</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Phase change temperature</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Supercooling temperature</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Initial temperature of PCM</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_f$</td>
<td>HTF temperature</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_{amb}$</td>
<td>Ambient temperature</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$T_r$</td>
<td>Reference temperature</td>
<td>$[\degree C]$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>$[s]$</td>
</tr>
<tr>
<td>$t_f$</td>
<td>Time of full solidification of PCM</td>
<td>$[s]$</td>
</tr>
<tr>
<td>$U$</td>
<td>Overall heat-transfer coefficient</td>
<td>$[\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}]$</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
<td>$[\text{m}^3]$</td>
</tr>
<tr>
<td>$V_{CO_2}$</td>
<td>Volume of CO$_2$</td>
<td>$[\text{m}^3]$</td>
</tr>
<tr>
<td>$V_{g,i}$</td>
<td>Initial volume of gas</td>
<td>$[\text{m}^3]$</td>
</tr>
<tr>
<td>$V_{hyd}$</td>
<td>Volume of formed hydrate</td>
<td>$[\text{m}^3]$</td>
</tr>
<tr>
<td>$w_{salt}$</td>
<td>Mass fraction of salt in the solution</td>
<td>$[\text{g} \cdot \text{g}^{-1}]$</td>
</tr>
<tr>
<td>$x_{CO_2}$</td>
<td>Mole fractions of CO$_2$ in liquid phase</td>
<td>$[\text{mol} \cdot \text{mol}^{-1}]$</td>
</tr>
<tr>
<td>$y_{CO_2}$</td>
<td>Mole fractions of CO$_2$ in vapour phase</td>
<td>$[\text{mol} \cdot \text{mol}^{-1}]$</td>
</tr>
<tr>
<td>$Z$</td>
<td>Compressibility factor</td>
<td></td>
</tr>
<tr>
<td>$\Delta r$</td>
<td>Spatial step in the discretization</td>
<td>$[\text{m}]$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time step in the discretization</td>
<td>$[\text{s}]$</td>
</tr>
</tbody>
</table>
1.1 Significance

Air conditioning industries have attracted attention due to the high electricity consumption and greenhouse gases emissions associated with the use of conventional space cooling technology. According to the *Australian Bureau of Statistics* [1], in 2014, nearly one half of Australian households (49%) used reverse cycle air conditioning as their main system of cooling. A further 10% of households used refrigerated air conditioners which cool only. Most of the air conditioners are electric-driven. According to a report of the Department of Climate Change and Energy Efficiency and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) *Energy consumption of 100 Australian residential air conditioners* [2], in the past 15 years, households consumed about 40% of residential energy in space heating and cooling. Such an electricity consumption results in not only a large energy usage, but also a heavy burden on electricity grids as power consumption may vary significantly during the day and night, especially in extremely hot climates. Moreover, electricity prices in Australia have dramatically increased in recent times. Prices increased nationally by 70% between June 2007 and December 2012. As a result, air conditioner use is becoming much less affordable.

As the energy efficiency of buildings becomes more valued and air conditioning becomes naturally a major factor for both residential and commercial buildings, increased electricity demand will be placed on the electricity grid. This demand is typically coincident, leading to high peak transmission stress on the grid infrastructure.

If an effective approach could be found to shift peak demand on electricity grids, it would serve several purposes: to increase utilisation of existing grid assets, thereby negating the need to augment the grid; lower the average cost of electricity; and aid the utilisation of renewable energy. It is well known that an effective CTES can shift peak demand to off-peak periods. For electric-driven air conditioning, CTES
stores the cooling capacity produced by the chiller during the night, and supplies it to the user during the daytime, thus offering a means to reduce the peak load on electricity grids. In addition to the lower cost of electricity, such operation of the air conditioner is more efficient than the daytime running due to the cooler condensing temperatures available. CTES also works compatibly with a wide range of cooling systems powered by renewable energy, such as solar thermal cooling systems and PV cooling systems. For solar thermal air conditioning systems, such as adsorption, absorption and ejector systems, CTES conserves excess cooling capacity created from solar thermal energy during the daytime and provides cooling into the evening. For PV cooling systems, usually PV panels integrate with a conventional electric-driven air conditioning system with a mechanical vapour compression refrigeration cycle, and there are two approaches for energy storage – battery storage and CTES. A battery conserves surplus electricity generated by solar panels; while CTES stores excess cooling capacity from chillers by means of latent heat or sensible heat. Generally, both storage approaches are able to store excess energy for later use, alleviate the intermittency of cooling supply, and deliver high primary energy saving by intensively utilising renewable energy. However, only a few investigations focus on the energy savings of CTES-aided renewable energy cooling systems, and we are not aware of any study that compares the energy savings of battery and CTES in a cooling system. In particular, the sensitivity of latent heat CTES to the operating conditions and the PCM properties are unclear. Furthermore, there is not a study that compares the energy saving of a latent heat CTES installation using different PCMs.

It is widely accepted that latent heat CTES has obvious advantages over sensible heat CTES. Sensible heat CTES usually utilises sensible heat capacity of materials, such as water and salt, to store thermal energy during temperature changes. This method is less favoured due to its low energy storage density. Current research mainly focuses on latent heat CTES that charges and discharges cooling capacity by the latent heat of PCM phase transition.

The advantages of latent heat CTES in air conditioning systems are:

1. The storage density of a PCM is usually 5–14 times higher than that of a sensible thermal storage material.
2. The phase change temperature can be adjusted to match the required delivery temperature, avoiding the entropy production caused by mixing the return water in the system.
3. The chiller’s set-point for charging the cold store can be the same as that for normal cooling supply due to the matched phase change temperature of the PCM; thus the chiller can operate under a single working condition.
4. The chiller’s efficiency can be improved due to the high evaporating temperature, and the chiller runs more efficiently at night.
5. The chiller can be downsized.
6. The temperature fluctuation of a PCM cold storage is smaller than that of a sensible thermal storage.
7. Demand management opportunities and additional extreme demand handling are possible.

Generally, PCMs for cold storage air conditioning systems should have the following properties:

1. A suitable phase change temperature
2. Large transition enthalpy per unit mass
3. Ability to fully reverse the phase transition
4. Sufficient thermal conductivity
5. Limited volumetric change in phase transition
6. Congruent freezing and melting with minimum supercooling without phase segregation
7. Chemical stability for long term use and compatibility with the container
8. Non-toxic and non-corrosive
9. Low cost.

Based on these criteria, many academics have been working on the selection and optimisation of an ideal PCM for cold storage.

Ice is a commonly used PCM. However, the evaporating temperature of a cooling system equipped with ice storage is lower than that of a conventional cooling system by 8–10°C, resulting in a decrease of 30–40% in the cooling system efficiency. Clathrate hydrates (or gas hydrates) have been proposed as a cold storage medium for CTES. Hydrates of natural gases are potential cold storage media to store cooling capacity, which can provide both suitable melting temperatures for space cooling and suitable freezing temperatures for the operation of conventional chillers. The properties of different cold storage media are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Cold storage medium</th>
<th>Water</th>
<th>Ice</th>
<th>Eutectic salt</th>
<th>Clathrate hydrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latent heat [kJ·kg⁻¹]</td>
<td>/</td>
<td>334</td>
<td>115</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Phase change temperature [°C]</td>
<td>0–10</td>
<td>0</td>
<td>8–12</td>
<td>5–12</td>
</tr>
<tr>
<td>COP of refrigerator</td>
<td>1</td>
<td>0.6–0.7</td>
<td>0.92–0.95</td>
<td>0.89–1</td>
</tr>
<tr>
<td>Heat transfer</td>
<td>Superior</td>
<td>Medium</td>
<td>Inferior</td>
<td>Superior</td>
</tr>
<tr>
<td>Investment</td>
<td>&lt;0.6</td>
<td>1</td>
<td>1.3–2</td>
<td>1.2–1.5</td>
</tr>
</tbody>
</table>
The phase change latent heat of clathrate hydrates is commonly close to that of ice, which leads to size and weight advantages compared to chilled water and other PCMs. The phase change temperature of clathrate hydrates is usually in the range of 5–12°C, which suits it to the characteristics of conventional air conditioning systems. Clathrate hydrate based CTES requires only one-half to one-third of the space of an equivalent eutectic salt CTES [3], and is approximately one-half the weight. Moreover, clathrate hydrates allow direct contact charging and discharging, thus improving the heat transfer efficiency to and from a cold store [4].

Most PCMs are expensive and many have negative impacts on the environment. CO₂ is a good option to form a clathrate hydrate on the grounds of safety, environmental impact and cost. However, using such a material for cold storage in practical cooling systems requires further investigation to overcome some difficulties, such as high formation pressure, large degree of supercooling, and long induction delay. These definitions will be introduced in detail in chapter 2. In addition, methods to characterise the phase change enthalpy are key to any application of PCMs. Currently, most characterisations of the latent heat of PCMs rely on the technique of Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). However, these methods are not very accessible to characterisation of large samples under high pressures. Thus they are not suited to determine the enthalpy of CO₂ clathrate hydrate.

This work focuses on demonstrating the energy saving potential of CTES for air conditioning applications, and developing and modifying the composition of a clathrate hydrate based cold storage material and its application in air conditioning systems. In this study, through both simulation and experimental work, the following questions are addressed:

1. What primary energy saving advantages can CTES provide in a PV cooling system comparing with electricity storage?
2. How can the phase equilibrium and formation behaviour of CO₂ clathrate hydrate be moderated for cold storage?
3. Is there a reliable and easy method to determine the phase change enthalpy of clathrate hydrates under certain pressures?
4. How does the modified CO₂ clathrate hydrate perform as PCM in a practical CTES cooling system?
5. What operating strategy can favour the energy saving of a cold storage based air conditioning system?

CO₂ clathrate hydrate is believed to be an ideal PCM for cold storage applications. We therefore seek to modify the CO₂ hydrate to achieve the following features:

- Variable freezing temperature between 0°C and 15°C
Safe and environmentally benign
High energy density
High round trip efficiency of thermal store
Standard engineering components to manufacture store
No maintenance
Cost effective.

1.2 Thesis outline

This thesis gives an all-round insight into the mechanics of CO₂ clathrate hydrate working as a PCM for cold storage applications. It includes a simulation work on the performance of a CO₂ hydrate based cold storage in a PV cooling system and an experimental study on both the phase change behaviour of CO₂ hydrate and its performance in a lab-scale cold storage system. Moreover, new methodologies are adopted to determine the thermal properties of the clathrate hydrate. This study provides data on CO₂ hydrate formation and dissociation at moderate pressures which are suitable to practical operating conditions of air conditioning systems.

Chapter 2 presents an introduction to current worldwide research activities on natural gas hydrates along with the application of some gas hydrates as PCMs in cold storage systems. It also summarises methods to modify natural gas hydrates for easy and fast formation.

Chapter 3 introduces a simulation work comparing the energy saving performance of a battery energy storage and a CTES in a PV-driven air conditioning system. The computer model of the air conditioning system is developed in the transient simulation software environment TRNSYS 17 [Thermal Energy System Specialists (TESS), 2007]. The latent cold storage component is programmed and compiled using the compiler Microsoft Visual Studio [Microsoft Corporation, 2010]. The simulation is conducted at three climatic locations (Shanghai, Madrid and Brisbane). In additions, influence factors of both storage approaches are investigated. The effect of PCM thermal properties on the primary energy saving of cold storage is discussed.

To develop a suitable cold storage medium, peralkyl-(ammonium/phosphonium) salts are used to lower the required formation pressure of CO₂ clathrate hydrates. Therefore, it is important to know the thermal properties of these quaternary salt hydrates before using them to aid the CO₂ hydrate formation. Chapter 4 focuses on the determination of the phase equilibrium and enthalpy of salt hydrates of tetra-n-butylammonium bromide (TBAB), tetra-n-butyaminunim fluoride (TBAF) and tetra-n-butyolphosphonium bromide (TBPB), as they are supposed to promote the hydrate formation by forming semi-clathrate structures. The phase equilibrium,
supercooling degree and induction time of salt hydrates at different concentrations and proportions are measured. Moreover, a T-history method is used to determine the formation enthalpy and specific heat of salt hydrates, and is proved to be a valid approach.

In chapter 5, characterisation of the formation and dissociation behaviours of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrates are conducted experimentally. The phase equilibrium of these hydrates at different concentrations is determined and the morphology of crystals during hydrate formation is presented. In particular, the effect of gas pressure, heat transfer fluid (HTF) temperature, secondary promoters and the memory effect on hydrate formation are examined. Methods are sought to reduce the hydrate supercooling and shorten the induction time. Promoters tested include SDS and TiO$_2$ nanoparticles. TBAF is also employed to accelerate hydrate formation according to its characteristics studied in chapter 4. As a result of this characterisation, a composition is composed to form the cold storage medium.

In chapter 6, the T-history method is employed again to determine the formation enthalpy and specific heat of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrates. This is the first time that this method is used for clathrate hydrates under elevated pressures. This investigation involves not only the CO$_2$ + quaternary salt + water system, but also more complex systems with secondary promoters.

Chapter 7 presents a lab-scale emulated cold storage air conditioning system. The aim of this exercise is to analyse how an increased volume of the CO$_2$ hydrate works in a cyclic charging–discharging process. The temperature variation as well as the energy charge and discharge of a CTES containing the CO$_2$ hydrate material are measured. This allows the performance of such a cold storage system to be investigated. In addition, the effect of chilled water return temperature, external flow rate and ultrasonic vibration on accelerating the formation and enhancing the charging rate during the charging process is evaluated.

Chapter 8 summarises the results and wraps the thesis work into a conclusion, showing that CO$_2$ semi-clathrate hydrate, once modified properly, can be an ideal PCM for cold storage air conditioning applications as it is safe and non-toxic, and reduces both initial cost and power consumption during charge and discharge.

1.3 Extracurricular work and publications

This PhD thesis is strongly orientated to applied research using both experimental and theoretical methods to come to a conclusion on the feasibility of using a CO$_2$ hydrate based PCM for use in cold storage air conditioning systems.
To gain an insight into the features and current research activities on clathrate hydrates, the author first conducted a literature review on clathrate hydrate based cold storage applications and reported the generalised ideas in a journal paper – ‘Clathrate hydrate technology for cold storage in air conditioning systems’, *Renewable and Sustainable Energy Reviews* 2014;36:34-51.

The significance of this work lies on determining whether CTES could promote the electricity saving of a cooling system. Therefore, the author conducted a simulation on a PV cooling system in a residential building. Such a system respectively employs a CTES and battery storage. The primary energy savings of different energy storage approaches are compared to a reference system without any energy storage as backup. The result of this work is presented in a journal paper – ‘Influencing factors on the energy saving performance of battery storage and phase change cold storage in a PV cooling system’, *Energy and Buildings* 2015;107:84-92.

The author participated at the 2015 IEA ECES Greenstock International Conference in Beijing, China, with an oral presentation and a conference paper to introduce the fundamental part of the simulation work – ‘A comparison of battery and phase change cold storage in a PV cooling system under different climates’, IEA ECES Greenstock International Conference, Beijing, 2015.

In order to utilise the CO$_2$ clathrate hydrate in practical a cold storage unit, the required formation pressure should be lowered. To understand how quaternary salts help to moderate hydrate formation, the author carried out experimental works on the phase change behaviour and influencing factors of the salt hydrates and reported the results in a journal paper – ‘An experimental study on the formation behaviour of single and binary hydrates of TBAB, TBAF and TBPB for cold storage air conditioning applications’, *Chemical Engineering Science* 2015;137:938–946.

The author determined the formation enthalpy and specific heat of the quaternary salt hydrates using the T-history method. In addition, a model of hydrate formation in a cold storage tube is established based on the enthalpy method to predict the cooling capacity and charging rate. These results are presented in a journal paper – ‘Characterisation of thermal properties and charging performance of semi-clathrate hydrates for cold storage applications’, *Applied Energy* 2016;167:59–69.

The formation and dissociation of CO$_2$–TBAB semi-clathrate were conducted by the author at low pressures applicable to the operating conditions of air conditioning systems. Using the T-history method, the formation enthalpy of this semi-clathrate hydrate was measured in a self-fabricated reaction tube. Also, secondary promoters were tested on the hydrate formation to increase gas uptake, decrease supercooling degree and shorten induction time. The results are reported in a journal paper – ‘Phase equilibrium and formation behaviour of CO$_2$–TBAB
semi-clathrate hydrate at low pressures for cold storage air conditioning applications’, *Chemical Engineering Science* 2016;155(22):294–305. A similar work on the formation and dissociation of CO$_2$–TBPB semi-clathrates has also been reported in another manuscript published as ‘Phase equilibrium and formation behavior of the CO$_2$–TBPB semiclathrate hydrate for cold storage applications’, *Journal of Chemical and Engineering Data* 2017;62:1083–1093.

In addition, main outcomes of the author’s PhD program have been summarised in a conference paper ‘Energy storage for air-conditioning using CO2 gas hydrates’, Asia–pacific Solar Research Conference, Canberra, 2016, and have been presented to the audience.

The author attended the 2014 Solar Cooling Workshop in Brisbane and the 2016 Solar Cooling Workshop in Melbourne as a member of ARIAH (Australia Institute of Refrigeration Air Conditioning and Heating), and gave oral presentations on the latest progress in the development of CO$_2$ clathrate hydrate for cold storage. The author has also been nominated as a Finalist in the Student of the Year category for the 2016 ARIAH Awards.

The annual Climate and Energy Student Expo was held in August 2015 at the Australian National University, aiming to foster an interactive community of researchers and promote the exchange of knowledge in the field of climate change and energy saving. The author showcased her research through an oral presentation on the topic of CTES in air conditioning applications and won the 2015 Climate and Energy Student Prize.

The author gave a guest lecture on the utilisation cold store in solar cooling in the course *Solar Thermal Technologies* to 3$^{rd}$-year undergraduate students at the College of Engineering and Computer Science of the Australian National University (ANU) in 2014, and tutored 3$^{rd}$-year undergraduate students in the course *Energy System Engineering* at ANU in 2015.

In addition, the author undertook training on Chemical Safety and Compressed Gases and Cryogenic Safety for safe experimental operations. This training has sharpened her technological skills in both laboratories and workplaces.
Chapter 2

Development of clathrate hydrate cold storage technology

2.1 Clathrate hydrates

Clathrate hydrates are crystalline solid compounds formed from water and gas molecules. Gas molecules (guest) are trapped in cages (host) that are composed of hydrogen-bounded water molecules. Fundamental studies on clathrate hydrates mainly concern the phase equilibrium, dissociation enthalpy, hydrate nucleation and growth rate. There are mainly structure I (SI), structure II (SII) and structure H (SH) type of clathrate hydrates, as shown in Figure 2.1 [5]. SI is a body-centred cubic structure forms with small natural gas molecules found in situ in deep oceans. SII is a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane. It represents hydrates which commonly occur in hydrocarbon production and processing conditions, as well as in many cases of gas seeps from faults in ocean environments. SH is named for the hexagonal framework, was discovered to have cavities large enough to contain molecules the size of common components of naphtha and gasoline [6].

Figure 2.1 Structure of different types of clathrate hydrate [5]
Phase diagram is used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases occur and coexist at equilibrium. The phase diagram for several components of natural gases is shown in Figure 2.2. The lines of equilibrium mark conditions under which multiple phases can coexist at equilibrium. H is used to denote hydrates, I for ice, V for vapour, and L\textsubscript{w} and L\textsubscript{HC} for aqueous and hydrocarbon liquid phases, respectively. Phase transitions occur along lines of equilibrium. For each component, the hydrate region is to the left of the three phase lines (I-H-V), (L\textsubscript{w}-H-V), (L\textsubscript{w}-H-L\textsubscript{HC}); to the right, phases exist for liquid water or ice and the guest component as vapour or liquid [5].

![Phase diagram](image)

Figure 2.2 Phase diagrams for some simply gas hydrocarbons that form hydrates [5]

Van der Waals-Platteeuw solid solution theory is commonly used for theoretical studies of phase equilibrium behaviour of clathrate hydrates [7]. For experimental measurements, a high-pressure cell is usually employed [8, 9]. The dissociation enthalpy can be calculated by Clapeyron equation based on the experimental data, or directly measured by an insulated boil-off chamber in a constant-temperature bath [10].

### 2.1.1 Refrigerant clathrate hydrates

Most refrigerant gases can form clathrate hydrates under supportive conditions. However, chlorofluorocarbon (CFCs) and hydrochlorofluorocarbon (HCFCs) have been gradually prohibited from use due to their ozone depletion and greenhouse impacts. As a consequence, hydrofluorocarbon (HFC) hydrates have been widely studied since 1992 when use of CFCs began to be phased out [11]. Equilibrium data
of HFC-134a, HFC-125 and HFC-143a hydrate were measured by Hashimoto et al. [9], and showed that HFC-134a hydrate has the lowest equilibrium pressure. The dissociation enthalpies of the three HFCs hydrates were all about 140 kJ·mol\(^{-1}\). The upper quadruple point \(Q_2\) for liquid gas–liquid water–hydrate–vapour (\(L_g\)-\(L_w\)-H-V) four-phase equilibrium was tested at 283.19 K/0.416 MPa for HFC-134a hydrate, 284.0 K/0.930 MPa for HFC-125 hydrate, and 283.3 K/0.838 MPa for HFC-143a hydrate. It is noticeable that, as long as one of the guest substances is in the gaseous state, the maximum possible hydrate formation temperature is \(T_{Q2}\). In order to utilise a fluid as the heat reservoir for heat release by hydrate formation, \(T_{Q2}\) must exceed the temperature of the fluid by several degrees [12]. Table 2.1 lists further properties of refrigerant gases, including the Ozone Depletion Potential (ODP) and the Global Warming Potential (GWP). HFC hydrates that have the potential to form PCMs for cold storage air conditioning are: HFC-236ca, HFC-236cb, HFC-245ca, HFC-245cb, HFC-245ea, HFC-245eb, HFC-254ca, HFC-254cb, HFC-254ea, HFC-254eb, HFC-254fa and HFC-254fb.

### Table 2.1 Properties of HFC gases

<table>
<thead>
<tr>
<th>Guest gas</th>
<th>Critical temperature /(^\circ)C</th>
<th>Critical pressure /MPa</th>
<th>Enthalpy of reaction /kJ·kg(^{-1})</th>
<th>Solubility in water /g·kg(^{-1})(25(^\circ)C)</th>
<th>ODP</th>
<th>GWP (100 yr)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCFC-141b</td>
<td>204.15</td>
<td>4.25</td>
<td>344</td>
<td>0.509</td>
<td>0.086</td>
<td>700</td>
<td>[13]</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>136.45</td>
<td>22.80</td>
<td>349</td>
<td>0.14</td>
<td>0.043</td>
<td>2400</td>
<td></td>
</tr>
<tr>
<td>HFC-134a</td>
<td>101.06</td>
<td>4.059</td>
<td>358</td>
<td>0.15</td>
<td>0</td>
<td>1300</td>
<td>[11, 13–18]</td>
</tr>
<tr>
<td>HFC-143a</td>
<td>72.89</td>
<td>3.776</td>
<td>383.9</td>
<td>\</td>
<td>0</td>
<td>3800</td>
<td>[15, 16]</td>
</tr>
<tr>
<td>HFC-125</td>
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<td>3.631</td>
<td>362</td>
<td>0.09</td>
<td>0</td>
<td>3400</td>
<td>[11, 14, 16, 17, 19]</td>
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<tr>
<td>HFC-152a</td>
<td>113.26</td>
<td>4.517</td>
<td>383</td>
<td>0.28</td>
<td>0</td>
<td>120</td>
<td>[13–16, 19, 20]</td>
</tr>
<tr>
<td>HFC-227ea</td>
<td>102.8</td>
<td>2.980</td>
<td>132.6</td>
<td>0.26</td>
<td>0</td>
<td>3220</td>
<td>[16, 21]</td>
</tr>
<tr>
<td>HFC-236fa</td>
<td>124.92</td>
<td>3.200</td>
<td>\</td>
<td>\</td>
<td>0</td>
<td>6300</td>
<td>[22, 23]</td>
</tr>
<tr>
<td>HFC-236ea</td>
<td>139.29</td>
<td>3.501</td>
<td>\</td>
<td>\</td>
<td>0</td>
<td>710</td>
<td>[21, 22]</td>
</tr>
<tr>
<td>HFC-245fa</td>
<td>154.35</td>
<td>3.651</td>
<td>\</td>
<td>\</td>
<td>0</td>
<td>820</td>
<td>[23-25]</td>
</tr>
<tr>
<td>HFC-365mfc</td>
<td>204.55</td>
<td>3.489</td>
<td>\</td>
<td>1.70</td>
<td>0</td>
<td>840</td>
<td>[26]</td>
</tr>
<tr>
<td>HFC-32</td>
<td>78.11</td>
<td>5.777</td>
<td>390.5</td>
<td>0.0043</td>
<td>0</td>
<td>675</td>
<td>[11, 16–18, 19, 27]</td>
</tr>
<tr>
<td>HFC-23</td>
<td>25.85</td>
<td>4.815</td>
<td>240.0</td>
<td>0.10</td>
<td>0</td>
<td>11700</td>
<td>[19, 27]</td>
</tr>
</tbody>
</table>

*ODP: Ozone Depletion Potential; GWP: Global Warming Potential*
2.1.2 CO₂ clathrate hydrate

Environmental issues related to the emission of greenhouse gases have become a big concern to the refrigeration industry [28]. The utilisation of CO₂ clathrate hydrate for cold storage has the potential to achieve a high energy storage density, due to its high dissociation enthalpy and large CO₂ uptake efficiency in a limited hydrate volume.

CO₂ molecules can form a sI clathrate structure and fit in 5₁₂₆² cages [29]. The clathrate hydrate has a critical temperature of 283.0 K and a critical pressure of 4.5 MPa [5]. By using DTA Laurence et al. [28] deduced that the total dissociation enthalpy of the solid formed from the CO₂–water mixture was 507 kJ·kg⁻¹ water. Thus, CO₂ hydrate slurry appears to have obvious advantages over many other types of slurries, such as ice (334 kJ·kg⁻¹) and TBAB (200 kJ·kg⁻¹). It has also been reported that when the global CO₂ mole fraction was 2.88 mol% and the temperature was 276.24 K, the hydrate fraction in the slurry was 2.8 vol% and the available enthalpy was up to 1.15×10⁴ kJ·m⁻³ water [30]. Therefore, CO₂ hydrate slurry is considered to be an alternative to multiphase secondary refrigerant.

The general structure of CO₂ hydrate equilibrium measurement system is shown in Figure 2.3 [31–37]. The system is mainly composed of a hydrate formation reactor cell, a gas supplying system and a measuring system. The reactor, which consists of an adiabatic cylindrical vessel, is installed on a magnetic stirrer with an agitator rotating within the liquid. The reactor is heated and cooled by an aqueous solution circulating into the jacket from a cryostat, and is linked to a gas storage vessel with a pressure valve that maintains a constant pressure. The pressure in the reactor is measured by a pressure transducer, while the temperature is measured by a probe in the liquid.
CO₂ hydrate formation has been examined from a chemical kinetics perspective. Jerbi et al. [38] investigated the formation kinetics of CO₂ hydrate in a semi-batch stirred tank, aiming to design a circulation loop for the secondary refrigeration application. They found that the hydrate growth was $1.45 \times 10^{-3} \%_{\text{hydrate}} \cdot \text{s}^{-1}$ for a stirring speed of about 450 rpm. For an isothermal circulation loop, the kinetic rate varied between $5.45 \times 10^{-3} \%_{\text{hydrate}} \cdot \text{s}^{-1}$ and $8.37 \times 10^{-3} \%_{\text{hydrate}} \cdot \text{s}^{-1}$.

Yang et al. [39, 40] built an engineering test module (Figure 2.4) to examine the effect of gas carrier, fluid velocity, slurry concentration and temperature on the heat transfer and formation kinetics of CO₂ hydrate. The system was mainly composed of a gas delivery system, a CO₂-saturated and raw water delivery system, a continuous flow reactor, a chiller, and a data acquisition system. It was found that when the flow pattern was maintained in an annular flow region, the hydrate formation rate was as high as 0.45 s⁻¹ under favourable conditions. However, as the flow changed to a slug or plug flow, the apparent rate constants decreased significantly (in the worst case falling to <0.01 s⁻¹), underscoring the importance of good inter-phase mixing. With vigorous mixing, the hydrate formation kinetics was favourable and the formation became heat-transfer limited.

![Figure 2.4 Schematic diagram of engineering test module system](image)

**2.1.3 Hydrocarbon clathrate hydrates**

Hydrocarbon gases can form sI, sII and sH hydrates. Small gas molecules such as methane and ethane can be encaged in lattice cavities of sI hydrates; larger gas molecules such as propane, butane, methane + propane, and methane + n-butane can be encaged in lattice cavities of sII hydrates. Methane + methylcyclopentane, methane + n-pentane, neohexane and isopentane all tend to form an sH structure.
A number of experiments have been carried out with respect to the kinetics of hydrocarbon clathrate hydrates. According to the work of Bergeron et al. [41], the average reaction rate constant of CH$_4$ hydrate formation was around $8.3 \pm 0.5 \times 10^{-8}$ m·s$^{-1}$ at an average temperature of 275.1 K, and $61.5 \pm 4.8 \times 10^{-8}$ m·s$^{-1}$ at an average temperature of 279.1 K. The reaction rate constant was found to increase with the rise in the temperature with the activation energy of 323 kJ·mol$^{-1}$.

An intrinsic kinetic model for the formation of CH$_4$ and C$_2$H$_6$ hydrates was proposed by Englezos et al. [42], and verified by experiments carried out in a semi-batch stirred tank. The formation rate was found to be proportional to the difference between the dissolved gas fugacity and the three-phase equilibrium fugacity. This difference is defined as ‘a driving force which incorporated the pressure effects’.

Moridis et al. [43] estimated the thermal properties and kinetic parameters of hydration reaction in porous media by simulation methods. They showed that the intrinsic rate constant of CH$_4$ hydrate dissociation was $1.78 \times 10^6$ kg·m$^{-2}$·Pa$^{-1}$·s$^{-1}$ with the activation energy of $8.97 \times 10^4$ J·mol$^{-1}$. Comparison with the results from pure CH$_4$ hydrate samples provided a measure of the effect of the porous medium on kinetic reaction. They also found the dissociation enthalpy of CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and i-C$_4$H$_{10}$ and found them to be 56.9, 71.1, 126.0, 130.4 kJ·mol$^{-1}$, respectively [44]. The liquid-hydrate-vapour (L$_w$-H-V) phase equilibrium data of hydrocarbon gases are detailed in Table 2.2.

<table>
<thead>
<tr>
<th>Hydrocarbon gas</th>
<th>Molecula r formula</th>
<th>Critical temperature / K</th>
<th>Critical pressure / MPa</th>
<th>Equilibrium temperature / K</th>
<th>Equilibrium pressure / MPa</th>
<th>Reference</th>
</tr>
</thead>
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<td>Methane</td>
<td>CH$_4$</td>
<td>\</td>
<td>\</td>
<td>273.7–285.9</td>
<td>2.77–9.78</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>274.3–285.8</td>
<td>2.92–9.54</td>
<td>[46]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>285.7–301.6</td>
<td>9.62–68.09</td>
<td>[47]</td>
</tr>
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<td></td>
<td></td>
<td>290.2–320.1</td>
<td>15.9–397.0</td>
<td>[48]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>305.1–320.5</td>
<td>98–493</td>
<td>[49]</td>
</tr>
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<td>Ethane</td>
<td>C$_2$H$_6$</td>
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<td>3.35</td>
<td>273.7–286.5</td>
<td>0.51–2.73</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>277.8–287.2</td>
<td>0.848–3.08</td>
<td>[50]</td>
</tr>
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<td></td>
<td></td>
<td>278.8–288.2</td>
<td>0.95–3.36</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>290–324</td>
<td>20–479</td>
<td>[52]</td>
</tr>
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<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>278.85</td>
<td>0.545</td>
<td>273.2–278.0</td>
<td>0.165–0.472</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>274.2–278.4</td>
<td>0.207–0.542</td>
<td>[54]</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>276.8–278.6</td>
<td>0.368–0.547</td>
<td>[55]</td>
</tr>
<tr>
<td>Isobutane</td>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>275.03</td>
<td>0.165</td>
<td>273.2–275.1</td>
<td>0.110–0.167</td>
<td>[56]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>273.2–275.0</td>
<td>0.115–0.169</td>
<td>[57]</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>C$<em>5$H$</em>{10}$</td>
<td>280.85</td>
<td>\</td>
<td>273.4–280.2</td>
<td>0.0069–0.0198</td>
<td>[58]</td>
</tr>
</tbody>
</table>
2.1.4 Multi-component clathrate hydrates

The phase equilibrium conditions of single clathrate hydrates sometimes cannot meet the requirements of cold storage systems. Therefore, multi-component clathrate hydrates are used to improve global properties, by utilising the complementary features of each component.

2.1.4.1 Multi-component system of refrigerant clathrate hydrates

Multi-component clathrate hydrates can provide a range of equilibrium pressures by changing the proportion of components. In the work of Akiya et al. [59], the critical dissociation temperature and pressure of HFC-32 + HFC-125 mixtures with the HFC-32 fraction of 0, 52.5% and 100 wt% were found to be 284.39 K/0.944 MPa, 291.55 K/1.429 MPa and 294.09 K/1.484 MPa, with the enthalpy of 135.0, 78.5 and 71.6 kJ·mol\(^{-1}\).

Kobayashi et al. [17] measured the vapour–liquid equilibrium data for pure, binary and ternary systems containing HFC-32, HFC-125 and HFC-134a. They found that, when the mole fraction of HFC-32 and HFC-125 was 0.485 and 0.250, respectively, the COP of such a system was higher than that of HCFC-22, resulting in 15% energy savings.

Lim et al. [60] used hydrocarbon gases with refrigerant gases to form hydrate. At 273.2 K, the equilibrium pressure of the propane + HFC-227ea system increased from 0.195 to 0.476 MPa; at 283.2 K, the equilibrium pressure increased from 0.280 to 0.632 MPa with the mole fraction of propane from 0 to 100%. HFC-134a/HCFC-141b [61], HFC-32/HFC-143a/HFC-134a [62], and HFC-134a/cyclopentane (CP) [63] were also found to be suitable for cold storage use. The properties of some commonly used multi-component refrigerant gases are listed in Table 2.3.

In addition, some refrigerant gas pairs are proposed to be feasible PCMs [14]: HFC-365mfc + HFC-134a, HFC-365mfc + HFC-152a, HFC-365mfc + HFC-227ea, HFC-236ea + HFC-134a, HFC-236ea + HFC-152a, HFC-236ea + HFC-227ea, HFC-245fa + HFC-134a, HFC-245fa + HFC-152a, HFC-245fa + HFC-227ea, HFC-236ea + HFC-134a, HFC-236ea + HFC-152a, HFC-236ea + HFC-227ea, CP + HFC-227ea and CP + HFC-152a.
### Table 2.3 Properties of multicomponent refrigerant gases

<table>
<thead>
<tr>
<th>HFCs</th>
<th>Components</th>
<th>Proportion</th>
<th>Critical temperature / °C</th>
<th>Critical pressure / MPa</th>
<th>ODP*</th>
<th>GWP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>R410a</td>
<td>R22/152a/124</td>
<td>53/13/34</td>
<td>107.3</td>
<td>4.61</td>
<td>0</td>
<td>1018</td>
</tr>
<tr>
<td>R410b</td>
<td>R22/152a/124</td>
<td>61/11/28</td>
<td>72.5</td>
<td>4.95</td>
<td>0</td>
<td>1221</td>
</tr>
<tr>
<td>R404a</td>
<td>R125/143a/134a</td>
<td>44/52/4</td>
<td>72.1</td>
<td>3.74</td>
<td>0</td>
<td>3922</td>
</tr>
<tr>
<td>R407a</td>
<td>R32/125/134a</td>
<td>20/40/40</td>
<td>75.7</td>
<td>4.24</td>
<td>0</td>
<td>2107</td>
</tr>
<tr>
<td>R407b</td>
<td>R32/125/134a</td>
<td>10/70/20</td>
<td>74.4</td>
<td>4.08</td>
<td>0</td>
<td>2804</td>
</tr>
<tr>
<td>R407c</td>
<td>R32/125/134a</td>
<td>23/25/52</td>
<td>86.7</td>
<td>4.62</td>
<td>0</td>
<td>1774</td>
</tr>
<tr>
<td>R408a</td>
<td>R125/143a/22</td>
<td>7/46/47</td>
<td>83.8</td>
<td>4.42</td>
<td>0</td>
<td>3036</td>
</tr>
<tr>
<td>R507a</td>
<td>R125/143a</td>
<td>50/50</td>
<td>70.9</td>
<td>3.79</td>
<td>0</td>
<td>3985</td>
</tr>
</tbody>
</table>

*ODP: Ozone Depletion Potential; GWP: Global Warming Potential

### 2.1.4.2 Multi-component system of hydrocarbon clathrate hydrates

Phase equilibrium data of binary hydrocarbon clathrate hydrate systems, such as CH\(_4\) + C\(_2\)H\(_6\), CH\(_4\) + C\(_3\)H\(_8\) and CH\(_4\) + i-C\(_4\)H\(_{10}\), have been studied [45, 47]. Thakore et al. [64] found that the presence of C\(_3\)H\(_8\) and i-C\(_4\)H\(_{10}\) brought down the equilibrium pressure of CH\(_4\) hydrate from 3.37 to 0.278 MPa and from 3.10 to 0.128 MPa, respectively (Figure 2.5). The equilibrium pressure of C\(_3\)H\(_8\) + i-C\(_4\)H\(_{10}\) hydrates varied slightly from 0.1013 to 0.1713 MPa at various proportions. Larger hydrate-forming molecules, such as propane, form hydrates with relatively low equilibrium pressures, and smaller molecules, such as methane, form hydrates with relatively high equilibrium pressures. Hydrates from mixtures of such larger and smaller molecules will have pressures nearer to the equilibrium pressure of the larger molecules [64].

The L\(_w\)-H-V phase equilibrium data of binary hydrocarbon clathrate hydrates are listed in Table 2.4. It can be seen that, in multi-component clathrate hydrate systems, the upper quadruple Q\(_2\) evolves into a line due to the fact that a single hydrocarbon is no longer present; instead, a combination of hydrocarbon and water vapour pressures creates a broader phase equilibrium envelope. However, since the quadruple line has a much higher gradient than the L\(_w\)-H-V line, and the pressure on this line rises dramatically with the increase in the temperature, the practical operations should be implemented below T\(_{Q2}\).
2.1.4.3 Multi-component system of CO$_2$/N$_2$ and hydrocarbon clathrates

Multi-component hydrates are sometimes composed of light alkane hydrocarbon gases and CO$_2$ and/or N$_2$. Uchida et al. [29] observed the formation of CH$_4$ + CO$_2$ hydrate by measuring the vapour-phase composition using gas chromatography and Raman spectroscopy. Results indicated that the kinetics of the mixed clathrate hydrate was controlled by the competition of both molecules to be enclathrated into the hydrate cages. CH$_4$ molecules were preferentially crystallised in the early stages of hydrate formation when the initial concentration of CH$_4$ was much less than that of CO$_2$ – thus pure CH$_4$ hydrates formed first. This phenomenon suggested that CH$_4$ molecules play important roles in hydrate formation.
<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Mole fraction of A / mol%</th>
<th>Mole fraction of B / mol%</th>
<th>Equilibrium temperature / K</th>
<th>Corresponding equilibrium pressure / MPa</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane(A) + Ethane(B)</td>
<td>1.60</td>
<td>98.40</td>
<td>283.9–287.8</td>
<td>1.81–3.08</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td>4.70</td>
<td>95.30</td>
<td>279.4–287.6</td>
<td>0.99–2.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.70</td>
<td>82.30</td>
<td>281.6–287.0</td>
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</tr>
<tr>
<td></td>
<td>56.40</td>
<td>43.60</td>
<td>214.8–283.2</td>
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<td>[45]</td>
</tr>
<tr>
<td></td>
<td>90.40</td>
<td>9.60</td>
<td>274.8–283.2</td>
<td>1.52–3.97</td>
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</tr>
<tr>
<td></td>
<td>98.80</td>
<td>1.20</td>
<td>274.8–280.4</td>
<td>2.86–5.09</td>
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<td>Methane(A) + Propane(B)</td>
<td>23.75</td>
<td>76.25</td>
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<td>0.263–0.830</td>
<td>[66]</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
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</tr>
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<td>0.552–1.56</td>
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<tr>
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<td>1.00</td>
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<td>1.63–4.36</td>
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<td>274.8–277.6</td>
<td>1.32–1.84</td>
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<td>275.2–279.7</td>
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<tr>
<td>Methane(A) + n-butane(B)</td>
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<td>5.82</td>
<td>277.99–281.43</td>
<td>2.05–3.29</td>
<td>[68]</td>
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<td>98.36</td>
<td>1.64</td>
<td>276.0–288.5</td>
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<td>Ethane(A) + Propane(B)</td>
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<td>72.00</td>
<td>276.5–277.9</td>
<td>0.46–0.66</td>
<td>[51]</td>
</tr>
<tr>
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<td>44.30</td>
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<td>275.9–277.4</td>
<td>0.05–0.72</td>
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<td>272.2</td>
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<td>3.90</td>
<td>274.2</td>
<td>0.228</td>
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<td>0.0732–0.0808</td>
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</tr>
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</tr>
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* mol% stands for mole fraction
The L-H-V phase equilibrium data of binary systems of hydrocarbon gases with CO₂ or N₂ are listed in Table 2.5. The phase equilibrium of multi-component systems (with more than two guest gases) of hydrocarbon gases with CO₂ and/or N₂ are detailed in Table 2.6. The variations of the equilibrium pressure of C₃H₈, i-C₄H₁₀ and n-C₄H₁₀ with CO₂ at given temperatures are plotted in Figure 2.6 [77]. It shows that the global equilibrium pressure went up slowly with the increase of CO₂ proportion at low CO₂ mole fractions, while it went up sharply at high CO₂ fractions (≥93%). However, there was a very slight pressure drop in each line at very high CO₂ mole fractions (≥98%).

![Figure 2.6 Equilibrium pressures of binary clathrate hydrates of CO₂ and hydrocarbon gas](image)

### 2.2 Modifications in the phase change behaviour

#### 2.2.1 Decrease of equilibrium pressure

In many cases, clathrate hydrates cannot reach phase equilibrium within the safe pressure range and operating temperatures of standard cold storage system components. As an example, CO₂ hydrate manifests high equilibrium pressure conditions, as shown in Figure 2.7 [84].
Tetra-n-butyl ammonium bromide (TBAB) in water can form a semi-clathrate structure in which TBAB molecules act as both the host and the guest. There are still small dodecahedral empty cages in this semi-clathrate hydrate, and thus it is able to uptake, store and separate small gas molecules under certain thermal conditions [85, 86]. Duc et al. [37] conducted experiments on CO₂–TBAB semi-clathrate hydrate. The results showed that using TBAB at a small concentration of 0.29 mol%, the equilibrium pressure of CO₂ hydrate at 279.3 K was reduced from 35.0 bar to 2.73 bar, as shown in Table 2.7. Generally, TBAB can decrease the formation pressure by a factor of 10–50.

Arjmandi et al. [87] measured phase boundaries of TBAB and different gas hydrates. The results showed that, in general, semi-clathrates of TBAB and guest gases are more stable than single gas hydrates at low pressures, and this stability is enhanced by raising TBAB concentration. The dissociation conditions are summarised in Table 2.8.

![Phase Equilibrium Curve](image)

**Figure 2.7 Phase equilibrium diagram of CO₂ clathrate hydrate**

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<th>P / bar</th>
<th>P (without TBAB) / bar</th>
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Table 2.8 Measured dissociation conditions of gas–TBAB clathrate hydrates

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<td>8.03</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>291.1</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>292.7</td>
<td>5.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>294.3</td>
<td>8.10</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>285.2</td>
<td>4.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>288.2</td>
<td>10.9</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>285.6</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>287.4</td>
<td>2.32</td>
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<tr>
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<td>289.3</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td>0.427</td>
<td>287.3</td>
<td>1.25</td>
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<td></td>
<td>288.8</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>290.2</td>
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<td></td>
<td></td>
<td>291.2</td>
<td>3.52</td>
</tr>
<tr>
<td>Natural gas</td>
<td>0.05</td>
<td>280.4</td>
<td>0.979</td>
</tr>
<tr>
<td>(87.32%methane +</td>
<td></td>
<td>282.4</td>
<td>2.07</td>
</tr>
<tr>
<td>5.67%ethane +</td>
<td></td>
<td>283.6</td>
<td>2.85</td>
</tr>
<tr>
<td>1.68%propane +</td>
<td></td>
<td>284.6</td>
<td>3.48</td>
</tr>
<tr>
<td>0.23%2-methyl</td>
<td></td>
<td>287.0</td>
<td>5.42</td>
</tr>
<tr>
<td>propane + 0.40%n-</td>
<td></td>
<td>291.0</td>
<td>9.52</td>
</tr>
<tr>
<td>butane + 0.10%2-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>methyl butane +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.24%nitrogen +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.36%carbon</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>dioxide) 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>283.2</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>284.2</td>
<td>1.72</td>
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<td></td>
<td>287.0</td>
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<td>289.1</td>
<td>5.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>286.2</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>0.43</td>
<td>290.7</td>
<td>4.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>292.5</td>
<td>7.97</td>
</tr>
</tbody>
</table>
In the experiments conducted by Wang et al. [88], semi-clathrates formed from gaseous mixtures of CO$_2$, H$_2$ and CO in TBAB solutions in an isochoric equilibrium cell with the TBAB concentrations of 0.05, 0.10 and 0.20 mol%. The equilibrium data for the hydrates are shown in Figure 2.8.

Meysel et al. [34] carried out experiments on semi-clathrate hydrate formation from CO$_2$ and N$_2$ (with CO$_2$ fraction of 0.75, 0.50 and 0.20, respectively) in solutions with the TBAB concentration of 0.05, 0.10 and 0.20 mol%. The results are shown in Figure 2.9.

Figure 2.8 Phase equilibrium for hydrates formation from CO$_2$ + CO + H$_2$ and TBAB solution
Li et al. [33, 89] investigated the effect of 0.29 mol% TBAB solution in conjunction with CP and dodecyl trimethyl ammonium chloride (DTAC) in CO₂ hydration by measuring gas uptakes, CO₂ separation efficiencies and induction time. Results of the above studies all revealed a similar tendency that, at certain temperatures the CO₂ hydrate formation pressure is remarkably lowered by adding TBAB and the formation pressure decreased as TBAB concentration increased.

Duc et al. [37] reported that the presence of TBAB in the hydration of natural gases decreased the formation pressure of both simple hydrates (CO₂ or N₂) and mixed hydrates (CO₂ + N₂) considerably. The gas storage capacity of mixed hydrates of CO₂ + N₂ + TBAB was about 35 vol(gas)/vol(hydrate). For gaseous mixtures, the hydrate equilibrium conditions were also proved to be related to the proportion of CO₂ in the mixture.

A hydrate-based CO₂ separation from CO₂/H₂ mixtures was studied by Xu et al. [90] in 0.29 mol% TBAB solution. It was found the equilibrium shifted to inapplicable conditions as the proportion of CO₂ decreased from 40% to 10%.

In the work of Tomita et al. [91], data on the time evolution of compositions were obtained on both the vapour phase and the hydrate slurry phase during long-term operations at 2.3 MPa and 273.2 K. In the experiments, the composition in the vapour phase and the hydrate phase reached a steady state in 15 h, when the composition of CH₄ and CO₂ in the slurry reached 0.61 and 0.76, respectively.

Other additives have been proposed to moderate hydrate formation conditions. Babu et al. [92] conducted experiments to study CO₂ hydrate formation kinetics in the clathrate process from a CO₂/H₂ mixture with the help of TBAB or
tetrahydrofuran (THF). The gas uptake, induction time and hydrate formation rate were determined in a temperature range from 274.2 to 279.2 K under 6.0 MPa. The results indicated that 3.0 mol% TBAB attained lower gas consumption than 0.3 mol% TBAB. A higher over-pressure driving force led to higher gas consumption and significantly reduced the induction time.

The equilibria of CO\textsubscript{2} semi-clathrate hydrates formed in water solutions of TBAB / TBAF / tetra-n-butyl ammonium chloride (TBAC) were measured by Li et al. [93] at 2.93×10\textsuperscript{-3} and 6.17×10\textsuperscript{-3} mol\% of the tetra-n-butyl ammonium halide. It was shown that all of them enhanced the hydrate stability. The equilibrium pressure of the CO\textsubscript{2} + TBAF + water system is lower than others at the same temperature.

In the work of Fan et al. [94], the effect of 0.293 mol\% TBAB and TBAF on hydrate formation rate and CO\textsubscript{2} separation efficiency was studied in a stirred reactor. The results showed the hydrate formation rate increased with increasing feed pressure and reached the maximum at 2.82×10\textsuperscript{-7} mol\textsuperscript{2}·s\textsuperscript{-1}·J\textsuperscript{-1} with TBAB and 8.26×10\textsuperscript{-7} mol\textsuperscript{2}·s\textsuperscript{-1}·J\textsuperscript{-1} with TBAF. They also revealed that TBAF effectively accelerated hydrate formation.

By employing various quaternary ammonium salts (TBAB, TBAC and TBAF), Kim et al. [95] investigated hydrate-based CO\textsubscript{2} capture. The thermodynamic stability of CO\textsubscript{2} (20\%) + N\textsubscript{2} (80\%) was examined using an isochoric method in a high pressure reactor. TBAF clathrates showed the largest reduction in equilibrium pressure at a specified temperature, while TBAC clathrates had the highest gas uptake. It was noted that both CO\textsubscript{2} and N\textsubscript{2} were enclathrated in the small cages of the clathrates, and the enclathration of gas molecules did not change the structure of the semi-clathrate.

The enclathration of gas in TBAC semi-clathrates was examined by Kim et al. [96] based on stability measurements and cage filling characteristics. The results clearly demonstrated that the thermodynamic stability of CH\textsubscript{4} (or CO\textsubscript{2}) + TBAC semi-clathrates was significantly enhanced. The best stabilization occurred at 3.3 mol\%, corresponding to the stoichiometric concentration of TBAC·29.7H\textsubscript{2}O. The dissociation temperature and enthalpy of TBAC semi-clathrates under atmospheric pressures were measured at 288.0 K and 204.8±1.7 kJ·kg\textsuperscript{-1}.

Xia et al. [97] presented a study on the kinetic and separation efficiency to purify simulated biogas (45.0 mol\% CO\textsubscript{2} and CH\textsubscript{4} mixture). Synergic additives comprising gas solvent (dimethyl sulfoxide (DMSO)) and hydrate formation promoter (THF or TBAB) were used to enhance the hydrate-based separation.

In the work of Babu et al. [98] it was concluded that the presence of TBAB, TBAC or tetra-n-butyl ammonium nitrate (TBANO\textsubscript{3}) could reduce the formation
conditions of clathrate hydrates for the applications of H₂ storage, CO₂ capture from flue gas, secondary refrigeration and cold storage.

A review of Veluswamy et al. [99] summed up that alkylammonium and alkylphosphonium salts (TBAB, TBAF, TBAC, TBANO₃ and TBPB) could promote H₂ uptake in clathrate hydrates. Roosta et al. [100] also reported that TBAB increased the CH₄ hydrate formation rate in an experimental work combined with a mathematic model.

Small amounts of THF can change the structure of CO₂ hydrate from sI to sII, thus decreasing its equilibrium pressure. Martínez et al. [101] studied the equilibrium pressure of CO₂–THF hydrate with 10wt% THF at 280 K. The equilibrium pressure reduced to 0.2 MPa comparing with 2.9 MPa of single CO₂ hydrate.

Delahaye et al. [35] tested the formation conditions of CO₂ + THF + water system using DTA and DSC. The results showed an average relative pressure decrease of 79% at a low initial concentration of THF (3.8 wt%). The formation pressure was lowered to 0.038 MPa in the presence of 15wt% THF. It is suggested that CP can also form sII clathrate hydrates with or without a help gas to fill small cavities and stabilise the structure [102]. Since CP only occupies large cavities, small gas molecules, such as H₂ and CO₂, can be more easily engaged in the small cavities.

The dissociation temperatures of H₂-CP hydrate at 2.7–11.1 MPa and CO₂–CP hydrates at 0.89–3.51 MPa were determined using a high-pressure Micro-DSC by Zhang et al. [103]. They found that the dissociation temperature of H₂-CP hydrate was higher than that of H₂–THF hydrate, but lower than that of H₂–TBAB hydrate;
while the dissociation temperature of CO₂–CP hydrate was slightly higher than that of both CO₂–THF hydrate and CO₂–TBAB hydrate.

Neopentane is also recognised as a potential formative agent of sII clathrate hydrate. Dissociation data for CP and neopentane in their binaries and ternaries with CH₄ and/or N₂ was reported by Tohidi et al. [83]. The predicted hydrate dissociation conditions (Figure 2.10) showed that CP and neopentane could lower the dissociation pressure to a larger extent than benzene and cyclohexane in their binaries with CH₄. The comparison with some other hydrate forming compounds indicated that CP was the strongest promoter, with neopentane in second place. In addition, tetrahydropyran, 2-propanol [104, 105], 1,4-dioxane and acetone [106], 3-methyl-1-butanol [36], methylcyclohexane (MCH) and cis-1,2-dimethylcyclohexane (cis-1,2-DMCH) [46] were also effective in moderating the equilibrium pressure of clathrate hydrates.

2.2.2 Increase of dissociation enthalpy

Dissociation enthalpy of clathrate hydrates is the most significant measure of the capability of a cold storage media. The addition of THF can change the hydrate sI to sII and increase the amount of entrapped guest species, thus leading to enhanced hydrate stability and dissociation enthalpy.

Enthalpies for pure and mixed CO₂ + N₂ gas, with or without THF, were measured by Kang et al. [78], as shown in Table 2.9. For G·nH₂O hydrates, n stands for the number of water molecules in the unit cell and G stands for the pure guest gas; for xCO₂·yN₂·46H₂O hydrates, x and y are the calculated number of CO₂ and N₂ molecules, respectively, in sI; and for xCO₂·yN₂·zTHF·136H₂O hydrates, x, y and z stand for the calculated number of CO₂, N₂ and THF molecules, respectively, in sII structures.

<table>
<thead>
<tr>
<th>Guest gases</th>
<th>Dissociation enthalpy / kJ·mol⁻¹</th>
<th>Hydrate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>65.22±1.03</td>
<td>n=7.23</td>
</tr>
<tr>
<td>N₂</td>
<td>65.81±1.04</td>
<td>n=5.94</td>
</tr>
<tr>
<td>0.17 CO₂ + 0.83 N₂</td>
<td>64.59±1.02</td>
<td>x=5.43, y=1.89</td>
</tr>
<tr>
<td>0.70 CO₂ + 0.30 N₂</td>
<td>63.41±1.00</td>
<td>x=7.08, y=0.25</td>
</tr>
<tr>
<td>0.17 CO₂ + 0.83 N₂ + 0.01THF + 0.99 H₂O</td>
<td>109.01±1.72</td>
<td>x=2.96, y=9.47, z=11.39</td>
</tr>
<tr>
<td>0.17 CO₂ + 0.83 N₂ + 0.03THF + 0.97 H₂O</td>
<td>118.94±1.87</td>
<td>x=2.35, y=7.42, z=12.53</td>
</tr>
<tr>
<td>0.70 CO₂ + 0.30 N₂ + 0.01THF + 0.99 H₂O</td>
<td>107.18±1.69</td>
<td>x=9.97, y=2.58, z=10.94</td>
</tr>
<tr>
<td>0.70 CO₂ + 0.30 N₂ + 0.03THF + 0.97 H₂O</td>
<td>113.66±1.79</td>
<td>x=8.11, y=2.19, z=13.16</td>
</tr>
</tbody>
</table>
Delahaye et al. [35] found that the dissociation enthalpy of CO$_2$–THF systems was two times higher than that of the single CO$_2$ hydrate. The enthalpy of the binary system was 147.4 kJ·mol$^{-1}$ at 278.7 K with 10.2 wt% THF, compared with 70.8 kJ·mol$^{-1}$ of the pure CO$_2$ hydrate at 278.7 K. Depending on the concentration of CO$_2$ and THF, the dissociation enthalpy of mixed hydrates was found to be in the region of 112.4–152.3 kJ·mol$^{-1}$ [107].

Mayoufi et al. [108] conducted DSC measurements of dissociation enthalpies of CO$_2$ hydrates with TBACl, TBANO$_3$ and TBPB (Figure 2.11). The CO$_2$–TBPB hydrate presented the highest dissociation enthalpy. It was noticed that the fusion heat of mixed hydrates increased significantly with the increase of CO$_2$ pressure, which could be explained by the fact that TBACl, TBANO$_3$ and TBPB could also accommodate CO$_2$ in semi-clathrates and stabilise the structures, thus raising the dissociation enthalpy. Under pressures of 1–2 MPa, the dissociation enthalpy of CO$_2$–TBPB hydrate was even higher than that of CO$_2$–TBAB hydrate [94, 109, 110]. SH hydrates can store the largest amount of small guest gas principally because the ratio of small to large cages is 5:1, compared to 2:1 for sII and 1:3 for sI [111].

Nakamura et al. [46] found the addition of MCH and cis-1,2-DMCH can change the structure of CH$_4$ hydrates to sH, which not only increased the enthalpy but also reduced the hydrate formation pressure. The enthalpy of CH$_4$-MCH hydrate was 374.1 kJ·mol$^{-1}$ at 274.1 K, and that of CH$_4$-cis-1,2-DMCH hydrate was 382.7 kJ·mol$^{-1}$ at 274.2 K.

![Figure 2.11 Enthalpy of CO$_2$ hydrate with different additives under various pressures](image-url)
2.2.3 Acceleration of formation process

Typically, hydrate nucleation and growth occur within the metastable region before entering the unstable region. Cooling into the unstable region, nucleation will occur readily, due to the high degree of supersaturation or driving force [5]. However, in the metastable zone there is substantial evidence that the hydrate induction period is not subject to correlation or prediction at lower driving forces of subcooling (the difference between the adopted HTF temperature and the equilibrium temperature of hydrate) or overpressure (the difference between the adopted pressure and the equilibrium pressure of hydrate) [5].

Supercooling temperature is the minimum temperature that a PCM has to undergo below its normal freezing temperature (without it becoming a solid) before reverting to its freezing temperature during solidification. The supercooling degree is the difference between the supercooling point and the freezing point.

Homogeneous nucleation is a solidification process occurring in the absence of impurities. It involves more molecules that could collide simultaneously. There is a sequential formation of clusters within the supercooled liquid of increasing cluster size, until the critical cluster size is reached. The critical cluster size (also called critical nucleus) is the cluster size that must be reached before nuclei/clusters can grow spontaneously, as shown in Figure 2.12. Before achieving the critical size, clusters of molecules form in the bulk metastable liquid, and these clusters may either grow or shrink as a result of density or composition fluctuations. When the cluster attains a critical size, monotonic growth may be interpreted by the excess...
Gibbs free energy between a small solid particle of solute and the solute in solution. In contrast, in the more usual case, heterogeneous nucleation occurs in the presence of a foreign body (e.g. dust micro-particles) or surface (e.g., fluid interface, container or pipe wall), at smaller supercooling than that required for homogeneous nucleation [5].

The induction time or lag time is the time of cooling before the hydrate formation is detected. It presents the period between cooling to the left of the line of equilibrium until the time of solid formation [5]. Induction times are very scattered, particularly at low driving forces; nucleation is stochastic and therefore unpredictable. Induction times are approximately proportional to the displacement from equilibrium conditions. In addition, induction times appear to be apparatus-dependent, for example, the times depend on the degree of agitation (cavitation or turbulence), surface area of the system and the rate of heat or mass transfer. Induction times also appear to be a function of time-dependent variables such as the history of the water, the gas composition and the presence of foreign particles. At high driving forces and with constant cooling, hydrate formation is less stochastic than that at a low driving force or at constant temperature.

The definitions of induction time, supercooling temperature, supercooling degree, and subcooling are summarised in Figure 2.13.

Fast hydrate formation (nucleation and growth) plays a critical role in efficient energy saving in the charging process of cold stores. However, hydrate nucleation is less predictable and is affected by many factors. It is a complex reaction kinetics problem in a multi-element and multi-phase heat flow system with irregular phase transition behaviour and anomalous transient state.
Clathrate hydrates generally form in the interface between two phases, and their further growth requires water or gas diffusing through the hydrate region; thus the crystallisation can be time-consuming.

The formation process of CO$_2$ hydrate was reported to be 100 min by Fournaison et al. [28] and 2 h by Delahaye et al. [112]. CH$_4$ hydrate formation was about three times longer than CO$_2$ hydrate formation [113]. For the purpose of accelerating clathrate hydrate formation, methods such as mechanical agitation, magnetic interference, additives and optimisations of storage structure are proposed.

2.2.3.1 Mechanical agitation and magnetic interference

Clarke and Bishnoi [114] conducted experiments in a semi-batch stirred tank reactor to study the intrinsic kinetics of CO$_2$ hydrate formation using in situ particle size analysis. It was found that when the rate of agitation was more than 400 rpm the effect of mass transfer became ignorable. Xie et al. [115] compared three mechanical hydration enhancement methods. It was found that continuous mechanical agitation improved the cold storage capacity, hydrate growth rate, and the general heat transfer coefficient, with an average hydrate growth velocity of 0.588 kg·min$^{-1}$. However, a large amount of energy was consumed by the continuous mechanical blending.

Linga et al. [116] obtained abundant gas uptake and separation efficiency by using a gas-inducing mechanical agitation system. Linga noted that hydrate crystallisation must be carried out without agitation if hydrates are to be used commercially. That is, for safety and economic reasons, it would be better to work in quiescent conditions during hydrate formation. In the study of Laugier et al. [117], it was found that ultrasound greatly improved gas-liquid mass transfer. This improvement was boosted at high pressures. In typical conditions of organic synthesis: 323 K, 1100 rpm, 10 bar, the gas-liquid mass transfer coefficient in liquid phase was multiplied by 11 with ultrasound (20 kHz/62.6 W). Liu et al. [118] verified that ultrasonic wave had an impact on refrigerant hydrate formation, and the range of ultrasonic wave power that promoted the hydrate formation was 58–1000 W.

2.2.3.2 Additives

Surfactants, such as SDS, sodium tetradecyl sulfate (STS) and sodium hexadecyl sulfate (SHS), cetyl trimethyl ammonium bromide (CTAB), dodecyl trimethyl ammonium bromide (DTAB), DTAC, linear alkyl benzene sulfonate (LABS), dodecyl benzene sulfonic acid (DBSA), sodium dodecyl benzene sulfonate (SDBS), ethoxylated nonylphenol (ENP), Tween and Span 20, can provide a nuclei to break through metastability, and thus are helpful to shorten the hydrate induction time.
The effect of three anionic surfactants, SDS, STS and SHS, on CH\textsubscript{4} hydrate formation was tested by Okutani et al.\cite{119} in an unstirred chamber. In each operation, hydrate formation lasted for a certain time and then ceased, leaving only a small proportion (<15\%) of the aqueous solution unconverted into hydrate crystals. The variations in the time-averaged rate of hydrate formation were 7.0 h for SDS at 2000 ppm, 6.4 h for STS at 100 ppm, and 8.2 h for SHS at 100 ppm. It was reported that the addition of CTAB (100 ppm) to the water shortened the hydrate pressure decay halftime to 45 min, indicating that the formation process could be catalysed. Such catalysts could specifically enhance the building of the hydrate structures of CO\textsubscript{2}\cite{120}.

The effect of SDS, LABS, CTAB and ENP on the formation and dissociation of CH\textsubscript{4} hydrate was investigated with three additive concentrations (300, 500 and 1000 ppm)\cite{121}. The effect of anionic surfactants DBSA and SDBS, cationic surfactants CTAB and DTAB, and non-ionic surfactants alkylpolyglucoside (APG), TritonX-100 (TX100), and dodecyl polysaccharide glycoside (DPG) on CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} hydrate formation were studied by ZareNezhad et al.\cite{122}. Li et al.\cite{89} estimated the effect of DTAC on the induction time of CO\textsubscript{2} hydrate formation in TBAB aqueous solution. In another work of Li et al.\cite{33}, the effect of 0.29mol% TBAB solution in conjunction with CP on hydrate-based CO\textsubscript{2} capture were studied. More than 80 mol\% of the amount of gas consumed was obtained within 400 s at 274.7–277.7 K and 2.5–4.5 MPa.

Structural revulsants, such as silver iodide and potassium oxalate monohydrate, are another kind of promoter which are used as template agents. Porous media, such as glass powder, silica gel, molecular sieve, poly HIPE, dry water and dry gel, can also accelerate the hydrate formation by promoting hydrate formation through the enhancement of mass transfer\cite{123}. Additionally, nanoparticles can be used to promote heat transfer between the gas and water, thus speeding up the growth of hydrate\cite{124}.

### 2.2.3.3 Structural optimisation of the reactor

The formation process can be accelerated by optimising the structure of the hydrate formation reactor. Okutani et al.\cite{119} examined CH\textsubscript{4} hydrate formation with the aid of a water-cooled cold plate, a steel flat-plate-type heat sink, vertically dipped into the aqueous phase across the gas/liquid interface. The increase in CH\textsubscript{4} uptake volume relative to its level in the absence of the cold plate was of a factor of 1.73. This factor exceeded that for the increase in the total surface area, 1.51, and that for the increase in the total horizontal perimeter, 1.62.

Hydrate formation was conducted by Linga et al.\cite{125} with one set of experiments conducted in a bed of silica sand, saturated with water (fixed fed column) and the
other experiment in a stirred vessel for each gas/gas mixture. It was shown that the rate of hydrate formation in the fixed bed column was significantly greater and thereby resulted in a higher percentage of water conversion of hydrate in less reaction time. For instance, after about 3 h, the gas uptake in a stirred bed was about 0.019 mol_{(gas)} \cdot \text{mol}^{-1}_{(water)}$, whereas in the case of the fixed bed reactor it was 0.083 mol_{(gas)} \cdot \text{mol}^{-1}_{(water)}.

Li et al. [126, 127] presented the effect of adding an iron rod on the nucleation and growth of HCFC-141b clathrate hydrate in a static water column. The rod that was combined with a surfactant improved the phase permeation between water and refrigerants, the hydrate formers, which were immiscible in general, thus considerably reducing the induction time and promoting the hydrate growth. When the temperature was 274.2–279.2 K, the nucleation occurred in 3–30 min and the hydrate formation completed in 1.5–8 h.

In addition, the size of pressure vessel has an effect on the formation of clathrate hydrates. McCallum et al. [128] found that the induction time of hydrate nucleation appeared to be greatly reduced by using a 72 L vessel which established the pressures and temperatures required for CH$_4$ and CO$_2$ hydrate stability compared with a 450 mL Parr vessel.

### 2.2.3.4 Memory effect

It was found that the induction time of hydrate formation in water that dissociated from previous hydrates was much shorter than that of hydrate formation in unused water. This phenomenon is known as the hydrate memory effect [129, 130]. It is suggested that for various species of clathrate in gas-liquid systems, such as CO$_2$/water and hydrocarbon gas/water, memory effect possesses a modified structure which allows easier hydrate re-formation [131]. Wu et al. [132] has carried out experiments in a pressure cell. In this study, from the first test to the fourth test, the induction time of the system was 129.5, 73.3, 37.9 and 16.9 min, respectively. However, when the dissociation temperature was higher than 25°C, the memory effect vanished. The memory effect for cyclopentane hydrate formation was investigated by Sefidroodi et al. [133] revealing that provided the superheating above the equilibrium temperature was no more than 2–3°C, the hydrates was obtained much faster than formed for the first time. Sun et al. [134] studied the clathrate hydrate formation in two systems: one with Tween-40 at $1 \times 10^{-3}$ mol·L$^{-1}$ and another with Tween-40 at $2 \times 10^{-3}$ mol·L$^{-1}$. It was concluded that the induction time was shortened by 10–20 times in the experimental system containing residual structures. The mechanism of the memory effect was reported [135] that the hydrate was observed to melt from the periphery outwards leaving a hydrate core. It is assumed that the residual structure of hydrate dissociation, as the source of the
memory effect, provides a site for mass transfer between host and guest molecules. Therefore, a driving force is created between the residual structures and its surrounding bulk phase to promote the hydrate nucleation.

### 2.2.4 Decrease of supercooling degree

Supercooling occurs when, in attempting to freeze the material, the temperature drops below the equilibrium point before solidification initiates [136]. In this state, the supercooled water is metastable. For clathrate hydrates, these structures comprise hydrogen-bonded water networks and/or water clusters (“cages”) that are the starting points to hydrate formation. Once the formation begins, the temperature rises to the equilibrium point, where it remains until the material is entirely frozen. [5]

Supercooling is undesirable in energy storage systems; if excessive, it can prevent the withdrawal of stored heat from the PCM. The reason for the high degree of supercooling is the fact that either the rate of nucleation (of crystals from the melt) or the rate of growth of the nuclei (or both) is very slow. Therefore, as the melt is cooled, it does not solidify at the thermodynamic melting point; thus the advantage of the material for energy storage is reduced [136]. Therefore, minimising the supercooling degree of clathrate hydrates relies greatly on the energy efficiency of air conditioning systems.

Supercooling can often be mitigated by adding nucleating materials. Some success has been attained by using additives with a crystal structure similar to that of the PCM. In homogenous nucleation, the nucleation rate of crystals from the melt is increased without adding any foreign materials. One way in which this can be done is to use ultrasonic waves to stir the liquid and thus the diffusion of ions in the melt is increased; ultrasonic waves also create cavities that act as nucleation centres and, finally, they break up the crystals and distribute them through the melt, creating new nucleation centres. In heterogeneous nucleation, the walls of the container, or some impurity present within the melt, act as a catalyst for nucleation by providing a substrate on which the nuclei can form [136].

It is feasible to decrease the supercooling degree by the use of additives. According to Isobe et al. [137] the magnitude of supercooling required for the inception of HFC-134a hydrate was reduced moderately by adding alumina or zinc powder to the water phase, in which HFC-134a was to be vapourised.

A larger reduction in supercooling can be achieved by adding a non-ionic surfactant. Calcium hypochlorite can boost rapid crystal nucleus formation, and is a versatile cleaning chemical to clear away impurities and a strong oxidizer that can break down and destroy organic debris, preventing it from adsorbing on the surface.
of the crystal nucleus or the growing crystal. Benzenesulfonic acid sodium salt can decrease the surface tension of water, decrease the diameter of bubbles and increase the rising frequency of bubbles, thereby decreasing the resistance of mass transfer between gas and water molecules. Also, it makes the liquid emulsify into tiny liquid drops; thus the effective interface area between the two phases can be increased and a great deal of hydrate nuclei are produced.

Bi et al. [138] achieved a decrease in supercooling from 2.33 to 1.55°C by adding 0.03% benzenesulfonic acid sodium salt. The drawback of adding a surfactant is an increase in the effective specific volume of the resultant clathrate hydrate, calling for a larger space to store a specified mass [137].

Although a larger secondary refrigerant flow rate can enhance the convection heat transfer between the PCM and the secondary refrigerant, it can also cause a non-negligible temperature rise of the PCM, resulting in a rise in supercooling degree. Bi et al. [139] investigated the influence of flow rate of the reactor on supercooling degree, presenting that when the flow rate was lower than 450 l·h⁻¹, the supercooling degree decreased quickly with the increase of the flow rate to a minimum of 1.97°C. When the flow rate was larger than 450 l·h⁻¹, the supercooling degree increased slightly with the increase of the flow rate. An optimised value of flow rate is recommended for the minimisation of supercooling degree of clathrate hydrates.

### 2.2.5 Enhancement of gas solubility

Gas solubility may strongly influence the equilibrium condition of some clathrate hydrates, such as H₂S hydrates and CO₂ hydrates, since the solubility of these gases in water is quite high even at low pressures. The influence of the gas solubility on the equilibrium of CH₄ and N₂ hydrates is also important due to their high equilibrium pressures. The root mean square deviation on the calculation of the dissociation pressures for CH₄ with and without solubility along the L_w-H-V line is respectively 2.63% and 4.97% [140]. The solubilities of some hydrocarbon gases are listed in Table 2.10.

<table>
<thead>
<tr>
<th>Guest gas</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>i-C₄H₁₀</th>
<th>n-C₄H₁₀</th>
<th>C₅H₁₀</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (×10⁻³) / kg⁻¹ mol⁻¹ (water)</td>
<td>2.48</td>
<td>3.10</td>
<td>2.73</td>
<td>1.69</td>
<td>2.17</td>
<td>3.32</td>
<td>1.19</td>
<td>60.8</td>
</tr>
</tbody>
</table>

Temperature and pressure are two important factors on gas solubility. Hashemi et al. [141] carried out predictions using Henry’s Law to estimate the solubility of CO₂. Under a pressure of 2 MPa, the solubility of CO₂ rose from 0.0150 mol% at
274.0 K to a peak of 0.0174 mol% at 277.5 K, and then dropped linearly back to 0.0150 mol% at 285.0 K. CO₂ solubility in pure water in the presence of CO₂ clathrate hydrate was measured at temperatures of 273.0–284.0 K and pressures from 2–6 MPa. It was found that the solubility increases with the increase of the temperature in the hydrate formation region; while in the absence of clathrate hydrate, the gas solubility increases with the decrease of the temperature. The amount of gas dissolved in liquid in the equilibrium with clathrate hydrates was 0.0163 mol% at 274.3 K and 0.0281 mol% at 283.0 K with the pressure maintained at 6 MPa [142].

Therefore, the solubility of the guest gas should be taken into consideration while selecting suitable temperatures and pressures for hydrate formation. In addition, co-solvents, such as dissolved propylene glycol (PPG) and polyethylene glycols (PEG), are also helpful to enhance gas solubility [143, 144]. However, how the co-solvents affect the crystallisation process of clathrate hydrates, especially at high concentrations, is still unknown.

2.3 Statistical modelling on clathrate hydrates

Besides experimental methods to determine the phase equilibria of hydrates and to modify the hydrate formation behaviour, thermodynamic and chemical methods have been widely applied. These statistical models provide a bridge between the molecular crystal structures and the macroscopic thermodynamic properties. They also offer a comprehensive means of correlation and prediction of all of the hydrate equilibrium regions of the phase diagram [5]. Thermodynamic modelling of clathrate hydrate mainly refers to phase equilibrium modelling and hydrate formation kinetics modelling.

Clathrate hydrates are solid crystalline inclusion compounds, in which the guest gas molecules are trapped in the cages of hydrogen bonded host molecules. The inclusion of gas molecules and the Van der Waals attraction between water and gases stabilize the hydrate structure [145]. After the determination of the hydrate crystal structure in the early 1950s, it was possible to generate theories for equilibria of macroscopic properties based in microscopic properties [5]. To determine the hydrate equilibria, the initial model was generated by Barrer and Stuart (1957), with a more accurate method by van der Waals and Platteeuw (1959) who are considered the founders of the method [5]. In this statistical model, the concentration of the non-water species in the hydrate was treated in a manner similar to the adsorption of a gas onto a solid [146]. Recent modelling methods of hydrate phase equilibrium are mainly based on the van der Waals and Platteeuw model. The effect of a tributylmethylphosphonium methylsulfate ionic liquid aqueous solution on the equilibrium conditions of CO₂ and CH₄ hydrates was
studied both by experiments and by a thermodynamic model in the work of Tumba et al. [147]. The model was developed based on van der Waals–Platteeuw solid solution theory accompanied with the Peng–Robinson equation of state (PR-EoS) and the non-random two-liquid (NRTL) activity model, and was successfully applied to represent and predict the obtained experimental data. Eslamimanesh et al. [148] proposed a thermodynamic model for representation and prediction of phase equilibria of semi-clathrate hydrates of CO₂, CH₄, or N₂ + TBAB aqueous solution. For modelling the hydrate phase, the van der Waals–Platteeuw solid solution theory is used, revised with two modifications for evaluations of Langmuir constants and vapour pressure of water in the empty hydrate lattice. The Peng–Robinson (PR-EoS) equation of state along with re-tuned parameters of Mathias–Copeman alpha function is applied for calculation of the fugacity of gaseous hydrate former. For determination of the activity coefficient of the non-electrolyte species in the aqueous phase, the Non-Random Two-Liquid (NRTL) activity model is used. It was shown that the model results were in acceptable agreement with the experimental hydrate dissociation data. Fukumoto et al. [149] applied a previous thermodynamic approach developed by Paricaud [150] to predict the dissociation conditions of semi-clathrate hydrates made with TBAB, TBAC, TBAF and TBPB. The SAFT-VRE equation of state was used to describe the properties of fluid phases, and a good description of osmotic and mean activity coefficients of electrolyte solution was obtained. The temperature–composition diagrams of water and salt binary systems were well described by the model. The van der Waals and Platteeuw theory was combined with the model to calculate the dissociation conditions of CO₂ semi-clathrate hydrates. The liquid-vapour-hydrate three-phase line was accurately described over wide pressure ranges and salt concentrations, by optimizing only one parameter per hydrate phase. Fan et al. [151] measured the hydrate formation conditions of CO₂ and CO₂-rich gas mixtures containing N₂/CH₄/C₂H₆ and (N₂ + CH₄ + C₂H₆) in the presence of aqueous solutions of ethylene glycol in a sapphire cell. Meanwhile, the hydrate models recently developed by this group and a typical literature-reported van der Waals–Platteeuw type model were tested against the hydrate formation data of CO₂-rich mixtures in water and aqueous solutions of ethylene/sodium chloride. The performance of various models is evaluated.

Clathrate hydrate formation kinetics properties can be modelled in two steps – nucleation and growth. The driving force is the fundamental question for modelling any hydrate nucleation. The driving force for the formation of a new phase is the chemical potential difference between the old phase and the new one (supersaturation). Kashchiev et al. [152] expressed the supersaturation for hydrate formation, and in their latter work [153], they applied the classic nucleation theory to develop the expression for the nucleation rate for one-component gas hydrates, concerning both homogeneous nucleation and different kinds of heterogeneous
nucleation. Also, they carried out demonstrative calculations for the effect of pressure and temperature on the nucleation rate of methane hydrate in isothermal and isobaric supersaturation processes, respectively [153]. Completing their analysis of hydrate nucleation, Kashchiev et al. [154] assumed a power-law crystallite growth to derive an equation for the temporal evolution of the gas consumption in the early nucleation stage, which led to the derivation of expressions for the induction times as a function of supersaturation. Anklam et al. [155] claimed that the assumption that the composition of the nucleated hydrate is constant and equal to the one at the three-phase equilibrium point for any supersaturation may not be valid if the operating conditions are far away from the gas-liquid-hydrate equilibrium conditions. To eliminate this limitation, they developed a new expression for hydrate nucleation. In addition, the diffuse character of the interface can be incorporated in the modelling of the nucleation process with the aid of phase field theory, and is proposed by Kvalme et al. [156] for CO₂ hydrate. The results indicated that the critical radius and the thickness of the interfacial region have the same order of magnitude and thus the classic nucleation theory could not be applied to this problem. For hydrate growth, models that are frequently used are:

- the model of Englezos-Kalogerakis-Dholabhai-Bishnoi that describes the kinetic experimental date for the formation of methane and ethane hydrates combining the theories of crystallisation and mass transfer at a gas-liquid surface [42, 157]
- the model of Skovborg-Rasmussen that removes PBE and assumes that all resistance to mass transfer during hydrate formation lay in the diffusion of the dissolved gas from the gas-liquid interface to the liquid bulk [158]
- the model of Herri-Pic-Gruy-Cournil that is based on the theory of crystallisation and considers PBE, and includes both nucleation and growth steps [159, 160]
- the model of Gnanendrn-Amin that is specifically for spray reactors of natural gas storage operating in semi-batch regime while the three previous models refer to stirred reactors [161].

2.4 Applications of clathrate hydrates in cold storage air conditioning systems

2.4.1 Clathrate hydrate based static cold storage

The use of clathrate hydrate as a cold storage medium or a secondary refrigerant is a novel technology in cold storage equipped air conditioning systems [5, 84]. Generally, clathrate hydrate based cold storage systems can be classified into direct and indirect contact types. A direct contact cold storage system has no intermediate
heat exchanger; this manifests as higher heat transfer efficiency and lower initial cost. However, it faces difficulties in the oil return to the compressor. In contrast, although an indirect contact system with intermediate heat exchangers has a higher initial cost, it can be operated under more practical conditions and has potential to be applied in large-scaled systems. The charging and discharging principle of a refrigerant clathrate hydrate based cold storage system is illustrated in Figure 2.14 [13, 162].

![Diagram of direct and indirect contact hydrate based cold storage system](image)

(a) Direct contact type

(b) Indirect contact type

Figure 2.14 Schematic diagram of direct and indirect contact hydrate based cold storage system

Mori et al. [163] carried out an observational study on clathrate hydrate formation in a cold storage tank incorporated into a vapour compression refrigerator loop. In Figure 2.15, the working fluid, R12, flowed into the cold storage tank and evaporated, resulting in the cooling of fluids and the formation of R12 hydrate. The hydrate appeared in two forms, making up separate layers in the tank: one in the form of slurry particle sediments at the bottom and the other in the form of
solidified foam floating on the free surface of the water phase. The hydrate layer built on the lower water/R12 liquid interface had the appearance of a dense slurry. A sufficient amount of liquid water still remained in the crystalliser to suspend the hydrate particles. This feature is favourable for high cold storage density.

Figure 2.15 Schematic diagram of the R12 hydrate based cold storage refrigeration system

Figure 2.16 illustrates the conceptual design of a gas hydrate-based refrigeration system contrived by Ogawa et al. [12]. It consists mainly of:

1. A compressor, in which gas and water are mixed and compressed
2. A formation reactor, in which the hydrate forms at a temperature higher than the ambient temperature, thereby releasing heat to the environment
3. A slurry pump for conveying the hydrate slurry and controlling the pressure difference between the two reactors
4. A dissociation reactor, in which the hydrate is dissociated, thereby absorbing heat from the conditioned space.

The pair of HFC-32 and CP was used as the working medium of this refrigeration system. The simulations revealed that, if the hydrate formation and dissociation temperature were 25.5 and 7.5°C, respectively, the COP of the system should be as high as 8.0. This fact indicated that the hydrate-based refrigeration system could surpass conventional refrigeration systems in thermodynamic efficiency. Meanwhile, in a lab-scale hydrate-based refrigeration system, HCFC-22 was used as the guest substance at a temperature of 5°C and a pressure of 0.4 MPa. The heat flow indicated that the system could be operated continuously over 2 h.
Jerbi et al. [164] presented a conceptual design of a refrigeration system in which CO₂ hydrate slurry was used as a two-phase secondary fluid, as is shown in Figure 2.17. The system allowed continuous formation and dissociation of CO₂ hydrate slurry. It was composed of a tank reactor for the formation and storage of CO₂ hydrate slurry and a circulation loop for the circulation and dissociation of CO₂ slurry. The tank reactor had a capacity of 25 L, which could resist a pressure about 4.5 MPa and provide a heat flux of 1–5 kW for a hydrate fraction between 10% and 30%. When CO₂ hydrate slurry flowed in the loop, the heat exchanger was chosen to allow the decomposition of the slurry and exchange the same heat flux as was provided in the reactor.

2.4.2 Clathrate hydrate slurry

In order to be a suitable secondary refrigerant, the slurry of clathrate hydrate has to fulfil satisfying flowing conditions:
1) The pressure condition should be within the safe working pressure range.
2) The temperature condition should suit to the characteristic of the air conditioning system.
3) The fluid should contain a relatively large fraction of solid phase to carry enough cooling capacity at stable temperature level.
4) The flow pattern should be supportive to preserve efficient heat transfer.

Clathrate hydrate slurries can be characterised by their apparent viscosity, which strongly depends on the mass fraction and the organisation of solid particles in the liquid phase related to the nucleation, hydrate growth, crystal shape/size distribution, and agglomeration, etc. The flow pattern and apparent viscosity data of different hydrate slurries from literatures are summed up in Table 2.11.

Although an ice slurry behaves like a Newtonian fluid for ice concentrations lower than 20 vol% [165], most of hydrate slurries manifest non-Newtonian fluid patterns – R141b hydrate slurry presents dilatant property that is undesirable for pumping; in contrast, peralkyl-(ammonium/phosphonium) salt hydrate slurries are all mainly pseudoplastic fluids. The fluid pattern of CO₂ hydrate slurry largely depends on the hydrate concentration. Apparently, the viscosity of all the slurries is much higher than that of water. The ice slurry viscosity of 20 vol% is 10.5–11.3 m·Pa·s [166], which is in the same order of magnitude with that of CO₂ hydrate slurry, higher than that of CH₄ hydrate and R141b hydrate slurry, and generally lower than that of peralkyl-(ammonium/phosphonium) salt hydrate slurries.

<table>
<thead>
<tr>
<th>Slurry</th>
<th>Flow pattern</th>
<th>Apparent viscosity/ m·Pa·s</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ hydrate slurry</td>
<td>4–20 vol% Herschel-Bulkley Fluid</td>
<td>4.5–34.9 (γ=500 s⁻¹)</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td>4–10 vol% Dilatant Fluid</td>
<td>3.8–42.2 (γ=400 s⁻¹)</td>
<td>[167]</td>
</tr>
<tr>
<td></td>
<td>10 vol% Bingham Fluid</td>
<td>1–3.5</td>
<td>[168]</td>
</tr>
<tr>
<td></td>
<td>10–20 vol% Pseudoplastic Fluid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄ hydrate slurry</td>
<td>Bingham Fluid</td>
<td>1–1.7 (γ=400 s⁻¹)</td>
<td>[169]</td>
</tr>
<tr>
<td>R141b hydrate slurry</td>
<td>Dilatant Fluid</td>
<td>3.8–42.2 (γ=400 s⁻¹)</td>
<td>[170]</td>
</tr>
<tr>
<td>TBAB hydrate slurry</td>
<td>Pseudoplastic Fluid</td>
<td>50–148 (γ=400 s⁻¹)</td>
<td>[171]</td>
</tr>
<tr>
<td></td>
<td>43–55 wt% Bingham Fluid</td>
<td>\</td>
<td>[172]</td>
</tr>
<tr>
<td></td>
<td>12–70 wt% Pseudoplastic Fluid</td>
<td>3.5–1000 (γ=1–1000 s⁻¹)</td>
<td></td>
</tr>
<tr>
<td>TBAF hydrate slurry</td>
<td>0–42 wt% Pseudoplastic Fluid</td>
<td>10–750 (γ=1–1000 s⁻¹)</td>
<td>[173]</td>
</tr>
<tr>
<td>TBPB hydrate slurry</td>
<td>0–28.2 vol% Pseudoplastic Fluid</td>
<td>4–41</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
<td>9.5–33 wt% Pseudoplastic Fluid</td>
<td>\</td>
<td></td>
</tr>
</tbody>
</table>
In the work of Zhou et al. [174], for the purpose of minimising the discrepancy between the energy supply and the cooling demand, a shell-and-tube fluidised bed heat exchanger, combined with a storage vessel, was designed to generate $\text{CO}_2$ hydrate slurry during the night. Such a system showed improved electricity saving with the COP 23–43% higher than that of conventional systems. With the continuous removal of formed hydrate slurry, the solid fraction was maintained at up to 35%.

During hydrate formation, agglomeration phenomena can easily occur and be responsible for bad circulation in circulation loops or preventing effective gas injection. Hydrate agglomeration depends on several parameters: stirring velocity, particle diameter, supersaturation and quantity of produced hydrates. However, it was shown that the presence of additives can reduce the agglomeration of particles and thus facilitate flow [38]. In all applications however, engineering creativity and strict attention to design details must be practiced in order to achieve trouble free system operation regarding avoiding ice slurry agglomeration, distribution system plugging, and minimizing pumping power requirements [175].

2.5 Conclusion

Clathrate hydrates, if used as cold storage medium, have obvious advantages over water for the high cold storage density; over ice for the compatible phase change temperature; and over eutectic salts for the superior heat transfer properties and ageing resistance.

For the purpose of evaluating and promoting the utilisation of clathrate hydrates in cold storage air conditioning systems, a review of recent research progress was presented in this chapter, concerning the characteristics of clathrate hydrates, modification of the properties, and clathrate hydrate based cold storage systems. Refrigerant, carbon dioxide, hydrocarbon and multi-component clathrate hydrates were introduced. Moreover, clathrate hydrates based cold storage air conditioning systems are evaluated, and the optimising methods of the system performance are summarised. Some topics remain to be addressed as follows.

The area of the phase equilibrium of clathrate hydrate has reached a high level of maturity; however, data for hydrate formation and dissociation equilibrium in the presence of additives that alter the phase diagram are needed [176].

Semi-clathrate hydrates that employ TBAB [148], TBAF [177, 178], TBAC, TBPB, TBMAC [179], TBACl and TBANO$_3$[108], have been proposed. It was found that the semi-clathrate structure is suited to rapid hydrate formation with larger phase change enthalpy; thus it is worthy of application to air conditioning systems.
Nanoparticles are widely used to enhance the heat transfer performance of PCMs. However, unlike clathrate hydrates, most PCMs charge and discharge via solid-liquid phase change and are little related to the vapour phase. The stability of nanoparticles in clathrate hydrates and its effect on the L\textsubscript{w}-H-V phase equilibrium is also to be studied.

Additives are usually used to modify the phase equilibrium behaviour and thermal properties of clathrate hydrates – such as to lower the equilibrium pressure, to raise the formation rate, and to enlarge the phase change enthalpy. However, the effect of additives on the long-term use of clathrate hydrates as cold storage media is still unknown.

Methods to determine the phase change enthalpy of clathrate hydrates are more challenging than that of normal PCMs, since maintaining the clathrate structure requires high pressures. The high-pressure DSC is typically used for this test. However, such appliances are expensive and the allowed samples in the test are too small to manifest mass-dependent properties of clathrate hydrates. An easy and reliable method is needed to determine hydrate enthalpy under high pressures.

There is little data on the practical performance of clathrate hydrates in a cold storage system. A lab-scale demonstration system will be helpful to make a direct evaluation on hydrate-based cold storage for potential commercialisation.

CO\textsubscript{2} hydrate manifests obvious merits among all the gas hydrate candidates for its safety and low cost. Besides its use in space cooling [180], CO\textsubscript{2} hydrate gained its applications in many other aspects, such as CO\textsubscript{2} gas capture [96, 181, 182], hydrate-based desalination [183], and engine generator design [184]. Hence, a comprehensive study on the formation and dissociation of CO\textsubscript{2} clathrate hydrate is of great significance.
Modelling battery and cold storage in PV cooling

The cooling of buildings over summer periods has been a major contributing factor to the increasing power consumption and grid load over the past decades. This is mainly due to the prevalent use of conventional air conditioning systems with mechanical vapour compression refrigeration cycle. To alleviate electricity grid load, PV powered cooling systems are being implemented. Such systems use a PV array as the primary generation source, converting solar energy into electricity and operating in parallel with the electricity grid. PV cooling technology is proved to be advantageous over other solar-driven cooling systems for its energy efficiency. A simulation work on a PV cooling system and a solar thermal cooling system was conducted under different climates and the energy saving performance of each one was evaluated [185]. The results showed that the electricity saving was improved with the PV case, which covered almost half of the energy demand with a consequent primary energy saving of 50%. The near coincidence of building cooling demand and PV sourced electricity assists to lessen peak electricity demand from buildings.

However, the intrinsic intermittent nature of PV generation must be addressed if high displacement of grid electricity is to be achieved. Thermal energy storage is preferable in supplying on-site loads during solar outages and peak load hours [186–190]. For PV cooling systems, current storage methods typically use battery storage to conserve surplus electricity produced by solar panels, or CTES to store excess cooling capacity generated by a chiller by means of latent heat or sensible heat. Generally speaking, both battery and CTES can conserve sufficient energy for later use and potentially deliver higher energy saving by intensively utilising available solar energy. However, we are not aware of any study that compares the energy performance of electricity storage and CTES for air conditioning applications. In particular, the sensitivity of the store design to the heat load characteristic and PCM characteristics are unclear. Additionally, there is no study that compares the energy saving of different PCMs in a CTES installation in cooling system.
This chapter will present modelling work based on TRNSYS to predict the primary energy saving of a PV cooling system with a battery energy storage and a phase change CTES, respectively, for the cooling of the same residential building under the climates of Brisbane, Madrid and Shanghai. The CTES will be modelled on the properties of ice, the eutectic of capric acid and lauric acid, and CO$_2$ clathrate hydrate, using each one in turn as the cold storage medium.

‘Exergy change’ is the difference between the energy input and output of a thermal storage excluding the exergy loss which is due to the finite temperature difference that drives the heat exchange [191]. The exergy change and energy storage efficiency will be examined for both single CTES and single battery storage. Based on this, the power consumption and primary energy saving ratio (PESR) of the cooling system will be used to evaluate the system performance during the whole cooling season. The primary energy saving is the difference between the primary energy consumption and the cooling capacity supplied by the cooling system [192–194]. In this way, the PESR is defined as the ratio of the cooling capacity produced by the system to the net power consumption (the power consumption minus the electricity supplied by PV).

The PESR will be analysed as a function of the cooling load (including the ratio of sensible load to latent load), the chilled water set-point and chiller COP, the store capacity and the cold storage material (for thermal storage cases only). Both storage approaches, as well as different PCMs in the CTES, will be compared with regard to the system energy saving.

### 3.1 Simulation background

The climates of the three locations contrast the proportions of sensible and latent heat loads. Figure 3.1 shows the monthly sensible and latent cooling load and solar radiation during the ventilation periods in each location. During the cooling season of Shanghai (July, August and September), the monthly proportion of latent load (61.6% of total load) outweighs the proportion of sensible load. In contrast, in Madrid (July, August and September), the monthly proportion of latent load (34.5% of total load) is quite low. In Brisbane (December, January and February), the proportions of each cooling load are, on average, approximately balanced. The average solar radiation of Shanghai, Madrid and Brisbane are 0.37, 0.43 and 0.46 kW·m$^{-2}$, respectively.

In this modelling, a residential building with a total area of 196.1 m$^2$ is air conditioned. The building includes one living room and three bedrooms. Details of each zone are listed in Table 3.1. The external wall is composed of a brick layer of 0.11 m thickness, a glass wool layer of 0.04 m and a gypsum layer of 0.01 m.
cooling load is defined by intermittent operation that can be expected by a working family. The scheduled air conditioning and ventilation period is 6:00–9:00 AM and 5:00–10:00 PM. Ventilation is at a rate of 1.5 air changes per hour. Outside air is drawn into the building during these times at a rate of 50 L·s⁻¹. The target indoor conditions are 22°C/60% RH.

(a) Shanghai, Asia

(b) Madrid, Europe
Figure 3.1 Cooling load of the building during ventilation periods under different climates

Table 3.1 Parameters and schedules for the simulated multi-zone building

<table>
<thead>
<tr>
<th>Zones</th>
<th>Living room</th>
<th>Bedroom 1</th>
<th>Bedroom 2</th>
<th>Bedroom 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>90 m²</td>
<td>30.5 m²</td>
<td>35.6 m²</td>
<td>40 m²</td>
</tr>
<tr>
<td>Internal gain (equipment)</td>
<td>1100 W (cooking)</td>
<td>300 W</td>
<td>300 W</td>
<td>530 W (computer)</td>
</tr>
<tr>
<td>Internal gain (lighting)</td>
<td>449.5 W</td>
<td>152.5 W</td>
<td>177.8 W</td>
<td>200 W</td>
</tr>
<tr>
<td>Occupation rate</td>
<td>0.1</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

3.2 System configuration

The system configurations are shown in Figure 3.2. In all cases, PV modules are connected to an electric water-cooled chiller via a power inverter.

A reference case (a) is built with no storage backup. The power consumption of the reference case is totally covered by the electricity grid.

For the battery storage case (b), direct current is produced by the PV modules and used to charge a battery. However, electrical energy drawn from PV modules or from the battery must first be inverted into alternating current by the inverter before being supplied to the chiller. In this way, the battery is available to the inverter/battery controller for charging when solar energy is in surplus, or for discharging when cooling demand exceeds PV supply. The chiller only runs during
ventilation periods in the battery storage case. The battery is never charged from grid electricity.

Figure 3.2 Diagram of the PV cooling system

For the CTES case (c), a cold storage tank is placed in parallel with the space cooling load. In this case, the chiller runs when PV electricity is available and the chilled water produced by chiller is used to charge the cold store by solidifying the PCM. For cooling supply, the building return water is chilled by heat transfer with PCM melting in the cold store. Any load that cannot be directly met by energy
stored within the system is met by supplying the chiller with grid electricity. The chiller then directly supplies the building with chilled water to meet the load.

In the cooling system, the chiller is sized to meet the peak demand of the building during the ventilation period. Initial trials of the model indicated that a 20 kW capacity is required.

The chiller’s performance model is based on an air cooled vapour compression chiller with performance tables sourced from manufacturer’s data. The PV panels used in this study are SPV module manufactured by Rajasthan Electronic Instrumentation Ltd Jaipur with 17.0 V rated voltage and 4.12 A rated current for each module. The PV array is sized to cover 65% of the total power consumption of the battery storage case, with the balance covered by grid electricity. Since the solar radiation and cooling load both differ in three locations, through a preliminary test of the model, the required array areas for Shanghai, Madrid and Brisbane are 50.4, 42.4 and 49.3 m², respectively. The battery charger and voltage regulator in the PV system are assumed to have an efficiency of 78%; the DC/AC inverter has an efficiency of 96%.

<table>
<thead>
<tr>
<th>PCM</th>
<th>Ice</th>
<th>C-L eutectic</th>
<th>CO₂ hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase change temperature, °C</td>
<td>0</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Density, kg·m⁻³</td>
<td>934.0</td>
<td>839.7</td>
<td>1090.0</td>
</tr>
<tr>
<td>Dissociation enthalpy, kJ·kg⁻¹</td>
<td>334.0</td>
<td>115.1</td>
<td>313.4</td>
</tr>
<tr>
<td>Thermal conductivity(s), W·m⁻¹·K⁻¹</td>
<td>2.18</td>
<td>0.57</td>
<td>0.80</td>
</tr>
<tr>
<td>Thermal conductivity(l), W·m⁻¹·K⁻¹</td>
<td>0.58</td>
<td>0.42</td>
<td>0.60</td>
</tr>
<tr>
<td>Heat capacity(s), kJ·kg⁻¹·K⁻¹</td>
<td>2.05</td>
<td>1.83</td>
<td>2.48</td>
</tr>
<tr>
<td>Heat capacity(l), kJ·kg⁻¹·K⁻¹</td>
<td>4.18</td>
<td>2.21</td>
<td>3.50</td>
</tr>
<tr>
<td>Cold storage size, m³</td>
<td>2.6</td>
<td>8.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

To compare the PESR of the battery storage case and the CTES case, the CTES component is sized at 3.26 m³ (including the volume of coils) to provide a rated cooling capacity of approximately 140 kWh. To compare the performance of different PCMs, the CTES component is sized at various sizes to provide the same cooling capacity that is stored with a balanced volumetric proportion of the PCM and the HTF. The PCMs compared in the CTES component are ice, eutectic of capric and lauric acid (C-L eutectic), and CO₂ clathrate hydrate, with the thermal properties listed in Table 3.2. The phase change temperature of CO₂ hydrate (at a certain pressure) is 7°C, the dissociation enthalpy is 313 kJ·kg⁻¹, and the specific heat is 2.48 kJ·kg⁻¹·K⁻¹. The chiller set-point is 7°C for BC case. The cold store phase change temperature is fixed at 7°C to allow latent loads to be
addressed. However, this requires that the chilled water is produced at a lower temperature of 5°C to allow for heat exchange losses in the cold store. It is noted that many PCMs, such as water and hydrates, undergo induction time before phase transition. Since induction times are stochastic and therefore unpredictable, it is assumed that the induction time is zero in all the phase change cases in this model.

Full-storage strategy is adopted, i.e. from 9:00 AM to 5:00 PM electricity converted from solar energy is totally charged in battery in the battery storage case, or totally used to produce cooling capacity and stored in cold storage in the CTES case. Between 5:00–10:00 PM and 6:00–9:00 AM, the electricity is discharged from the battery and turned to cooling capacity in the battery storage case, or the cooling capacity is released from the cold storage in the CTES case, as is shown in Figure 3.3. The black shadowed area of solar energy is used to offset the red shadowed area of cooling demand.

In the transient simulation software environment TRNSYS 17 [Thermal Energy System Specialists (TESS), 2007], a PV cooling system is developed. A simplified flow diagram for the modelled system is shown in Figure 3.4. The TRNSYS deck (configuration) file is composed of a multi-zone building, a cooling supply and storage module (an electric chiller integrated with a CTES in parallel with fan-coils in the conditioned space) and a PV-battery electricity supply and storage module. The component of a lead-acid battery operates in conjunction with solar array and power conditioning components. It specifies how the battery state of charge varies over time, given the rate of charge or discharge. Control signals are given to the inverter, chiller, pumps and fan according to the ventilation schedule and indoor temperature and humidity feedback.

![Diagram of cooling load, electricity, and solar energy over time](image)
Figure 3.3 Energy flow chart of full-storage operating strategy

The CTES component is programmed and compiled using the compiler Microsoft Visual Studio [Microsoft Corporation, 2010] based on a validated effectiveness–NTU model [198, 199]. This technique has been used in a computational fluid dynamics model of a tube-in-tank PCM system [198] and a mathematical model for tubes in phase change thermal energy storage [199], with the results experimentally validated. Simulations based on this technique have been widely used and validated in several studies [200–203] and results from our model were within the uncertainty of these experimental results.

Figure 3.4 TRNSYS diagram of the PV cooling system
The effectiveness, which is described as a ratio of the actual heat discharged to the theoretical maximum heat that can be discharged, is found to be a function of the mass flux. It represents the average NTU of the storage system, which can be presented by the average thermal resistance between the HTF and the PCM at the phase interface:

$$\varepsilon = 1 - \exp(-NTU)$$  \hspace{1cm} (3.1)

$$NTU = \frac{UA}{(\dot{m}c_{p,HTF})} = \frac{1}{R_T\dot{m}c_{p,HTF}}$$  \hspace{1cm} (3.2)

Considering the cooling coil in the CTES is a long tube surrounded by a certain volume of PCM, the total thermal resistance $R_T$ can be expressed as:

$$R_T = R_{HTF} + R_w + R_{PCM} = \frac{1}{2\pi r_i \alpha} + \frac{\ln(r_o/r_i)}{2\pi k_w L} + \frac{\ln\left[\frac{\varphi(r_o^2 - r_0^2) + r_o^2}{r_o}\right]}{2\pi k_{PCM} L}$$  \hspace{1cm} (3.3)

The heat transfer between HTF and PCM can be correlated to the energy gain/loss of the HTF. Consequently, the heat transfer and the outlet HTF temperature can be calculated from:

$$Q = \varepsilon \dot{m}c_{p,HTF}(T_i - T_m) = \dot{m}c_{p,HTF}(T_o - T_i)$$  \hspace{1cm} (3.4)

### 3.3 System performance indicators

The evaluation the single energy storage and the whole cooling system is based on some system performance indicators. The dimensionless assessment criteria used to evaluate the battery are the self-consumption ratio, which is the ratio of the PV power used for charging ($Q_{BC}$) to the overall produced PV power ($Q_{PV}$), and the self-sufficiency ratio, which describes the share in the load power ($Q_{LP}$) that is discharged from the battery ($Q_{BD}$) [204]. For cold storage, the ‘energy efficiency’ is defined as the ratio of energy drawn from the cold store to energy put into the store over an equivalent range of storage capacity. Furthermore, exergy analysis gives information on the amount of the available energy transferred in the latent heat storage [205]. The output exergy, the difference between the input exergy and the ‘destroyed exergy’ in terms of loss of useful temperature, due to temperature offsets in heat exchange and thermal gains, is an index for evaluating the system energy saving. For the cooling system, the primary energy consumption of both cases is mainly attributed to the electric energy consumed by the chiller, pumps and fans. The expressions of all indices are listed in Table 3.3.
Table 3.3 Expressions of system performance indicators

<table>
<thead>
<tr>
<th>Object</th>
<th>Index</th>
<th>Expression</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery</td>
<td>Self-consumption ratio</td>
<td>( \gamma_c = \frac{Q_{BC}}{Q_{PV}} )</td>
<td>[204]</td>
</tr>
<tr>
<td></td>
<td>Self-sufficiency ratio</td>
<td>( \gamma_s = \frac{Q_{BD}}{Q_{LP}} )</td>
<td></td>
</tr>
<tr>
<td>CTES</td>
<td>Storage energy efficiency</td>
<td>( \eta_{CS} = \frac{Q_o}{Q_i} - \frac{Q_f}{Q_f} ) [191, 205]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exergy output</td>
<td>( \Delta E = E_o - E_i = mC_p(T_o - T_i) - T_{amb}ln\left(\frac{T_o}{T_i}\right) ) [191]</td>
<td></td>
</tr>
<tr>
<td>System</td>
<td>Power consumption</td>
<td>( Q_{\text{Consum}} = Q_{ELEC_CHILLER} + Q_{ELEC_PUMP} + Q_{ELEC_FAN} ) /</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Primary energy saving ratio</td>
<td>( PESR = \frac{Q_{\text{output}}}{Q_{\text{input}}} = \frac{Q_{\text{heat exchange in cooling coil}}}{Q_{\text{consumed energy}} - Q_{\text{saved energy}}} ) /</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Results and discussions

3.4.1 Energy change on a typical summer day

Based on the full-storage strategy, the variation of energy and temperature of both cases on a typical sunny summer day in Brisbane is shown in Figure 3.5. In the battery storage case (a), the cooling supply is 89.6 kWh, and the total system power consumption is 69.0 kWh with the PV panels covering 42.8 kWh. On this specified day illustrated in Figure 3.5, the battery is charged to 98% during the daytime, and is discharged to 45% during the night, and then to 11% in the next morning. In the CTES case (b), the total electricity consumption of the day is 77.7 kWh. There are 118.1 kWh cooling capacity charged and 88.9 kWh discharged. During the discharge, the PCM temperature is always at the phase change temperature with the liquid fraction of the PCM varying from 15.6% to 79.1%.
Figure 3.5 Energy and temperature variation of a summer-day’s operation

3.4.2 Energy change during the cooling season

The cooling supply and power consumption of both cases during the entire cooling season under different climates are shown in Figure 3.6. Owing to the difference in the cooling load, the energy supply and the power consumption in Shanghai and Brisbane are both larger than those in Madrid. However, since the solar radiation in Shanghai is inferior to that in the other two locations, the PV electricity supply in
Shanghai is relatively lower. The high electricity consumption but low electricity supply in Shanghai eventually leads to a situation that the cooling supply is much more dependent on the electricity grid unless a larger PV panel is used.

Figure 3.6 Energy change of both cases under different climates during cooling season
In the battery storage case, the PV power cannot be stored sometimes due to the battery being fully charged. The CTES case also faces energy loss caused by the fully charged CTES. However, the major energy loss is that the discharged cooling capacity is less than the charged due to the heat gain from the ambient during the energy conservation.

In addition, there are obvious discrepancies between the power consumptions of the two cases. The leading factor is the secondary pump in the CTES case that results in 11% extra energy expenditure. Secondly, the chilled water is set at a lower temperature in the CTES case for heat transfer in the cold store, which leads to a lower chiller COP and consequently a higher energy cost. Furthermore, CTES suffers a certain amount of heat gain during the thermal energy conservation period, while advanced battery systems do not have significant charge losses in normal operation due to leakage or local current which has been justified [206]. Typically, among rechargeable batteries, lithium-ion batteries exhibit the least amount of self-discharge (around 2–3% discharge per month) compared to lead-acid batteries at 4–6%, while nickel-based batteries are more seriously affected by the phenomenon (nickel cadmium, 15–20%; nickel metal hydride, 30%), with the exception of low self-discharge NiMH batteries (2–3%) [207]. Last but not least, energy loss in the battery is electricity at the expense of solar energy; while in the cold store it is the cooling capacity produced at the expense of electricity; hence, the CTES is considered to deplete more “high-grade” energy.

**3.4.3 PESR during whole cooling season**

The PESR and energy storage efficiency of both cases are illustrated in Figure 3.7.

![Figure 3.7 PESR and storage efficiency of both cases under different climates](image-url)
Due to the reasons discussed above, the storage efficiency of the CTES (0.77 on average) turns out to be less than that of the battery (0.89 on average). The PESR of the CTES case (average of 4.25 for Shanghai, 5.54 for Madrid and 4.24 for Brisbane) is also obviously less than that of the battery storage case (average of 6.06 for Shanghai, 7.08 for Madrid and 7.64 for Brisbane), signifying that to reach a comparable PESR the PV panel of the CTES case needs to be larger than that of the battery storage case. On the other hand, the PESR of both cases obviously outweigh that of the reference case without any storage (average of 2.49). The PESR of the battery storage and CTES case is respectively 2.8 and 1.9 times higher than that of the reference case.

3.4.4 Influencing factors of a single battery/CTES

Beside the analysis of the cooling system based on the one-day’s operation and the cooling season’s operation, the influencing factors of a single battery and a single cold thermal store are studied by a simplified simulation system that only considers variations in the inputs and outputs of the storage component.

In the system, PV panels with a set of two modules in series and three modules in parallel are arranged, charging a field of 24 V × 16.5 Ah batteries with three cells in parallel. The influence of solar radiance on the charging process of the battery is analysed in Figure 3.8.

Figure 3.8 Charging performance of the battery with different solar radiation
Figure 3.9 Discharging performance of the battery with different load power

The charging rate and power loss rate both grow proportionally with the increase in the solar radiation. Consequently, the self-consumption ratio increases linearly until the solar radiation reaches 0.9 kW·m\(^{-2}\). After this, the excess PV power is dumped. The charging time declines rapidly as the solar radiation rises before 0.2 kW·m\(^{-2}\); while it drops slowly after this point. The effect of load power on the battery discharge is illustrated in Figure 3.9. Although the discharging rate grows with the increase in the load power, the self-sufficiency ratio declines from 0.89 to 0.72 when the load rises from 0.10 to 0.21 kW.

Figure 3.10 Charging performance of the CTES with different HTF temperature
Figure 3.11 Discharging performance of the CTES with different cooling load

The effect of HTF temperature and cooling load on the exergy output of cold store is studied based on a 1 m³ tank with a rated storage capacity of 43.0 kWh. The flowrate of HTF is constant at 0.3 kg·s⁻¹. In the charge of the cold store, as is shown in Figure 3.10, the increase in the HTF temperature results in a decline in the energy efficiency and a greatly extended charging time (from 7.45 to 50.5 h). Meanwhile, the average exergy output of the cold store declines linearly with the growth of the HTF temperature, indicating that the “exergy charging rate” drops proportionally with the reduction in the heat transfer temperature difference. In the discharge in Figure 3.11, owing to the increase in the cooling load, the time required for discharge drops, leading to a decrease in surface heat gain during the discharging period. As a consequence, the energy efficiency increases with the rise of the cooling load. The deflection occurs at 2.1 kWh, after which the effect of cooling load on the energy efficiency and the charging time becomes insignificant. The average exergy output is in direct proportion to the cooling load. The effect of cooling load (including the ratio of the sensible load to the latent load), the chiller set-point and COP, and the storage sizes on the PESR of a PV-battery cooling system and a CO₂ hydrate based PV-cold storage cooling system will be discussed in the next section.

3.4.5 Influencing factors of the PV cooling system with different storages

3.4.5.1 Cooling load

A correlation is performed between the cooling load and the PESR by aggregating cooling loads from typical days of each climate (Figure 3.12). For both cases, the
system power consumption rises with the increase in the cooling load. However, the PESR of the battery storage case (a) increases with big fluctuations as the load grows; while the PESR of the CTES case (b) ascends with the increase of the cooling load before the load reaches 55.6 kWh, and declines as the load exceeds this value. This indicates that there is an optimal store size for a given load and that the cold store may need to be larger in energy capacity than a battery store for a given cooling load.

Figure 3.12 The influence of cooling load on the PESR of both cases
The effect of latent load on the PESR is discussed by classifying the daily cooling loads into three groups – where the sensible load is less than, approximately equal to, or more than the latent load. These classifications are marked in Figure 3.13 as “sen/lat <1”, “sen/lat =1” and “sen/lat >1”, respectively.

(a) Battery storage case

(b) CTES case

Figure 3.13 The influence of sen/lat cooling load ratio on the PESR of both cases

For the battery storage case, the highest PESR is obtained for balanced loads. For both cases, the PESR tends to be low for moderate loads with a high latent heat proportion. However, as the total daily load increases, it becomes clear that the battery storage case can still perform well while the PESR of CTES case dropped
drastically. Upon investigation, these high loads are attributable to latent heat demand. The temperature loss of heat exchange on the extraction of cooling effect from the cold store results in a chilled water temperature higher than the dew point temperature at some times. Grid electricity is required to overcome this limitation, and this will result in a decrease in the PESR. However, quantitative study on the effect of cold store sizing and heat exchange effectiveness on the PESR requires further investigations.

3.4.5.2 Chiller COP and chilled water set-point

The effect of the chiller COP and the chilled water set-point are studied for both cases by comparing the daily grid electricity consumption and PESR in Brisbane (Figure 3.14). The COP varies between 1.2 and 4.4 reflecting a range of ambient temperatures to which chiller’s condenser heat must be rejected. The chilled water set-point varies in the range of 5–9°C for the battery storage case, and 1–5°C for CTES case.

In the battery storage case, the PESR is slightly affected by varying the chilled water set-point but is very sensitive to the change in the chiller COP. In the CTES case, the PESR is markedly affected by both factors, since both the chiller’s efficiency and the heat transfer efficiency in cold store are crucial to the system power consumption.

(a) Battery storage case
Figure 3.14 The influence of chiller COP and chiller set-point on the PESR of both cases

The power consumption drops and PESR grows notably as the COP increases. The power consumption is the largest when the set-point is 1–2°C due to the power consumed by the chiller. However, the largest PESR also occurs when the set-point is 1°C, which reveals that the enhancement of heat transfer in the CTES outweighs the extra energy consumed by the chiller for a lower set-point. Therefore, the rise in the PESR with the decrease in the set-point on the whole can be justified.

3.4.5.3 Storage size

The storage capacity should be matched to the cooling load to realise the best cost and energy benefits. The sizing ratio is normalised as the ratio of storage capacity to the total cooling load. Studies are carried out with the weather profile of Brisbane.

For the battery storage case (Figure 3.15a), the sizing ratio in the range from 0.43 to 1.50 by varying the battery size is chosen, with a fixed PV panel sized according to the fixed load energy. The battery is only able to accept charge when electricity is being produced and discharges over the 8 hour ventilation period. As can be seen, the energy loss due to the fully charged battery declines rapidly as the sizing ratio grows; while it drops to and stays at 0 after the ratio exceeds 1.08, indicating that no energy is lost by overcharging. The PESR increases gradually as the sizing ratio rises to 1.10, and it tends to be constant at 3.33 afterwards. The charging time first climbs slowly with the increase in the ratio until the ratio reaches 0.96 where it starts to surge up rapidly. However, the full charge of battery cannot be fulfilled within 8 h when the sizing ratio exceeds the deflection point of 1.30. It is noted that
this deflection point appears after the sizing ratio exceeds 1, and the value depends on the PV panel sizing and local solar radiation.

**Figure 3.15 The influence of storage size on the PESR of both cases**

For the CTES case (Figure 3.15b), the load coverage ratio of the cold store is also 0.43–1.50, corresponding to a tank volume from 1.0 to 3.6 m³. The volume ratios of HTF and PCM vary from 0.5 to 2.0. Around the ratio of 1.24, the average liquid fraction of CTES peaks at 0.84, signifying a superior discharging performance. After this point, due to the inferior heat transfer between the HTF and the PCM resulted from large storage size, the discharge is suffocated. At different sizing
ratios, the line for PESR is an approximate normal distribution with the peak located when the sizing ratio is about 1. As the $V_{HTF}/V_{PCM}$ ratio increases, the heat transfer in CTES is enhanced; thus the PESR grows by 0.5–0.8. It is noted that applying a storage capacity equivalent to the cooling load can improve the system energy saving; however, the increase in the size also enlarges thermal resistance and surface heat gain thus leading to an inferior energy saving [186, 208].

3.4.6 Effect of PCM on energy saving of the CTES case

The study on exergy change, energy storage efficiency and charging/discharging time of the cold store at different HTF temperatures is also based on a 1m$^3$ tank of different PCMs. The HTF mass flow rate is 0.3 kg·s$^{-1}$. The temperature difference between the PCM and the HTF is in a range of 1–7$^\circ$C. The chiller set-point was 3$^\circ$C for C-L eutectic storage and CO$_2$ hydrate storage and –4$^\circ$C for ice storage case, with 4$^\circ$C temperature difference driving heat transfer.

3.4.6.1 Exergy change of the single CTES

In the charge period (Figure 3.16a), the average exergy change per unit volume is the largest in the ice store while smallest in the C-L eutectic store due to the large difference in thermal conductivity. CO$_2$ hydrate storage has the longest charging time attributed to its large phase change enthalpy and relatively small thermal conductivity. The charging time of the C-L eutectic storage appears smaller than that of the other two, which is attributed to the fact that the phase change enthalpy of C-L eutectic is only about one third of those of the others. The energy storage efficiency of all PCMs exceeds 97%, with CO$_2$ hydrate storage the highest. This is due to its considerable enthalpy and moderated phase change temperature (7$^\circ$C) that can reduce heat gain at ambient temperatures better than ice. On the other hand, both the exergy change and storage efficiency increase with the rise in the temperature difference between the PCM and the HTF.

In a similar way, Figure 3.16b illustrates the energy variations in the discharge. The exergy change of ice storage during the discharge is more prominent than those of the other PCMs due to the larger thermal conductivity of solid ice. This is also the reason why in the discharge, ice storage achieves higher storage efficiency than CO$_2$ hydrate storage.
3.4.6.2 Power consumption and PESR of the CTES case with different PCMs

The seasonal cooling supply and grid electricity consumption of each cold storage system with various PCMs for each climate are shown in Figure 3.17. Considering
the effect of chiller set-point on the PESR and the performance of a single CTES, the chiller set-point was 3°C for C-L eutectic and CO₂ hydrate storage and –4°C for ice storage case. The size of each storage case was previously mentioned in Table 3.2.

As for the results in the last section, more grid electricity is consumed in the all the CTES cases than in the battery storage case. Comparing three PCMs, ice storage is likely to store the largest amount of cooling capacity due to its large enthalpy and thermal conductivity, which also accelerates the charging/discharging process. However, it also suffers the largest heat gain, attributed to its phase change temperature (0°C) that is much lower than the ambient. Furthermore, since the required chiller set-point for ice storage is –4°C, more power is consumed by the chiller. C-L eutectic storage is capable of reducing heat gain since its storage temperature (7°C) is higher than for ice and its thermal conductivity is low in both solid and liquid phases. However, a large tank volume is required because of its low phase change enthalpy. This will lead to an increased surface area, and consequently a large heat gain to the cold store. CO₂ hydrate storage seems advantageous over the other two PCMs. This material transitions phase at relatively higher temperatures (7°C) with large latent heat. This ensures the cold store can reserve a large amount of cooling capacity with less heat gain from the ambient compared to ice storage. However, it has limited thermal conductivity in the solid phase and may require a large heat exchange surface area in the store to prevent the store from being heat rate limited.

![Graph showing energy consumption by different storage types in Shanghai](image-url)
Figure 3.17 Cooling supply and power consumption of each case during cooling season

The average PESR and energy storage efficiency of the reference case and all the storage cases across the entire cooling season are plotted in Figure 3.18. Compared with the reference case without energy storage, all the storage cases can manage to achieve a higher PESR. The battery store achieves the highest PESR of all the cases studied. For various PCM cold stores, the average PESR of CO\textsubscript{2} clathrate hydrate cold storage (4.18) is higher than that of ice storage (2.66), and C-L eutectic storage
The average PESR of CO₂ hydrate storage is 56% higher than that of ice storage.

![Figure 3.18 PESR and storage efficiency of battery and CTES with different PCMs](image)

### 3.5 Conclusion

Promising energy saving performance of CTES is predicted in this chapter through a TRNSYS simulation that compares battery storage and phase change CTES with different PCMs in a PV cooling system across three geographic locations.

In the battery storage, the charging rate and self-consumption ratio are both in proportion to the solar radiation within a certain range; and the discharging rate increases with the rise in the load power while the self-sufficiency ratio declines with it. In the CTES, an increase in HTF temperature leads to a reduction in energy efficiency and an extended charging time. The average exergy output is in linearity with the cooling load.

During the cooling season, on average the PESR of the battery storage case is 2.8 times higher than that of the reference case without any storage; while the PESR of the CTES case is 1.9 times higher than that of the reference case. The excess power consumption due to the heat gain and the relatively low chiller’s efficiency in the CTES case is blamed for the lower capability of the CTES case compared to the battery storage case.

It is also worth mentioning that the PESR is sensitive to the proportion of latent load in the cooling demand. It is also affected by the chilled water set-point, the chiller COP, and the storage size (with different volumetric ratio of HTF and PCM...
in cold storage). This is true for both the battery storage and CTES case. In the battery storage case, a high PESR can be achieved for high cooling loads; while in the CTES case a moderate cooling load seems more favourable. The PESR for the CTES case increases notably with the rise in chiller COP. In addition, there is an optimal storage size of both battery and CTES.

Compared with ice and C-L eutectic, CO₂ hydrate is more capable in cold storage performance due to its high enthalpy and thermal conductivity, and suitable phase change temperature. The C-L eutectic storage manifests a similar average PESR to that of the CO₂ hydrate storage, and its energy storage efficiency is even slightly higher than that of the CO₂ hydrate storage. However, the energy storage density of CO₂ hydrate is much higher than that of C-L eutectic, which means less PCM and smaller storage size is required in the CO₂ hydrate storage case.
Chapter 4

Phase equilibrium and enthalpy of TBAB, TBAF and TBPB hydrates

Since the formation of most natural gas–water hydrates normally requires high pressures, the practical applications of natural gas hydrates are dependent on the use of quaternary ammonium/phosphonium (TBA⁺ or TBP⁺) salts to form semi-clathrate structure at reduced phase equilibrium pressures. Before conducting experiments on CO₂ semi-clathrate hydrates, the phase equilibrium of quaternary salt hydrates in the absence of CO₂ gas are studied and modified for the following reasons:

1. Semi-clathrate hydrates of TBA⁺ or TBP⁺ salts can offer a suitable phase change temperature at certain mass fractions, and thus can be a suitable cold storage material. Their phase equilibrium is worthy of further investigation.

2. It is helpful to design and assess the experimental procedures for semi-clathrate hydrates and CO₂ semi-clathrate hydrates in a manner that allows direct comparison of the results.

3. An understanding of the phase change behaviour of TBA⁺ or TBP⁺ salt hydrates, such as the maximum induction temperature and the induction time, contributes to the design of the experimental procedures to from CO₂ semi-clathrate hydrate.

4. Promoters are used to minimise the supercooling and to accelerate the induction period of the hydrate. A surfactant can provide a nucleus, around which a crystal forms and creates a solid, thus it helps to break through the metastability [4]. Frequently used surfactants are SDS, STS, SHS, CTAB, DTAB, DTAC, LABS, DBSA, SDBS, ENP, Tween and Span20, etc. In addition, nanoparticles can accelerate the hydrate formation by enhancing the thermal conductivity of the gas–water system thus speeding up the growth of crystals [124, 209–212]. Since the base of the gas hydrates is the semi-clathrate structure of TBA⁺ or TBP⁺ salt hydrates, the functions of these promoters can be firstly tested on TBA⁺ or TBP⁺ salt hydrates on the ground of safety and simplification.
5. The T-history method to determine the formation enthalpy of clathrate hydrate can be validated in the test of semi-clathrate hydrates of TBA\textsuperscript{+} or TBP\textsuperscript{+} salts. In other literature, the hydrate dissociation process is usually used to determine the phase equilibrium data. This avoids factors leading to uncertainty in the hydrate formation, such as supercooling and formation memory effect \cite{213–220}. The formation behaviour of hydrate is of great importance to the charging process of a cold store and is a determinant of the energy saving of the cooling system.

The aim of this chapter is to study the formation properties of TBAB, TBAF and TBPB semi-clathrate hydrate, namely the formation temperature, induction time and supercooling degree. For this purpose, single and binary salt–water systems are prepared with the various mass factions in the range 10–40 wt\%. The hydrate formation is induced by stepwise cooling the samples and the equilibrium temperature is determined not only by the visibility of formed solids but also by the variations in the cooling curve. Different crystal shapes are also presented. Formation promoters are tested as means to alleviate supercooling and shorten the hydrate induction period. SDS is employed as a promoter with the concentration of 0.05, 0.1 and 0.5 wt\%; TiO\textsubscript{2} nanoparticles in the size of 20 nm and 80 nm are also tested. Finally, the memory effect is studied through 10 cycles of formation and dissociation of the fresh and used samples.

In addition, the measurement on phase change enthalpy, heat capacity and thermal conductivity of hydrates formed from single and binary TBAF water solutions is conducted. The enthalpy method is used to investigate energy change during hydrate formation in a tubular vessel. The enthalpy method derives the accumulated cooling capacity and variations of the charging rate. The effect of HTF temperature, tube size, thickness and thermal conductivity of the tube wall the charging performance of the salt hydrate are to be studied. This work will be helpful to determine the thermal properties of semi-clathrate hydrates and predict the energy variation in a cold storage tube.

4.1 Determination of formation behaviour

4.1.1 Experimental setup and procedures

To determine the hydrate formation temperature, samples of TBAB, TBAF and TBPB water solutions (each 20 g) were prepared at mass fractions of 10–40 wt\%. In binary systems, the proportion of components (TBAB + TBPB, TBAB + TBAF and TBPB + TBAF) was 75:25, 50:50 and 25:75, respectively. The purity and source of the materials used in the experiments are provided in Table 4.1. These samples were contained in a thin-wall glass tube with a diameter of 20 mm.
The experimental system is shown in Figure 4.1. It is composed of a thermostatic bath, test tubes and a data acquiring system. The tubes containing the samples were submerged in a propylene glycol water solution (the HTF) in a thermostatic bath. The HTF temperature is controlled by the bath. A platinum resistor is located in each tube to measure the hydrate temperature. The mass of salt and distilled water was measured by an electronic balance with the uncertainty of 10 mg; therefore, the uncertainty of the mass fraction of solutions was estimated to be $\pm 1.00 \times 10^{-4}$. The temperature fluctuation of the thermostatic bath was $\pm 0.05^\circ C$. The uncertainty of the platinum resistors was $\pm 0.1^\circ C$.

![Figure 4.1 Schematic diagram of the formation temperature measuring system](image)

1–thermostatic bath; 2–test tube; 3–platinum resistor; 4–tube holder; 5–data logger; 6–computer

### Table 4.1 Purity and source of the materials

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS Number</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra-n-butylammonium bromide</td>
<td>CAS 1643-19-2</td>
<td>98%</td>
<td>SIGMA-ALDRICH</td>
</tr>
<tr>
<td>Tetra-n-butylammonium fluoride</td>
<td>CAS 429-41-4</td>
<td>75 wt% in water</td>
<td>SIGMA-ALDRICH</td>
</tr>
<tr>
<td>Tetra-n-butylphosphonium bromide</td>
<td>CAS 3115-68-2</td>
<td>98%</td>
<td>SIGMA-ALDRICH</td>
</tr>
<tr>
<td>Sodium dodecyl sulphate</td>
<td>CAS 142-87-0</td>
<td>99%</td>
<td>VETEC</td>
</tr>
</tbody>
</table>

The first trial experiment was conducted using the continuous cooling method. The samples were placed in the bath. The bath temperature was reduced by a constant cooling rate at $0.2^\circ C \cdot min^{-1}$ before reaching $0^\circ C$. The bath temperature was then maintained at $0^\circ C$. The temperature of salt solution typically underwent a valley shaped response (due to the supercooling) before climbing (due to the exothermic hydrate formation), and finally reaching a peak (due to the phase equilibrium) before dropping to the bath temperature (Figure 4.2).

However, by continuous cooling, the peak failed to indicate the phase equilibrium temperature accurately, since the uncertainty was increased by the high cooling rate in the unsteady state. The valley cannot manifest the maximum induction temperature (defined as the maximum bath temperature that can trigger the hydrate nucleation, which also indicates the minimum supercooling degree), since the
sample temperature gravitated towards and then constantly stayed at the bath temperature during the long-time nucleation. It is considered that the continuous cooling method in hydrate formation may potentially result in poor repeatability in the measurement of phase equilibrium data. Therefore, a stepwise method was used in this study.

Figure 4.2 Typical temperature curves of salt hydrates by continuous cooling

The stepwise cooling procedure consists of a number of steps. The bath temperature was initially at 15°C for TBAB and TBPB and 30°C for TBAF, which were estimated high enough to avoid any hydrate formation at the start of the experiment. When the system temperature was stable, the bath temperature was decreased in steps of 0.5°C and was maintained for at least 6 h at each step to ensure a steady state was achieved. The hydrate formation was identified from the temperature curve as well as by observing the formed crystals. If a solid crystal occurred in the tube, or an increase in the temperature curve took place, the bath temperature was maintained for another 6 h for full completion of the hydrate formation. If no visible hydrate was observed or the temperature remained constant, the bath temperature was decreased by one step and it was repeated until the formation was detected. The formation temperature was obtained from the peak in the temperature curve. At this point, the coexistence of the solid and the liquid in the tube lasted for a long time (i.e. the formed hydrate was stable in the solution). After this, the system quickly developed into a fully frozen solid. Once the hydrate formation was detected at a certain step, the bath temperature at this step was taken as the maximum induction temperature.

In order to study the natural nucleation of semi-clathrate hydrates in a static CTES, neither crystal seeds nor mechanical vibration/agitation was used to artificially induce the nucleation. The measurements on each sample were conducted at least
three times to examine repeatability of the results. If a low repeatability was found, the test will be repeated until there are three points of data obviously close to each other and this point is recorded as the result.

4.1.2 Formation temperature of salt hydrates

The appearance of samples of TBAB, TBAF and TBPB water solutions at mass fractions of 10, 15, 20, 25, 30, 35, 40 wt% at an ambient temperature of 4°C is shown in Figure 4.3. It is noted that, TBAF solutions at all mass fractions formed hydrates at 4°C. For TBAB and TBPB, the mass fraction of 15–35 wt% and 25–35 wt%, respectively, were most conducive to forming hydrate at such an ambient temperature.

Figure 4.3 Appearance of TBAB/ TBAF/TBPB water solutions at 4°C
Figure 4.4 Formation temperature of single salt hydrates as a function of mass fraction

The formation temperature of hydrates formed from TBA$^+$ and TBP$^+$ salts and water system as a function of salt mass fraction are shown in Figure 4.4, compared with the phase equilibrium data determined from dissociation in other literatures [213, 215, 218, 219, 221, 222].

The formation temperature of TBAF hydrate is overall much higher than that of the other two across the entire mass fraction range tested. It also reveals a tendency that the formation temperature of all the hydrates firstly climbs with the increase in the mass fraction, and peaks around a value, which is 30 wt% for TBAF hydrate, 35 wt% for TBAB and TBPB hydrate. After the peak point, the formation temperature drops as the mass fraction rises. This peak is defined as the congruent point, at which the solid and liquid phases of the salt–water system have the same composition (i.e. the two-component system can be seen as a one-component system) [216]. This indicates that the most stable hydrate is available at this mass fraction [214], and it corresponds to mole fraction of 2.87 mol% for TBAF, 2.92 mol% for TBAB and 2.78 mol% for TBPB, or hydration number of 33.89 for TBAF, 33.26 for TBAB and 35.01 for TBPB.
It is also noted that the formation temperature is different to the dissociation temperature. The existence of supercooling in hydrate formation enlarges the difference between the phase equilibrium temperature and the bath temperature that is set, thus a larger overall transient cooling rate results. When the volume of the sample is small, the heat flux is relatively large; consequently, the measured temperature curve is more or less affected by the bath.

The formation temperature of binary hydrates of TBAB + TBPB, TBAB + TBAF and TBPB + TBAF at proportions of 75:25, 50:50 and 25:70 are illustrated in Figure 4.5 and detailed in Table 4.2. The maximum induction temperature of binary hydrate is also shown. As can be seen, TBAB + TBPB systems show a very narrow formation temperature range that is 1.1–5.9°C; while the range for TBAB + TBAF and TBPB + TBAF is 5.7–24.3°C and 5.5–24.6°C, respectively.

Notably, hydrate formation in the presence of TBAF usually requires less energy than TBAB or TBPB, thus is favoured to form at high temperatures. This is because the fluoride ion is easier to link to the water lattice and replace water molecules than the bromide ion. On the other hand, in binary systems with TBAF (Figure 4.5(b) and 4.5(c)) the formation temperature curves for binary hydrates at various mass fractions are within the curves for single hydrate.
In contrast, there is a eutectic point (indicating the composition corresponding to the lowest melting point of a compound PCM) in the system of TBAB + TBPB (Figure 4.5(a)), which is at the proportion of 25:75. In other cases, the formation temperature increases in the TBAB + TBPB system as the proportion of TBAB rises. This is owing to the fact that the size and shape of TBA$^+$ can better fit to the framework of semi-clathrate hydrate than TBP$^+$ [218]. Moreover, the butyl group of TBA$^+$ can be trapped not only in large T cavities ($5^{12}6^2$, consisting of 12 pentagonal and 2 hexagonal faces) and P cavities ($5^{12}6^3$, consisting of 12 pentagonal and 3
hexagonal faces), but also in small D cavities (512, consisting of 12 pentagonal dodecahedron) of water lattice [223], revealing a better thermodynamic stability.

### Table 4.2 Measured formation temperature of binary salt hydrates

<table>
<thead>
<tr>
<th>w_{salt} of TBAB+TBPB</th>
<th>Proportion of TBPB in the binary system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x_{TBPB}=0</td>
</tr>
<tr>
<td>0.10</td>
<td>1.6</td>
</tr>
<tr>
<td>0.15</td>
<td>4.1</td>
</tr>
<tr>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>0.25</td>
<td>6.6</td>
</tr>
<tr>
<td>0.30</td>
<td>8.2</td>
</tr>
<tr>
<td>0.35</td>
<td>10.3</td>
</tr>
<tr>
<td>0.40</td>
<td>5.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>w_{salt} of TBAB+TBAF</th>
<th>Proportion of TBAF in the binary system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x_{TBAF}=0</td>
</tr>
<tr>
<td>0.10</td>
<td>1.6</td>
</tr>
<tr>
<td>0.15</td>
<td>4.1</td>
</tr>
<tr>
<td>0.20</td>
<td>5.0</td>
</tr>
<tr>
<td>0.25</td>
<td>6.6</td>
</tr>
<tr>
<td>0.30</td>
<td>8.2</td>
</tr>
<tr>
<td>0.35</td>
<td>10.3</td>
</tr>
<tr>
<td>0.40</td>
<td>5.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>w_{salt} of TBPB+TBAF</th>
<th>Proportion of TBAF in the binary system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x_{TBAF}=0</td>
</tr>
<tr>
<td>0.10</td>
<td>2.7</td>
</tr>
<tr>
<td>0.15</td>
<td>3.2</td>
</tr>
<tr>
<td>0.20</td>
<td>3.5</td>
</tr>
<tr>
<td>0.25</td>
<td>3.7</td>
</tr>
<tr>
<td>0.30</td>
<td>4.0</td>
</tr>
<tr>
<td>0.35</td>
<td>4.4</td>
</tr>
<tr>
<td>0.40</td>
<td>2.3</td>
</tr>
</tbody>
</table>
4.1.3 Morphology of hydrate crystals

Sequential photographs were taken along the formation of 25 wt% TBAB, TBAF and TBPB hydrate at the start point, peak point and completion point, respectively, as is marked in Figure 4.2.

In Figure 4.6, for TBAB hydrate, after the nucleation seed crystals were observed in columnar shape with the thickness between 0.2 and 0.4 mm and the length around 1.0 mm (a). Large crystals gradually grew from the seeds taking shape of radial pattern with the columnar branches of 2.0–3.0 mm long (b). The growth continued until the intervals among the radial crystals were filled with solids, and the bulk of hydrate appeared pure white, uniform and compact (c). After this, no more noticeable crystal growth was observed. By comparing the crystal shape with that described in the literature [224], it can be confirmed that the TBAB hydrate in this study mostly has a type B characteristic.
In Figure 4.7, the seed crystals of TBAF hydrate were also in columnar shape, with the thickness similar to that of TBAB hydrate, while the length was about three times larger than that of TBAB hydrate (a). Straight after the nucleation, more needle-like crystals piled up from the bottom of the tube where seed crystals first occurred (b). Finally, crystals packed the tube and the bulk seemed as compact as that of TBAB hydrate but in pale yellow (c).

The crystal morphology of TBPB hydrate (Figure 4.8) was a hexagonal plate with 0.5–0.8 mm on each side (a). This differs from the crystal shape of TBAB and TBAF hydrate. After nucleation, the formation proceeded and the crystals grew into a relatively non-compact framework that was composed of larger hexagons (b). The appearance of the bulk of TBPB hydrate at the completion point was flocculent, and the layout of crystals was disordered (c).

4.1.4 Effect of additives on hydrate formation

As previously mentioned surfactants and nanoparticles are likely to favour hydrate formation as formation promoters. To investigate the effect of promoters on the hydrate formation, 25 wt% salt solutions were used. SDS was added at various mass fractions (0.05, 0.1 and 0.5 wt%) and TiO$_2$ was employed in different particle sizes (20 and 80 nm). Hence, eight samples of various additive combinations were prepared for each salt hydrate.

The samples of TBAB, TBAF and TBPB were cooled by a bath temperature of 5, 20 and 2$^\circ$C, respectively, which is set according to the maximum induction temperature measured by the stepwise cooling and the possibility of additives to bring down the supercooling temperature. The measured formation temperature, supercooling degree, induction time (from the start to the cease of induction) and deflection time (from the start to the peak point) are shown in Figure 4.9, and are further discussed in Table 4.3.

It can be concluded that, SDS at some concentrations is helpful to reduce the induction time and deflection time of all the hydrates. The formation temperature of TBAB hydrates decreases with the rise in the SDS mass fraction, while that of TBAF and TBPB hydrates increases with it. In addition, the supercooling degree of the three salt hydrates can be reduced by increasing SDS concentration. However, the effect of TiO$_2$ nanoparticles is less controllable.

By observing the shape of the peak in the formation temperature vs promoter concentration plot, it is found that to some extent SDS tends to make the peak flatten and wide, while TiO$_2$ makes the peak sharp and narrow. This also incarnates in the difference between the induction time and deflection time.
When SDS and TiO₂ are used together, in most cases the effect of SDS overwhelms the effect of TiO₂ in both the peak shape and the hydrate formation behaviour. It is believed that SDS mainly favours the induction by shortening the time for nucleation, while TiO₂ nanoparticle mainly accelerates the hydrate growth by enhancing thermal conductivity of the multi-phase and multi-component system.
Figure 4.9 Formation behaviour of salt hydrates with different additives

Table 4.3 Effects of SDS and TiO$_2$ on the formation of salt hydrates

<table>
<thead>
<tr>
<th>Salt</th>
<th>Additive</th>
<th>Induction time and deflection time</th>
<th>Formation temperature</th>
<th>Supercooling degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAB</td>
<td>SDS</td>
<td>Reduced as SDS fraction increased</td>
<td>Reduced as SDS fraction increased</td>
<td>Reduced as SDS fraction increased</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Slightly reduced by 20 nm</td>
<td>Slightly enlarged by both sizes</td>
<td>Slightly reduced by both sizes</td>
</tr>
<tr>
<td>TBAF</td>
<td>SDS</td>
<td>Reduced as SDS fraction increased</td>
<td>Enlarged as SDS fraction increased</td>
<td>Reduced by SDS fraction increased</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Slightly reduced by 80 nm</td>
<td>Slightly reduced by both sizes</td>
<td>Slightly reduced by 20 nm; largely reduced by 80 nm</td>
</tr>
<tr>
<td>TBPB</td>
<td>SDS</td>
<td>Reduced as SDS fraction increased</td>
<td>Reduced before 0.05 wt%; enlarged after it</td>
<td>Reduced as SDS fraction increased</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Reduced by both sizes</td>
<td>Reduced by 20 nm; enlarged by 80 nm</td>
<td>Reduced by 20 nm; enlarged by 80 nm</td>
</tr>
</tbody>
</table>

4.1.5 Effect of subcooling driving force on hydrate formation

The subcooling (the difference between the formation temperature and the bath temperature to cool the sample) is a driving force to the hydrate nucleation. To
investigate the effect of subcooling driving force on the rate of nucleation and hydrate growth during the latent heat transfer period, 25 wt% TBAB, TBAF and TBPB solutions were prepared with/without SDS (0.5 wt%) or TiO$_2$ nanoparticle (20 nm). Hydrate formation was induced at three bath temperatures (5.0/2.5/0.0$^\circ$C for TBAB, 20.0/13.0/6.0$^\circ$C for TBAF, and 2.0/0.5/–1.0$^\circ$C for TBPB) starting from the maximum induction temperature. The subcooling was enlarged by decreasing the bath temperature. The results are shown in Figure 4.10.

Overall, shorter induction time is driven by larger subcooling (lower bath temperature), since the overall heat transfer can be enhanced by larger temperature difference. It is also notable that, for all the hydrates tested, a dramatic decrease in both the induction time and the deflection time takes place when decreasing the bath temperature from the maximum induction temperature. The induction time and deflection time are both the shortest in the TBAF hydrate.

In addition, repeatability of the formation temperature can be examined. From the results, unrepeatability occurs in the measured formation temperatures, especially when decreasing the bath temperature from the maximum induction temperature. The unrepeatability is 22.5%, 22.2% and 6.0% in average respectively for TBAB, TBAF and TBPB, by lowering the bath temperature from the maximum induction temperature. It is known that hydrate formation conditions depend on many factors, such as rate of cooling, degree of subcooling, water history, etc., thus it may not be repeatable [225]. Many studies have shown that the repeatability can be improved to some extent by increasing the subcooling driving force [226].

(a) 25 wt% TBAB hydrate formation at different subcooling
4.1.6 Memory effect on hydrate formation

Memory effect has been found to reduce the induction time of hydrate formation in water that dissociated from previous hydrates [129, 130]. It is assumed that the residual structure of hydrate dissociation provides a site for mass transfer between host and guest molecules. Therefore, a driving force is created between the residual structures and its surrounding bulk phase to promote the hydrate nucleation [135]. Hydrate formation in a system containing fresh water usually leads to highly scattered results due to the stochastic nature of hydrate crystallization. On the other
hand, hydrate formation in a system containing water that has previously experienced hydrate formation and decomposition can improve the repeatability of results. Thus this memory effect is also believed a way to enhance the repeatability of test results [226].

To study the memory effect, 25 wt% TBAB, TBAF and TBPB solution with/without SDS (0.5 wt%) and TiO$_2$ nanoparticle (20 nm) were used again. The temperature variation of samples was recorded during 10 cycles of formation and dissociation at a constant bath temperature of 0.5$^\circ$C. The 1$^{st}$, 4$^{th}$, 7$^{th}$ and 10$^{th}$ hydrate formation is shown in Figure 4.11.
For TBAB (a) and TBPB hydrate (c), the completion of the 1\textsuperscript{st} formation takes 206 and 192 min, respectively, and the required time reduces steadily as the cycles proceed. The time for the 10\textsuperscript{th} formation of TBAB hydrate accounts for only 48.5\% of the time used for the 1\textsuperscript{st} formation, and that of the 10\textsuperscript{th} TBPB formation accounts for 73.3\% of the 1\textsuperscript{st} TBPB formation. In contrast, TBAF hydrate (b) has a much shorter formation time on the whole (completed in 25 min for the 1\textsuperscript{st} formation), and the formation time decreases slightly as the cycles are repeated.

It is also noted that for TBPB and TBAF hydrate, the supercooling degree, induction time and deflection time are all the largest in the fresh case due to the memory effect. However, these parameters do not always reduce as cycles proceed. Taking TBAF with 0.5 wt\% SDS and 20 nm TiO\textsubscript{2} as an example, the induction time reduces steadily by 4.2\%, 14.0\% and 14.6\%, respectively at the 4\textsuperscript{th}, 7\textsuperscript{th} and 10\textsuperscript{th} time of formation; whereas, the deflection time decreases by 26.1\% and 5.7\% at the 4\textsuperscript{th} and 7\textsuperscript{th} formation but increases by 1.4\% at the 10\textsuperscript{th} formation. For TBAB hydrate, a notable randomness in the variation of the time and temperature parameters is found, which especially differs with additives. By contrast, samples with TiO\textsubscript{2} show best repeatability with an average error of 0.65\textdegree C for TBAB, 0.75\textdegree C for TBAF and 0.11\textdegree C for TBPB.

The memory effect is desirable for a practical cold store since it can increase the rate at which the cold store can absorb cooling power as well as reducing the induction time.
4.1.7 Effect of sample mass on hydrate formation

It has been reported that repeatability of the hydrate formation is much less than that of the hydrate dissociation [225]. One reason is that the formation behaviours, such as the supercooling and induction period, are influenced by the mass of the hydrate sample, since the heat flux is largely affected by mass during heat transfer. Hence, a test on the effect of mass on the hydrate formation and dissociation behaviour is conducted by comparing the cooling and heating curve of an 8 g and an 80 g 25 wt% TBAB solution. Results are shown in Figure 4.12.

![Cooling and heating curve of salt hydrates of different masses](image)

(a) 8 g hydrate sample of 25 wt% TBAB

(b) 80 g hydrate sample of 25 wt% TBAB

Figure 4.12 Cooling and heating curve of salt hydrates of different masses
The 1st derivative of the temperature curve is also plotted to illustrate the variation of temperature. For the 8 g sample, in Figure 4.12 (a) the derivative of temperature during the cooling process reaches a peak owing to the temperature rise in hydrate formation. The formation point is indicated by the deflection point where the 1st derivative of temperature drops to 0 for the first time and the temperature of the sample peaks (marked as point “A” in Figure 4.12 (a)). In the heating process, the 1st derivative of temperature increases to a large positive value and then drops gradually, since the sample is heated and the heating rate reduces. The point where the derivative of temperature is closest to 0 is recognised as the dissociation point (marked as point “B” in Figure 4.12 (a)). Similarly, the formation point and dissociation point are found in the 80 g sample, and are marked as point “A” and “B” in Figure 4.12 (b).

It is noted that the formation temperature is 6.20°C and the dissociation temperature is 9.63°C for the 8 g sample; while the formation temperature is 9.19°C and the dissociation temperature is 9.98°C for the 80 g sample. The discrepancy between the formation and dissociation point is 3.43°C for the small mass and only 0.79°C of the large mass. The supercooling degree for the small mass (5.15°C) is found to be larger than that for the large mass (4.12°C). In addition, the dissociation value is quite similar for both masses, while a big difference is found between the formation temperatures for both masses, revealing the intrinsic low repeatability in hydrate formation.

4.2 Characterisation of formation enthalpy and specific heat

4.2.1 Methodology

4.2.1.1 T-history theory

Phase change enthalpy of PCMs is the determinant of cooling capacity that can be stored by a CTES of fixed volume. Various types of thermal capacity characterisation solutions are available, such as DSC and DTA [227]. Nonetheless, these methods are limited: only a small mass can be tested, which would affect the thermal response; repeatability may not be reached when analysing heterogeneous samples; in the case of composite materials, the main component may interfere in the signal [228–230]. In most cases, PCMs show volume dependent effects, such as phase separation and supercooling, and thus require a sufficient sample volume to assure the sample is representative for the bulk material. Also, the rapid cooling and heating cycles usually lead to inaccuracy in the measurements.
Compared with DSC and DTA, the T-history method offers an easier way to characterise PCMs. The T-history method, first proposed by Yinping Zhang [231] in 1999 and developed by researchers in the past decades, offers a means to carry out enthalpy and heat capacity determination and is used for non-homogeneous samples with supercooling with better accuracy.

Lázaro et al. [232] verified the correct setup and data analysis of a T-history installation using standard materials with known properties. These materials included gallium, water and hexadecane, as well as two commercial PCMs, RT27 and sodium acetate trihydrate graphite compound. The results confirmed that the T-history method can be used to correctly analyse different kinds of PCM.

Marín et al. [233] described a further evaluation on the measurement of heat capacity and heat convection coefficient as temperature dependent values using the T-history procedure. To some degree, the original T-history method has restrictions on the measurement accuracy owing to the physical assumptions. To modify it, Rady et al. [234] conducted a thermal analysis to characterise a granular phase change composite using the T-history method with further modification of the method to handle the granular material undergoing phase change over a temperature range. The accuracy of the T-history method was improved and then applied to PCMs, such as paraffin and lauric acid, with no or a low degree of supercooling [235].

Similarly, Chiu et al. [230] adopted a modified T-history method to characterise the thermal properties of a salt hydrate and paraffin for the use in a thermal storage model.

Peck et al. [236] improved the T-history method without decreasing its simplicity by setting the tube horizontally.

Stanković et al. [237] investigated the impact of different thermistor linearization techniques on the uncertainty of the T-history characterisation of a RT21 (RUBITHERM® GmbH) PCM, and found that the technique employed may considerably affect the usability of latent heat storage density of PCMs in a certain temperature range. Suffice to say, the T-history method has been modified and adopted in the determination of thermal properties of PCMs, including typical PCMs, commercial PCMs and self-developed PCMs.

The sketch of the T-history installation used in our work (Figure 4.13) is quite similar to that in Figure 4.1; however, the samples are placed in a thermostatic chamber and are cooled and heated by air rather than propylene glycol. In the preparation of the experiment, aqueous solutions of single TBAF and binary compounds of TBAF with TBAB or TBPB at proportions of 25:75, 50:50 and 75:25 and mass fractions of 15–40 wt% (each 20 g) were placed in a glass tube with an
inner diameter of 24 mm. To acquire the cooling curve along the hydrate formation, a thermocouple was placed within each tube near its centre. The tubes were in the thermostatic chamber and cooled by air at a constant temperature of 3°C. The samples of binary solutions of TBAF were tested as the PCM sample, and distilled water of the same quantity was tested as the reference sample according to the T-history procedure. The mass of the salt solution and distilled water was measured by an electronic balance with the uncertainty of 10 mg; thus the uncertainty of the mass fraction of solution was estimated at ±1.00×10⁻⁴. The uncertainty related to temperature measurement amounted to ±0.1°C.

![Figure 4.13 Schematic diagram of the T-history setup for salt hydrates](image)

The typical T-history curves of the PCM sample and the reference are shown in Figure 4.14 (a) and (b), respectively. The temperature of PCM is initially uniform at \( T_o \) \((T_o > T_m)\), and the temperature of HTF is maintained at \( T_f \) \((T_f < T_s)\) throughout the test. The PCM temperature undergoes three stages: the liquid-phase sensible heat transfer period, the latent heat transfer period, and the solid-phase sensible heat transfer period. Due to the fact that the supercooling degree in the hydrate formation varies with different cooling rates, purity and water history \([235]\), \( T_s \), \( T_m \) and \( T_r \) are identified from the temperature curve according to the points of “Peak, Top and Valley” in the first deviation difference curve, as was introduced by Li et al. \([238]\). \( A_1 \), \( A_2 \) and \( A_3 \) are to be obtained by integrating the temperature difference between PCM and HTF with respect to time.

The T-history method is based on the lumped capacitance method, which requires uniformity of temperature profile throughout the transient process. This requires that thermal resistance of the PCM must be much less than the thermal resistance of the convective/conductive heat transfer to the outside surface of the material, i.e. a small Biot number \((\text{Bi} = \frac{ar}{2k} < 0.1)\) is adopted \([231]\).
Taking the tube and the contained PCM as a whole, the three stages of cooling can be presented respectively by: integrating both sides of the energy balance equation:

\[ mc_p \frac{dT}{dt} = -\alpha A_c (T - T_f) \quad (4.1) \]

To integrate Equation (4.1), from initial time to \( t_1 \) the PCM is in liquid-phase:

\[ A_1 = \int_{t_0}^{t_1} (T - T_f) \left( m_t c_{p,t} + m_p c_{p,l}(T_0 - T_s) \right) = \alpha A_c A_1 \quad (4.2) \]

From \( t_1 \) to \( t_2 \) phase change occurs:

\[ A_2 = \int_{t_1}^{t_2} (T - T_f) \quad m_p h = \alpha A_c A_2 \quad (4.3) \]
From \( t_2 \) to \( t_3 \) the PCM is in solid-phase:

\[
A_3 = \int_{t_2}^{t_3} (T - T_f) \quad (m_{t}c_{p.t} + m_{p}c_{p.s})(T_s - T_r) = \alpha A_c A_3
\]

(4.4)

As in shown in Figure 4.14(b), the characteristic temperatures in reference curve are the same \( T_o, T_s, T_r \) and \( T_f \) as is marked in the PCM curve in Figure 4.14(a). Since \( T_f \) is higher than the freezing point of water, the reference sample stays at liquid-phase all the while. Using the same energy balance equation, it can be obtained that:

\[
\begin{align*}
(m_{t}c_{p.t} + m_{w}c_{p.w})(T_0 - T_s) &= \alpha A_c A_1' \\
(m_{t}c_{p.t} + m_{w}c_{p.w})(T_s - T_r) &= \alpha A_c A_2'
\end{align*}
\]

(4.5)

The convection coefficient \( \alpha \) and specific heat of the tube \( c_{p.t} \) are calculated from Equation (4.5). As a result, the phase change enthalpy, \( h \), specific heat of the liquid and solid PCM, \( c_{p,l} \) and \( c_{p,s} \), can be obtained from Equation (4.2)–(4.4).

### 4.2.1.2 Determination of PCM thermal conductivity

To measure the thermal conductivity, an experimental tube containing salt water solution at a uniform temperature is submerged in the thermostatic bath at a constant temperature of \( T_f \) until the PCM is totally frozen. The tube has a length of 250 mm and an inner diameter of 15 mm. The temperature variation in the centre of the tube is recorded. After the hydrate formation, the experimental tube that contains the frozen hydrate is as shown in Figure 4.15.

![Figure 4.15 The experimental test tube containing a salt hydrate](image)
As the phase change proceeds, the phase boundary in the PCM moves, as is illustrated in Figure 4.16. According to Zhang et al. [231], if the ratio of the length to the diameter of the tube is larger than 15, it is justifiable to assume that the heat transfer is approximately one dimensional. Thus, the heat diffusion equation is:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T(r,t)}{\partial r} \right) = \frac{1}{\sigma} \frac{\partial T(r,t)}{\partial t} \quad (\delta < r < r_i, \ t > 0)
\] (4.6)

The initial condition

\[T(\delta=r_i) \equiv T_m \quad (t = 0)\] (4.7)

The boundary condition

\[k_s \frac{\partial T}{\partial r} \bigg|_{r=r_i} = \alpha(T_f - T) \quad (t > 0)\] (4.8)

For the interface between the two phases

\[T(r=\delta) = T_m\] (4.9)

\[k_s \frac{\partial T}{\partial r} \bigg|_{r=\delta} = \rho h \frac{d\delta}{dt} \quad (0 < t < t_f)\] (4.10)

From above equations, the solid thermal conductivity can be obtained by

\[k_s = \frac{\rho r_i^2 h}{4t_f(T_m-T_f)}\] (4.11)

To reduce error, using the perturbation method and neglecting the second order term of the perturbation expansion, the thermal conductivity of the solid PCM can be calculated from:

\[k_s = \left[1 + \frac{c_p, s(T_m-T_f)}{h} \right] / 4\left(t_f(T_m-T_f)\frac{1}{\rho r_i^2 h} - \frac{1}{\alpha r_i}\right)\] (4.12)

It was found that in most cases \(t_f(T_m-T_f)\frac{1}{\rho r_i^2 h} \gg \frac{1}{\alpha r_i}\); thus the term \(\frac{1}{\alpha r_i}\) can be neglected [231]. For a PCM in solid-phase in the same tube in a bath at a temperature higher than \(T_m\), the thermal conductivity of liquid PCM \(k_l\) can be acquired in a same way.
4.2.2 Measured enthalpy and specific heat of salt hydrates

Using the T-history method, the calculated average heat convection coefficient of air in the chamber is 5.78 W·m⁻²·K⁻¹. If the thermal conductivity of the PCM is assumed to be 0.40 W·m⁻¹·K⁻¹, the resultant Biot number is 0.087. These conditions satisfy the lumped capacitance method requirements. The measured enthalpy and heat capacity of liquid and solid phases are detailed in Table 4.4. The calculated TBAF hydrate enthalpy is also shown in Figure 4.17(a) compared with the measured enthalpy of TBAF·32H₂O and TBAF·29H₂O from other studies [239]. The results in the present study are a little lower than those from Rodionova et al. [239], which resulted from the assumption of the lumped capacitance method and the incidental heat gain. The T-history method showed consistency over several runs for each sample and is a reliable technique for thermal property characterisation.

The measured formation enthalpy is dependent on the mass fraction of salt. It first increases as the salt mass fraction rises, peaks at a value, and then decrease as the mass fraction continues rising. Before the peak, the mole ratio of TBAF to water is lower than the stoichiometric mole ratio in the hydrate (1:32 or 1:29); therefore, the amount of hydrate formed depends on the amount of TBAF in the solution and there is always free water left. The higher the mass fraction and the more TBAF is contained in the solution, the more hydrates can form, and thus the more enthalpy is measured. After the peak, the mole ratio of TBAF to water is higher than the stoichiometric mole ratio, and in this case TBAF salt becomes the one left and water is completely consumed in forming the hydrate. Hence, the higher the TBAF mass fraction, the less water is in the solution, the less hydrates can form, and thus the less enthalpy can be measured. The ratio of the measured enthalpy to the salt mass fraction in this section is illustrated in Figure 4.17(a) showing that the ratio also achieves the maximum around the stoichiometric ratio of TBAF to water in the hydrate.

In Figure 4.17(b) and 4.17(c), the measured enthalpy and the ratio of the enthalpy to the mass fraction of the binary system of TBAF + TBAB and TBAF + TBPB are shown. A similar tendency occurs that the measured enthalpy and ratio both peak around 35 wt% in both cases. In addition, both the enthalpy and ratio of the binary system are on the whole lower than that of the single TBAF–water system, and they both increase with the rise of TBAF proportion.
Table 4.4 Measured thermal properties of single/binary salt hydrates

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(a) TBAF hydrate

(b) TBAF + TBAB binary hydrate
4.3 Modelling charging process of selected hydrate in a cold storage tube

4.3.1 Enthalpy method

The transient heat and mass transfer problems associated with solidification-melting are known as ‘moving boundary problems’ or Stefan problems, which is a particular boundary value problem for a partial differential equation adapted to the case in which phase boundary moves with time. The enthalpy method is widely used for solving Stefan problems. It provides an easy way to model heat conduction with phase change by giving the solid-liquid interface as a part of the solution without explicit tracking of finite volumes.

To calculate the energy variation during phase change, the enthalpy method is commonly used for its ease of implementation. Ahmmed et al. [240] presented a study of laser induced melting and solidification of crystalline silicon using the enthalpy method. The model considered temperature dependent thermos-physical properties of silicon and was verified by experiments on a nanosecond pulsed laser annealing of silicon. An excellent agreement was observed with the experimental results for both the melting depth and the melting duration.

Wang et al. [3] applied the enthalpy method to simulate a cold storage spherical capsule containing an organic eutectic compound, by which the energy change of
the capsule along the charging and discharging process was predicted. Within a certain temperature range, the predicted temperature variations agreed well with the experimental results.

Bhattacharya et al. [241] employed the enthalpy method in a micro-scale model of the solidification of eutectic alloys. The capability of the model was successfully verified.

Brusche et al. [242] compared a temperature based method with the enthalpy method to resolve the Stefan problem associated with mark formation on the crystalline background of the phase-change layer in optical rewritable recording media. The result revealed the temperature method outperformed for small and medium range Stefan number (the ratio of sensible heat to latent heat), while the enthalpy method exceeded the temperature method for melting problem with large Stefan number.

In our work, the mathematical model of a PCM freezing in a tube is established by the enthalpy method [243]. To use this method, assumptions are made:

1. The temperature in the tube is uniform at the initial time.
2. The heat transfer in the tube is mainly heat conduction and the natural convection within PCM is negligible.
3. The phase change temperature is singular and constant.
4. There is no phase separation taking place.
5. The thermal properties of liquid and solid phase are temperature independent.
6. The phase change interface moves regularly from the wall to the centre of tube during phase transition.

The supercooling degree is hard to quantify. It is affected by the applied HTF temperature, composition of the solution, memory effect [226, 244], status of the liquid [245, 246], etc. Hence, in the modified model, the supercooling degree was set as an input with the value from experimental results.

Under these assumptions, the governing equation of the unsteady heat diffusion in each layer is [247]:

$$\rho \frac{\partial h}{\partial t} = k_1 \frac{1}{r} \frac{\partial^2 (rT)}{\partial r^2}$$ \hspace{1cm} (4.13)

where \( \rho \) and \( k \) are defined as: \( \rho, k = \begin{cases} \rho_s, k_s & h < h_s^* \\ \rho_l, k_l & h > h_l^* \end{cases} \) \hspace{1cm} (4.14)

The relationship between temperature and enthalpy can be expressed as:
\[ T - T_m = \begin{cases} \frac{h-h_s^*}{c_{p,s}} & h < h_s^* \\ 0 & h_s^* \leq h \leq h_i^* \\ \frac{h-h_i^*}{c_{p,l}} & h > h_i^* \end{cases} \]  \tag{4.15}

The initial condition is:
\[ T(\delta=R) = T_0 \]  \tag{4.16}

The boundary condition is consistent with Equation (4.8).

Figure 4.18 Spatial discretization of the cold storage tube

As is shown in Figure 4.18, the PCM inside the tube is discretised into layers with the nodes at the middle of layers. Hence, the above equations can be adopted separately in each control volume according to the position of the nodes.

For node \( i \) (\( i = 2, 3, 4, \ldots, N-1 \)), the adoptable heat balance equation is:
\[ \frac{(T^n_{i-1} - T^n_{i})A_{i-1}}{\frac{dr}{2k_{i-1}}} + \frac{(T^n_{i} - T^n_{i})A_{i}}{\frac{dr}{2k_{i}}} = \frac{V_i \rho_i c_p}{\Delta t} (T^{n+1}_i - T^n_i) \]  \tag{4.17}

For node 1 (at the centre layer), the heat balance equation is:
\[ \frac{(T^n_{1} - T^n_{1})A_{1}}{\frac{dr}{2k_{1}+2k_{1}}} = \frac{V_1 \rho_1 c_p}{\Delta t} (T^{n+1}_1 - T^n_1) \]  \tag{4.18}

For node N (at the outermost layer), the heat balance equation is:
\[ \frac{(T^n_{N-1} - T^n_{N-1})A_{N-1}}{\frac{dr}{2k_{N-1}}} + \frac{T^n_{i} - T^n_{N}}{R_1 + R_2 + R_3} = \frac{V_N \rho_N c_p}{\Delta t} (T^{n+1}_N - T^n_N) \]  \tag{4.19}

Where \( R_1 = \frac{1}{4\pi r_o^2 \alpha} \) is the thermal resistance of heat convection on the external surface of the tube; \( R_2 = \frac{1}{4\pi k_w \left( \frac{1}{r_i} - \frac{1}{r_o} \right)} \) is the thermal resistance of heat conduction of the tube wall; and \( R_3 = \frac{dr}{2k_4 \pi r_i^4} \) is the thermal resistance of heat conduction of the half thickness of PCM at the outermost layer. The problem is solved by C++ program with the simulated time step of 1 s and the number of layers of 20. Hence
the cooling capacity, charging rate, charging time and temperature variation within the heat transfer tube during the charging process can be predicted.

### 4.3.2 Model validation

To validate the model of the cold storage tube, water was used firstly as the PCM. The temperature variation of water during solidification were measured at various HTF temperatures (–5, –7 and –9°C) and compared with the results from the model (Figure 4.19). On the whole, the freezing time in the experiment is shorter than that in the simulation, which may be attributed to the ignorance of heat convection in the liquid PCM in the assumption. The average error in the freezing time is around 7%.

![Figure 4.19 Model validation using water at variable HTF temperatures](image)

An analysis was conducted on the grid-independence of the model. By running the model under the same conditions (the HTF temperature is 7°C, the tube inner diameter is 12.0 mm, the tube wall thickness is 1.0 mm, and the wall material is glass) while using different numbers of layers (i.e. N=5, N=10, N=15 and N=20). The temperature and cooling capacity was obtained, as shown in Figure 4.20. As can be seen, except for the case of N=5 which results in low accuracy, other cases are all in good agreement. The charging time is 89.5 min for both N=20 and N=15, and 89.6 min for N=10. The accumulated cooling capacity is 3.43 kJ for N=20, N=15 and N=5, and 3.42 kJ for N=10. Therefore, the model shows good grid-independence.
4.3.3 Selection of hydrate

The formation temperature of single and binary TBAF semi-clathrate hydrates as a function of mass fraction determined in the previous study [248] is shown in Figure 4.21. The red hatched area (5–12°C) is marked as the suitable temperature range for conventional air conditioning systems. The phase change temperature, the determined phase change enthalpy and heat capacity in section 4.2.2 are also considered.
Based on the above results, the 30 wt% TBAF+TBPB semi-clathrate hydrate with the proportion of 25:75 was selected from all the candidates to be used in the numerical model, as it has a suitable phase change temperature and a relatively large enthalpy. Its thermal conductivity was measured by the method described in section 4.2.1.2, and its density was obtained by direct measuring the mass and volume. All the characterised properties of the hydrate and dimensions of the cold storage tube are detailed in Table 4.5. These parameters are to be implemented in the numerical model. In this way, the accumulated cooling capacity and instantaneous energy charging rate of hydrate formation can be predicted.

<table>
<thead>
<tr>
<th>Formation temperature / °C</th>
<th>Thermal conductivity, ( l ) / W·m⁻¹·K⁻¹</th>
<th>Thermal conductivity, ( s ) / W·m⁻¹·K⁻¹</th>
<th>Density / kg·m⁻³</th>
<th>Specific heat, ( l ) / kJ·kg⁻¹·K⁻¹</th>
<th>Specific heat, ( s ) / kJ·kg⁻¹·K⁻¹</th>
<th>Phase change enthalpy / kJ·kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.26</td>
<td>0.353</td>
<td>0.469</td>
<td>1054.8</td>
<td>4.70</td>
<td>2.47</td>
<td>108.3</td>
</tr>
</tbody>
</table>

### Dimensions of cold storage tube

<table>
<thead>
<tr>
<th>PCM mass / g</th>
<th>Internal diameter / mm</th>
<th>Wall thickness / mm</th>
<th>Wall thermal conductivity, ( W·m^{-1}·K^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>24</td>
<td>1</td>
<td>0.80 (glass)</td>
</tr>
</tbody>
</table>

### 4.3.4 Charging performance of the cold storage tube

The temperature variation and the energy change in the cold storage tube are shown in Figure 4.22. During the charging period, the temperature drops quickly in the initial 10 min; then it is held at the supercooling temperature before increasing to the phase change temperature. After the phase change, the temperature continues to gradually decrease to the HTF temperature. The total charging time from the simulation is 8.10 min (10.3%) shorter than that from the experiment due to the induction time prior to hydrate formation. This effect cannot be predicted by the model.

The hydrate enthalpy rate (the charging rate) is the greatest before phase change owing to the large temperature difference for sensible heat transfer of the liquid PCM. It drops dramatically to 0.23 W, followed by a sudden peak at 2.96 W caused by supercooling. After the peak, the rate continues to drop gradually during phase change and is as low as 0.12 W at the end of phase change. The total accumulated cooling capacity is 3.24 kJ by the end of the charging process (when the charging rate is 0), while it is 3.22 kJ and 3.11 kJ, respectively, at the moment when the rate is 0.1 W and 0.2 W. By stipulating an early end of charge condition, 12.7% and
26.0% of the charging time can be saved by losing only 0.62% and 4.01% cooling capacity, as shown by the grey dash lines in Figure 4.22.

![Figure 4.22 Temperature and energy change of the selected hydrate in the charging process](image)

4.3.5 Influencing factors of the cold storage tube

The cooling capacity is crucial to the energy storage performance of a cold storage unit, and the charging time plays an important role in the overall effectiveness of the cooling system. The analysis on the influencing factors of the charging process, that is, the HTF temperature, tube size, and the thickness and thermal conductivity of the tube wall – will focus mainly on these two parameters.

4.3.5.1 HTF temperature

Figure 4.23 demonstrates the effect of HTF temperature on the cooling capacity and the charging time. The charging time is recorded from the start of cooling till the charging rate drops to 0.1 W. The tube has properties listed in Table 4.5.

There is a linear reduction in the cooling capacity as the HTF temperature increases, which is attributed to the decrease in the heat transfer temperature difference. However, compared with latent heat, sensible heat plays only an insignificant role in the energy storage capacity, and thus the resultant reduction is minimal. To be specific, the charged cooling capacity only drops by 0.05 kJ with the each 1ºC rise in the HTF temperature. In contrast, the charging time increases dramatically, from 38.8 min to 198.3 min, as the HTF temperature increases from 1 to 9ºC. The charging time climbs rapidly, especially after the HTF temperature exceeds 7ºC.
The simulated results of the charging time are in agreement with, but on average 9.0% larger than, the experimental results.

Figure 4.23 Cooling capacity and charging time with different HTF temperatures

4.3.5.2 Tube diameter

The cooling capacity and charging time of the cold storage tube with different tube diameters are illustrated in Figure 4.24. This modelling was conducted at a HTF temperature of 7°C. The tube wall is of 1 mm thick and the material is glass.

Figure 4.24 Cooling capacity and charging time with different tube sizes
Both parameters are determined by ending the charge at three moments – when the charging rate equals 0, 0.1 or 0.2 W. As can be seen, the cooling capacity and charging time both increase as the tube diameter rises. The former is attributed to the increased PCM volume while the latter is affected by both the increased volume and the rise in conduction thermal resistance at the radial direction. In addition, compared with stopping the charging process when charging rate is 0 W, stopping charging when charging rate is 0.1 and 0.2 W can reduce the charging time by 12.6% and 23.9% respectively on average, resulting in a small reduction in the cooling capacity by only 0.62% and 3.49% on average.

In summary, large chiller power consumption and pump power consumption can be saved at the cost of a small decrease in the CTES cooling capacity. Therefore, for wise control strategy, the charging rate can be an index to determine the cessation of charge.

4.3.5.3 Tube wall thickness and thermal conductivity

The model of the cold storage tube employs different materials as the tube wall – namely polyvinyl chloride (PVC), polythene (PE), glass, nickel-copper, stainless steel, copper alloy and carbon steel with increasing thermal conductivity. In this way, the effect of thermal conductivity and thickness of the tube wall on the charging time can be observed, as is shown in Figure 4.25. This modelling was conducted at a HTF temperature of 70°C and the tube inner diameter is 24 mm.

![Figure 4.25 Charging time with various tube wall thickness and thermal conductivity](image)

With the same wall thickness, the charging time drops within a certain range as the wall thermal conductivity increases. The charging time is almost constant when the
thermal conductivity is above 13.0 W·m⁻¹·K⁻¹ (for nickel–copper). In addition, the charging time increases linearly with the increase in the wall thickness at a certain thermal conductivity below 0.80 W·m⁻¹·K⁻¹, while it decreases slightly with the increase in the wall thickness at a certain thermal conductivity above 13.0 W·m⁻¹·K⁻¹. The former is owing to the fact that a thicker wall results in a larger thermal resistance, while the latter can be attributed to the observation that, in the case that the wall thermal conductivity is large enough for effective heat conduction, a larger wall thickness can offer a larger heat transfer surface area, thus leading to a better heat convection between the external tube wall and the HTF outside.

The variations of cooling capacity and charging rate of the cold storage tube of four different materials (PVC, PE, glass and nickel–copper) with the same thickness of 1.0 mm are compared in Figure 4.26. As is shown, the total charged cooling capacity is almost the same for all cases. The average charging rate is accordingly higher for larger thermal conductivity. The required charging time for PE, glass and nickel–copper case is respectively 11.3%, 13.6% and 16.1% shorter than that of the PVC case.

![Figure 4.26 Energy variations with different tube wall materials](image)

**4.4 Conclusion**

This work presents an experimental study on the formation and dissociation of semi-clathrate hydrates of TBAB, TBAF and TBPB. Morphology studies on seed crystals are provided. To modify formation behaviour, SDS and TiO₂ nanoparticles are added to the salt–water systems. This work also includes the characterisation of thermal properties of semi-clathrate hydrates and a model of the charge process of a cold storage tube. The topics covered in this chapter are summarised following.
The formation temperature of all the salt hydrates peaks around a value (30 wt% for TBAF, 35 wt% for TBAB and 35 wt% for TBPB). The formation temperature is adjustable by changing the mass fraction and proportion of salts in the solution. Hence, a suitable formation temperature can be designed for air conditioning use.

SDS can help all the three semi-clathrate hydrates to alleviate supercooling and decrease induction time, while the effect of TiO$_2$ nanoparticle is less controllable. The formation temperature of TBAB hydrate decreases, while that of TBAF and TBPB hydrate increases, as the SDS mass fraction rises. Lower bath temperature leads to faster formation, with poor repeatability of the formation temperature. The memory effect manifests that the induction time in the 1st formation is usually much longer than that in the repeated formations. It is noted that fast induction and small supercooling degree cannot both be usually satisfied at the same time. Modification and optimisation methods for faster and easier hydrate formation are required by means of additives and proper operating conditions.

From the results of the enthalpy and heat capacity determined using the T-history method, among all the salt hydrate candidates, TBAF + TBPB semi-clathrate hydrate (30 wt%, 25:75) is considered the most suitable to be a cold storage medium. By comparing the results with those from other studies, it is also proved that the T-history method is reliable to determine the phase change enthalpy of salt hydrates.

By employing the enthalpy method, a model of a cold storage tube is established to predict the cooling capacity and charging rate of a selected hydrate. By using the model, the influencing factors of cooling capacity and charging time can be studied. It is revealed that the required charging time can be shortened by reducing the HTF temperature, tube size and wall thickness or by increasing the thermal conductivity of the tube wall.
Phase equilibrium of CO$_2$ semi-clathrate hydrates with TBAB and TBPB

CO$_2$ hydrate can be generated by direct CO$_2$ gas injection into a cold aqueous solution. It offers a large energy storage density due to its high dissociation enthalpy. Air conditioning systems usually require the phase change temperature of the cold storage material to be 5–12$^\circ$C and the phase equilibrium pressure of CO$_2$ hydrate at such temperatures is typically very high.

Yang et al. [183] investigated the characteristics of CO$_2$ hydrate and concluded that 5.0 MPa is good for hydrate-based CO$_2$ capture. However, this pressure is too high to be safe and cost effective for normal air conditioning systems. At the current stage, studies mainly focus on decreasing the hydrate formation pressure and increasing the formation rate and gas uptake [249]. For this purpose, quaternary salts, such as TBAB, TBAF and TBPB introduced in chapter 4, are reported to aid gas hydrate formation.

TBAB has been subjected to intensive studies to modify the phase change condition of clathrate hydrates [34, 37, 85, 86, 88, 90, 250]. It has been reported that generally TBAB can decrease the formation pressure by a factor of 10–50 [37]. It was also indicated that continuous operations of hydrate-based CO$_2$ separation were able to be put into practice [91].

Besides TBAB, other salt additives can also moderate hydrate formation conditions, such as TBAF [93–95], TBAC [93, 95] and THF [92]. TBAF also forms semi-clathrate hydrates with water under atmospheric pressure conditions, and the dissociation temperature of the cubic structure with a hydration number of TBAF·29·7H$_2$O [251]. From the results in chapter 4, the benefit of stabilised hydrate equilibrium conditions is greater for TBAF than TBAB, and TBAF hydrate manifests shortest induction time. However, due to the presence of dodecahedral cages that are partially filled with water molecules, TBAF shows a relatively lower
gas uptake than TBAB. Furthermore, since its phase equilibrium temperature is high, to use TBAF its mass fraction must be very low to adjust the temperature into a suitable range for conventional air conditioning systems. This is likely to result in low CO₂ enclathration and thus low enthalpy of hydrate formation.

TBPB has similar formation behaviour to TBAB and its phase equilibrium temperature range is suitable for air conditioning use. Even though there are fewer studies on TBPB than on TBAB, TBPB also shows feasibility for use as a PCM.

In another work of Mayoufi et al. [221], the phase equilibrium behaviour of simple and mixed semi-clathrate hydrates formed from CO₂–TBPB water mixtures was studied using a pressure-controlled DSC. It was found that adding 0.0058 mol% TBPB to water decreased the formation pressure of CO₂ hydrate from 3.5 to 0.5 MPa at 281.6 K.

Zhang et al. [219] experimentally measured the phase equilibrium data of TBPB hydrates with or without CO₂ at the TBPB mass fraction of 0.10, 0.20, 0.35 and 0.50 wt% in a wide temperature range of 281.0–292.0 K and a pressure range of 0.4–4.0 MPa. The data were compared with that of TBAB hydrates. It was found that at 0.10 wt% the phase equilibrium data of CO₂–TBAB hydrates are almost consistent with those of CO₂–TBAB hydrates. However, at 0.20 wt% and at a high pressure they are different.

In the study of Clain et al. [173], experimental data were obtained by DSC on the phase equilibrium and enthalpy of CO₂–TBPB hydrate. A model based on CO₂ mass balance was built to determine the hydrate fraction from the pressure and temperature conditions. These studies all revealed that TBAB semi-clathrate hydrate was a potential solution for CO₂ hydrate based cold storage in refrigeration applications. Therefore, this study will continue using TBAB and TBPB to aid CO₂ semi-clathrate hydrate formation, and the results will be presented in this chapter.

Induction delay and supercooling are two crucial problems in the CO₂ hydrate formation. To reduce both the induction time and the supercooling degree, some secondary promoters are reported to aid hydrate formation. The most frequently used additives are surfactants.

Experiments were carried out by Zhong et al. [252] on hydrate formation for CO₂ removal from a gaseous mixture of 40 mol% CO₂ and 60 mol% CH₄ at 277.15 K in a pressure range of 2.8–6.7 MPa. The experiments were conducted in a batch mode respectively using 140 cm³ deionised water, 1 mol% THF solution, and 1 mol% THF solution containing 550 ppm SDS. SDS was employed by ZareNezhad et al. [253] from 1000 to 5000 ppm, and energy savings of the electric power consumed at the impeller at different operating conditions were compared. It was found that at 1⁰C/27 bar it was possible to achieve a CO₂ gas to hydrate conversion of 95% in
less than 8 h in the presence of 4000 ppm SDS without other additives at a completely quiescent condition.

Similarly, Li et al. [33, 89] studied the effect of DTAC and CP on the induction time and CO\(_2\) separation efficiency of the hydrate formed from a CO\(_2\) + N\(_2\) gaseous mixture. The results showed that the addition of CP remarkably shortened the induction time and enhanced the CO\(_2\) separation. The initial pressure of 1.66 MPa in conjunction with the DTAC concentration of 0.028 mol% is the most favourable for CO\(_2\) separation among those tested. Besides surfactants, nanoparticles are helpful to accelerate CO\(_2\) hydrate formation by improving the heat transfer of the bulk solution. Aluminium oxide nanoparticles were used to increase CO\(_2\) hydrate formation rate [254] and copper oxide nanoparticles were used to reduce the solidification time [209].

To use CO\(_2\) hydrate in a cold store, it is important to ensure the hydrate formation can occur at low pressures that are suitable for practical air conditioning systems. The objective of this chapter is to investigate the phase equilibrium of CO\(_2\) hydrate modified by TBAB and TBPB at low pressures in a completely quiescent condition.

Experiments are carried out in a self-fabricated reaction tube on TBAB solutions at the mass fraction of 10, 20 and 32 wt% and TBPB solutions at the mass fraction of 10, 20, 30 and 37 wt% with secondary promoters, namely TBAF, SDS and TiO\(_2\) nanoparticles. The hydrate formation behaviour, such as the CO\(_2\) uptake, induction time, supercooling degree, and the discrepancy between the formation and dissociation temperature, is studied. The effects of feed pressure, HTF temperature, promoter concentration and the memory effect on the formation behaviour are discussed. The morphology of the hydrate formation and dissociation is provided.

### 5.1 Methodology

#### 5.1.1 Calculation of CO\(_2\) solubility

To calculate the CO\(_2\) solubility, the model of Henry’s law is employed [255, 256]. It is assumed that the activity coefficients for the solvent and the solute are unity and the Poynting correction is negligible. Thus, the solvent is modelled as:

\[
x_{CO_2} K_H = y_{CO_2} \phi_{CO_2} P
\]  

(5.1)

The Henry’s constant expressed on a mole fraction basis was developed as [257]:

\[
ln(K_H) = -6.8346 + 1.2817 \times \frac{10^4}{T} - 3.7668 \times \frac{10^6}{T^2} + 2.997 \times \frac{10^8}{T^3}
\]  

(5.2)
The CO₂ fugacity coefficient $\phi_{CO_2}$ can be found from vapour-phase volumetric properties as given by an equation of state [258]. Therefore, CO₂ solubility $x_{CO_2}$ at different pressure-temperature states along hydrate formation can be obtained. It is noted that the solubility of CO₂ in liquid water is not altered by the presence of hydrates [30].

Lin et al. [259] determined CO₂ solubility in a TBAB solution at 283.1 K with the TBAB concentration from 4.43 to 10.0 wt%. The results indicated that the TBAB concentration had no significant influence on the CO₂ solubility in a pressure range from 0.5–1.6 MPa. Therefore, in this study both the effect of TBAB or TBPB, or the formed hydrates on CO₂ solubility in water is neglected, i.e. CO₂ solubility is only affected by the pressure and temperature conditions.

5.1.2 Determination of hydrate composition

To determine the CO₂ uptake, a clear hydrate composition is necessary to estimate the number of moles of CO₂ in the formed hydrate. Lin et al. [259] determined the formula of the hydrate of CO₂, TBAB, and H₂O to be 2.51CO₂·TBAB·38H₂O in the case that the amount of type A hydrate of CO₂–TBAB was much less than that of type B hydrate. It is known from literature that the hydration number of TBPB hydrate is 32 [218, 260]. In the present study, the hydrate composition of CO₂–TBAB and CO₂–TBPB semi-clathrate hydrate is determined in the same way. To obtain $a$ in the formula of $aCO_2\cdot TBPB\cdot 38H_2O$ and $aCO_2\cdot TBPB\cdot 32H_2O$, the number of moles of hydrate $n_{hyd}$, which equals to that of TBAB/TBPB in hydrate phase $n_{salt,hyd}$, can be calculated as:

$$n_{hyd} = n_{salt,hyd} = \frac{w_{salt} m_{solution}}{M_{salt}}$$

(5.3)

The number of moles of the enclathrated CO₂ can be obtained as:

$$n_{CO_2,hyd} = n_{CO_2,initial} - \frac{PV_{CO_2}}{Z_{gas const} nT} - \frac{x_{CO_2}}{1-x_{CO_2}} (n_{salt,solution} + n_{H_2O,solution})$$

(5.4)

where $n_{CO_2,initial}$ can be found from the initial status.

5.1.3 Calculation of CO₂ uptake

A typical CO₂ hydrate formation curve in a pressure-temperature diagram is shown in Figure 5.1. Figure 5.1 (a) illustrates the variation of pressure and temperature versus time; while Figure 5.1 (b) illustrates the correlation between pressure and temperature of the system corresponding to the same formation process. The system of CO₂ + TBAB + H₂O and CO₂ + TBPB + H₂O is firstly pressurised from an initial point I to point A. It is then cooled by HTF, for which the pressure and
temperature both drop until the L$_w$-H-V three-phase equilibrium curve is reached. It is shortly followed by the rupture of the metastability from point B to point C. After that, the hydrate formation proceeds and the pressure and temperature both head toward the L$_w$-H-V curve. Finally, the formation ends at point D. The mass of CO$_2$ uptake can be calculated by using the mass conservation at point B and D.

![Diagram of CO$_2$ hydrate formation process](image)

(a) Pressure and temperature vs time

(b) Pressure vs temperature

Figure 5.1 Typical P-T diagram of the CO$_2$ hydrate formation process

At point B, there is no CO$_2$ gas trapped in clathrates. The amount of CO$_2$ dissolved in water is $(n_{CO_2,l})_B = (x_{CO_2})_B \frac{m_{H_2O}}{M_{CO_2}}$ and the amount of gaseous CO$_2$ is $(n_{CO_2,g})_B = \left(\frac{P}{ZT}\right)_B \frac{V_{g,i}}{R_{gas\ constant}}$.

At point D, the hydrate growth and CO$_2$ uptake are finished. The amount of CO$_2$ dissolved in water is $(n_{CO_2,l})_D = (x_{CO_2})_D [m_{H_2O,i} - (n_{H_2O,hyd})_D M_{H_2O}]$ and the amount of gaseous CO$_2$ is $(n_{CO_2,g})_D = \left(\frac{P}{ZT}\right)_D \frac{V_{g,i} + (n_{H_2O,hyd})_D M_{H_2O}}{R_{gas\ constant}} - V_{hyd}$.

By establishing the mass conservation equation $(n_{CO_2,l})_B + (n_{CO_2,g})_B = (n_{CO_2,l})_D + (n_{CO_2,g})_D + (n_{CO_2,hyd})_D$ and substituting above equations we have $(n_{CO_2,hyd})_D$ and
\( (n_{H2O,hyd})_D \) unknown. By using the correlation of \( n_{hyd} = \frac{1}{a} (n_{CO2,hyd})_D = \frac{1}{32} (n_{H2O,hyd})_D \) in the above equations and knowing the value of \( a \) in the hydrate formula, \( n_{hyd} \) can be found.

5.2 Experimental setup

To test the formation and dissociation of \( CO_2-TBAB \) and \( CO_2-TBPB \) semi-clathrate hydrates at various pressure and temperature conditions, an experimental setup featuring horizontal reaction tube with side windows was fabricated (Figure 5.2). The tube was assembled with a pressure-proof glass tube (with an inner diameter of 10 mm and a length of 160 mm) and an outer brass sleeve tube. With O-rings and bolted joints on two ends, the tube was able to work safely at up to 10 bar. Hydrate formed in the horizontal tube and hydrate crystals were viewed from the side windows. The tube was kept horizontal not only to diminish the gravitational movements of the solid in the liquid [236] but also to enlarge the contact surface between gas and water. The latter was intended to enhance the heat and mass transfer for hydrate formation. A thermocouple was mounted at the centreline of the tube. The vertical assembly connected to the end of the tube was composed of a liquid inlet, a gas inlet, a relief valve and a pressure sensor. As the valves were all closed, the tube could offer a constant volume system for experiments. The entire tube was insulated to minimise the effect of cooling and heating rate on the hydrate formation. The mass of additives and water was measured by an electronic balance with an uncertainty of 10 mg; therefore, the uncertainty of the mass fraction of the solution was \( \pm 1.00 \times 10^{-4} \). The uncertainty of temperature measurement was \( \pm 0.1^\circ C \) and of pressure measurement was \( \pm 0.05 \) bar.

Figure 5.2 Reaction tube of the T-history method
5.3 Experimental procedure

To determine the phase equilibrium of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrate, 30 g TBAB/TBPB solution was trickled into the reaction tube. The tube was filled until the solution level just exceeded the centreline of the tube and submerged the thermocouple. The liquid inlet valve was closed and CO$_2$ gas was injected in the tube until it reached the design pressure and the gas inlet valve was shut. The tube was left standing to let the pressure in the tube drop naturally for the dissolving of CO$_2$ in water. When the pressure was stable, the tube was totally immersed in a thermostatic bath and cooled at a constant HTF temperature. A stepwise method was adopted to seek the maximum valid HTF temperature that could trigger the hydrate formation. The tube was first cooled by HTF at a temperature that was higher than but close to the estimated formation point. If neither a temperature peak nor an obvious pressure drop occurred in 3 h, the HTF temperature was decreased by 0.5°C, and the above procedures were repeated until a temperature peak or a pressure drop was observed. After hydrate formation, the tube was heated in air at a constant temperature to dissociate the formed hydrate. Experiments were conducted at various salt mass fractions, feed pressures, HTF temperatures and promoter concentrations.

The procedure to determine the hydrate composition was slightly different – 3 g TBAB/TBPB solution was used in the sample and the initial pressure was 10 bar. This was to ensure that the amount of CO$_2$ was greater than that of TBAB/TBPB, so that TBAB/TBPB could be totally enclathrate and sufficient overpressure driving force could be maintained along the hydrate formation.

5.4 Results and discussions

5.4.1 Phase equilibrium condition

A formation-dissociation process of CO$_2$–TBAB semi-clathrate hydrate (20 wt%) is shown in Figure 5.3. At the beginning of cooling, the reaction tube at 21°C under 8.8 bar was cooled by the HTF at 7°C (step 1). After more than 3 h, the temperature and pressure were almost constant, indicating that the HTF temperature was not low enough to trigger hydrate formation. Then the HTF temperature was reduced to 6.5°C (step 2). It was found that a great pressure drop took place, followed by a peak in the temperature revealing that the hydrate formation was occurring. Meanwhile, a downtrend of the 1$^{st}$ derivative of pressure was observed, indicating intensive CO$_2$ uptake. The formation temperature is recognised from the peak temperature. The onset point of the formation is identified as the point where the 1$^{st}$ derivative of pressure deviates from 0; and the end point is identified as the point...
where the 1\textsuperscript{st} derivative of pressure reverts to 0. At the end of formation, the 1\textsuperscript{st} derivative of pressure returned to 0.

The heating process was then started by moving the tube out of the bath and placing it in air at a constant temperature of 21°\textsuperscript{C}. Sequentially, the 1\textsuperscript{st} derivative of pressure jumped to positive values, reached a peak and dropped to 0 at the end. The dissociation point was from the inflection point in the temperature curve, which was accompanied by a peak in the 1\textsuperscript{st} derivative of pressure.

![Figure 5.3 A formation-dissociation process of CO\textsubscript{2}–TBAB hydrate](image1)

![Figure 5.4 P-T correlations in the formation-dissociation process of CO\textsubscript{2}–TBAB hydrate](image2)

Corresponding to Figure 5.3, the route of the hydrate formation and dissociation is illustrated in Figure 5.4 as the correlation of pressure and temperature. The onset,
peak and end point in the formation as well as the inflection point in the dissociation are marked accordingly. In the cooling process, a temperature rise occurred in step 2 due to the exothermic hydrate formation. A large decrease in the pressure also took place due to the incorporation of CO$_2$ in hydrate phase. In step 1, the pressure drop was only caused by the changes in the gas state (PV=nRT) and the CO$_2$ solubility. In step 2, the pressure drop resulted from three aspects – CO$_2$ uptake in the hydrate phase, and the changes in the gas state and the CO$_2$ solubility. In the heating process, both temperature and pressure grew gradually, and a deflection point indicated the equilibrium.

![Figure 5.5 Phase equilibrium of CO$_2$–TBAB hydrate at various mass fractions](image)

Figure 5.5 shows the dissociation equilibrium of CO$_2$–TBAB semi-clathrate hydrate with the TBAB mass fraction of 10, 20 and 32 wt%. The data is compared to other literature [93, 218, 259, 261]. In the dissociation, the required pressure at a certain temperature is considerably reduced by the rise in TBAB mass fraction. These data are also compared with those from other literature and show consistency. This reveals that the addition of TBAB is helpful to allow increased HTF temperature in the charging process of the cold store under a certain pressure range thus improving the coefficient of performance of the chiller.

A formation-dissociation process of CO$_2$–TBPB semi-clathrate hydrate (10 wt%) is shown in Figure 5.6. The variations of temperature and pressure are shown as lines, and the 1$^{st}$ derivative of pressure is shown as scatters. In the beginning of cooling, the tube at room temperature at 6.0 bar was cooled by HTF at 2.5$^\circ$C (step 1). After 2 h, neither temperature nor pressure had any notable change (the 1$^{st}$ derivative of pressure was constantly at 0) indicating that this HTF temperature was not low enough to trigger the hydrate formation; therefore, the HTF temperature was
decreased by 0.5°C and held for at least 1 h (step 2). The reduction of the HTF temperature was repeated until a peak in the temperature curve was observed (step 4). Meanwhile, a greater pressure drop was observed, indicating the hydrate formation and intensive CO₂ uptake. The heating process was started subsequently after the end point of formation, by moving the tube out of the bath and placing in air at a constant temperature of 24°C. The peak point in the 1st derivative of pressure curve indicates the largest CO₂ releasing rate, which is recognised as the dissociation point.

Figure 5.6 A formation-dissociation process of CO₂–TBPB hydrate

Figure 5.7 P-T correlations in the formation-dissociation process of CO₂–TBPB hydrate
Corresponding to the formation and dissociation in Figure 5.6, the correlation of pressure and temperature is plotted in Figure 5.7 clarifying the route that the system undergoes.

![Figure 5.8 Phase equilibrium of CO₂–TBPB hydrates at various mass fractions](image)

To acquire the applicable pressure for CO₂ enclathration at a certain temperature with the help of TBPB, the dissociation equilibrium data of the CO₂ + TBPB + water system with the mass fraction of 10, 20, 30 and 37 wt% are plotted in Figure 5.8 and compared to other literatures [219, 221, 262]. The equilibrium temperature was measured with the pressure varied between 1.5 and 7.5 bar. By increasing the TBPB mass fraction from 10 to 20 wt%, the corresponding pressure was considerably reduced. This helps to reduce the cost of the system to maintain high pressures and enhance the system stability. However, when it exceeds 20 wt%, the TBPB mass fraction no longer affects the CO₂ hydrate equilibrium effectively, which makes the curve for 20, 30 and 37 wt% close to each other. The data are compared with those from other literature and manifest good consistency.

### 5.4.2 Hydrate morphology

Sequential photographs were taken along the CO₂ hydrate formation from 10 wt% TBAB solution at a feed pressure of 6.0 bar. Figure 5.9 (a), (b) and (c), respectively correspond to the onset point, peak point and end point marked in Figure 5.4.

In Figure 5.9 (a), columnar-shaped seed crystals with high light transmittance are observed dispersing in the solution. The thickness of the seed crystals is around 0.5 mm and the length is around 1.0 mm. The crystals then cluster, pile up from the bottom, and continue growing upwards, as shown in Figure 5.9 (b). The bulk of
hydrate finally appears compact, uniform and ice-like in Figure 5.9 (c). The dissociation of formed hydrates then starts and crystals first melt with small bubbles rising, as is shown in Figure 5.9 (d). In Figure 5.9 (e), larger bubbles rise more frequently as the dissociation proceeded. Solid crystals disappear gradually and more liquid is seen.

By comparing the crystal shape with that described in the literature [224, 263], it can be confirmed that the CO₂–TBAB semi-clathrate hydrate in this study mostly has a type B characteristic. Therefore, it is reasonable that the method to calculate the hydrate composition in section 2.3 is adopted.

Sequential photographs were also taken in a trial of CO₂–TBPB hydrate formation from a 10 wt% TBPB solution at a feed pressure of 6.0 bar with the tube cooled at the HTF temperature of 1.5⁰C. Figure 5.10 (a)–(c) corresponds to the formation process; Figure 5.10 (d)–(e) corresponds to the dissociation process by heating the tube at a constant temperature and keeping the gas in the tube; Figure 5.10 (f)
corresponds to the dissociation process by heating the tube while releasing CO$_2$ gas from the tube.

In Figure 5.10 (a), after induction, seed crystals were seen dispersing in the liquid. The crystals then slowly grew, clustered and piled up, as is shown in Figure 5.10 (b). The bulk of formed hydrate appeared compact and ice-like in Figure 5.10 (c). After the end of formation, no more noticeable crystal growth was observed. The formed crystals were subsequently dissociated. In Figure 5.10 (d) crystals melted with small bubbles rising from the bulk of hydrate. In Figure 5.10 (e), as the dissociation proceeded, crystals dissociated and larger bubbles rose more frequently. The remaining crystals were in lamellar shape with high transparency. The dissociated liquid was uniform and clear.

(a) Formation – seed crystals dispersing

(b) Formation – crystals clustering

(c) Formation – crystals piling up

(d) Dissociation – little bubbles rising

(e) Dissociation – large bubbles rising

Figure 5.10 Morphology of CO$_2$–TBPB hydrate in the reaction tube
5.4.3 Hydrate composition

For CO\textsubscript{2}–TBAB semi-clathrate hydrate, a is calculated as 2.49, which is very close to the result of 2.51 in the work of Lin et al. [259]. The formula of CO\textsubscript{2}–TBAB hydrate is 2.49CO\textsubscript{2}·TBAB·38H\textsubscript{2}O. For CO\textsubscript{2}–TBPB semi-clathrate hydrate, a in this study is calculated as 2.84. Hence, the composition of the CO\textsubscript{2}–TBPB semi-clathrate hydrate is 2.84CO\textsubscript{2}·TBPB·32H\textsubscript{2}O.

To summarise the effect of TBAB and TBPB in the formation and dissociation CO\textsubscript{2} semi-clathrate hydrate, both of them managed to reduce the equilibrium pressure to below 7.3 bar, as is listed in Table 5.1. Suitable equilibrium temperature ranges for air conditioning use are achieved for 20 wt% TBAB, and 20 and 30 wt% for TBPB.

<table>
<thead>
<tr>
<th>Mass fraction (wt%)</th>
<th>T\textsubscript{form}(°C)</th>
<th>P\textsubscript{form}(bar)</th>
<th>T\textsubscript{diss}(°C)</th>
<th>P\textsubscript{diss}(bar)</th>
<th>Hydrate formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>10</td>
<td>1.8–3.7</td>
<td>2.6–6.4</td>
<td>5.9–10.2</td>
<td>2.5–6.8</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5.4–7.4</td>
<td>3.2–7.2</td>
<td>11.0–13.5</td>
<td>2.8–7.3</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>8.3–10.3</td>
<td>1.9–6.9</td>
<td>12.4–14.6</td>
<td>2.2–6.7</td>
<td>2.49CO\textsubscript{2}·TBAB·38H\textsubscript{2}O</td>
</tr>
<tr>
<td>TBPB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.5–4.1</td>
<td>3.5–6.6</td>
<td>7.1–9.7</td>
<td>2.9–6.6</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5.2–7.4</td>
<td>2.0–5.9</td>
<td>9.6–11.0</td>
<td>1.7–5.3</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>5.6–7.8</td>
<td>2.6–6.5</td>
<td>10.7–12.3</td>
<td>2.4–6.8</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>6.2–8.8</td>
<td>3.0–7.2</td>
<td>11.2–12.3</td>
<td>3.0–7.0</td>
<td>2.84CO\textsubscript{2}·TBPB·32H\textsubscript{2}O</td>
</tr>
</tbody>
</table>

5.5 Influencing factors on hydrate formation

The influencing factors on CO\textsubscript{2}–TBAB and CO\textsubscript{2}–TBPB hydrate formation are of great importance for their use as a cold storage medium. The ‘formation behaviour’ includes mainly CO\textsubscript{2} uptake, induction time and formation time, and supercooling degree. The induction time is the time from the moment when the temperature drops to the equilibrium temperature for the first time to the moment when the equilibrium is reached. The formation time is the period from the starting point of formation to the completion of hydrate formation.

5.5.1 Feed pressure

The effect of feed pressure on the CO\textsubscript{2} uptake during the hydrate formation was studied with 10 wt% TBAB (Figure 5.11) and 10 wt% TBPB solution (Figure 5.12).

As shown in Figure 5.11, at a feed pressure of 8.9, 6.5, 4.5 and 3.4 bar, it takes 283, 256, 218 and 164 min to complete the formation and the CO\textsubscript{2} uptakes are 0.279,
0.139, 0.104 and 0.059 g, respectively. By the end of hydrate formation none of the CO₂ gas, TBAB or water in the system has been totally enclathrated. Hydrate formation at a low feed pressure is restrained by overpressure driving force, which is crucial to triggering nucleation and providing enough CO₂ mass transfer during the hydrate growth. The pressure drops with the gas uptake, and when the pressure is too low to provide enough driving force the hydrate formation stops. This may also explain the tendency that the formation at lower pressure stops earlier. It is obvious that the feed pressure greatly impacts on the CO₂ enclathration. A big reduction of 78.9% in the CO₂ uptake is led by reducing the feed pressure from 8.9 to 3.4 bar.

Figure 5.11 CO₂ uptake in CO₂–TBAB hydrate formation at various feed pressures

Figure 5.12 CO₂ uptake in CO₂–TBPB hydrate formation at various feed pressures
As is illustrated in Figure 5.12, results show that at a feed pressure of 8.6, 7.4, 5.9 and 4.5 bar, the hydrate formation takes 159, 135, 125 and 124 min to complete, and the final CO₂ uptake is 0.247, 0.190, 0.147 and 0.118 g, respectively. Similar to the case of TBAB, by the end of hydrate formation, none of the CO₂ gas, TBPB and water in the system is enclathrated totally in the hydrate. A 52.2% reduction of in the CO₂ uptake results from decreasing the feed pressure from 8.6 to 4.5 bar.

The joint effect of feed pressure and TBAB/TBPB mass fraction on the CO₂ uptake is presented in Figure 5.13 and Figure 5.14, respectively, with regard to both the CO₂ uptake quantity and efficiency. This analysis was conducted at a feed pressure range of 2.3–9.4 bar with the mass fraction of 10, 20 and 32 wt% for the TBAB case.
and at 2.9–8.7 bar with the mass fraction of 10, 20, 30 and 37 wt% for the TBPB case.

In the results, the effect of feed pressure is in agreement with that in Figure 5.11 and 5.12 – that higher feed pressure leads to larger CO₂ uptake quantity and efficiency for all the TBAB/TBPB mass fractions studied. However, higher TBAB/TBPB mass fraction results in lower CO₂ uptake quantity and efficiency throughout the pressure range. This is especially obvious for 32 wt% TBAB and 37 wt% TBPB mass fraction at pressures lower than 7.0 bar. It is assumed that with sufficient overpressure driving force, CO₂ uptake mainly relies on the number of vacant cages (nucleation sites) in the hydrate structure. However, at a low feed pressure the trapping of CO₂ gas is less dependent on the number of vacant cages; instead, the mass transfer becomes a major restraint on the hydrate formation. In this case, a low salt mass fraction is more favourable since it provides more free water for CO₂ gas dissolution thus improves the mass transfer. This tendency is also attributed to the fact reported by Babu et al. [92] that the hydrate growth of 32 wt% TBAB may not be sustainable with its effect diminishing and this may result in an early stoppage of gas uptake. A similar finding is in the work of Fukunoto et al. [264] that the CO₂ separation factor dropped by increasing the TBAB and TBPB concentration.

### 5.5.2 HTF temperature

For CO₂–TBAB hydrate, the effect of HTF temperature on the hydrate formation is studied using 20 wt% TBAB solution. All the runs were carried out at the same initial pressure of 4.2 bar while various HTF temperature conditions were – 3.5, 4.5 and 5.5°C. The temperature during hydrate formation is plotted in Figure 5.15 and the 1st derivative of the pressure was calculated accordingly. The three runs all reach a temperature peak at around 7.1°C. The induction time is 116.6, 132.5 and 157.3 min and the formation time is 89.2, 102.0 and 167.4 min corresponding to the HTF temperature of 3.5, 4.5 and 5.5°C. It is indicated that a large reduction in both the induction time (25.9%) and the formation time (46.7%) is resulted from lowering the HTF temperature by 2°C. Moreover, the supercooling degree is 3.6, 2.4 and 1.3°C, corresponding to the HTF temperature of 3.5, 4.5 and 5.5°C.

For CO₂–TBPB hydrate, the effect of HTF temperature on the hydrate formation is analysed also taking 20 wt% TBPB mass fraction as an example. All the tests were carried out at the same initial feed pressure of 7.0 bar. The HTF temperature of 4.0, 4.5, 5.0 and 5.5°C was adopted. As can be seen in Figure 5.16, the four temperature curves all reach a peak at around 7.2°C. The induction time is 119.5, 129.0, 134.5 and 279.4 min and the formation time is 66.2, 80.2, 99.6 and 63.7 min at the HTF temperature of 4.0, 4.5, 5.0 and 5.5°C correspondingly. The induction time can be
reduced greatly by lowering the HTF temperature, especially from 5.5 to 5.0°C; whereas, the formation time is not always shortened by lower HTF temperature.

Figure 5.15 Temperature and pressure drop in CO$_2$–TBAB hydrate formation with different HTF temperatures

The supercooling degree is 2.75, 2.57, 1.95 and 1.55°C corresponding to the HTF temperature of 4.0, 4.5, 5.0 and 5.5°C. It is revealed that although the decrease in the HTF temperature can shorten the time for charging the cold store, it can also decrease the chiller's efficiency; therefore, an optimal point should be found in the operation of a cold storage system considering both the factors.

Figure 5.16 Temperature and pressure drop in CO$_2$–TBPB hydrate formation with different HTF temperatures
5.5.3 Secondary promoters

Experiments were carried out on the formation of CO$_2$-TBAB semi-clathrate hydrate with the help of a secondary promoter. The promoters tested in this study are TBAF, SDS and TiO$_2$ nanoparticles. Besides SDS and TiO$_2$, those have been tested to salt hydrate in chapter 4, TBAF is used together with TBAB for its promotion effect on fast hydrate formation. All of them were tested in 30 g samples of 20 wt% TBAB solution. TBAF was used at the mass fraction of 0.1, 0.5, 2.0 and 3.5 wt%, SDS was used at the mass fraction of 0.1, 0.3 and 0.5 wt%, and the nanoparticle of TiO$_2$ was added at a unique mass fraction of 0.1 wt% but in two particle sizes of 20 and 80 nm. All the tests were conducted at the same feed pressure of 5.0 bar and at the same HTF temperature of 4.0°C. The temperature variation and pressure drop along each formation process are shown in Figure 5.17.
The effect of different promoters on the CO$_2$ gas uptake (Figure 5.18), the induction and formation time (Figure 5.19), the equilibrium temperature and supercooling degree (Figure 5.20) are discussed. In the figures, the samples are marked with one letter (F for TBAF, S for SDS, T for TiO$_2$ nanoparticle and R for a reference case without promoters) with the mass fraction or particle size of the promoter.

In Figure 5.18, the CO$_2$ uptake is obviously reduced by the addition of TBAF, and larger reduction is led by higher mass fractions. However, CO$_2$ uptake is increased

Figure 5.17 CO$_2$–TBAB hydrate formation with TBAF/SDS/TiO$_2$

Figure 5.18 CO$_2$ uptake quantity and efficiency in CO$_2$–TBAB hydrate formation with different promoters
by adding SDS at all the mass fractions and TiO$_2$ nanoparticles in both sizes. The largest CO$_2$ uptake is achieved in the case of 80 nm TiO$_2$ nanoparticles with the uptake quantity of 0.178 g and the uptake efficiency of 41%.

In Figure 5.19, in the presence of different promoters, the induction time and formation time of CO$_2$–TBAB hydrate are largely different. TBAF reduces the induction time and formation time most dramatically. The higher the TBAF mass fraction is, the less the formation time is. The induction time is the shortest in the case of 0.5 wt% TBAF, which is only 14 min. The total completion time (induction time + formation time) is the shortest in the case of 3.5 wt% TBAF, which is only 89 min. SDS at low mass fractions is able to shorten the induction time and formation time; whereas, when the mass fraction rises from 0.3 to 0.5 wt%, the induction time gets much longer. TiO$_2$ nanoparticles of both sizes decrease the induction time and formation time to a large extent.

![Figure 5.19 Induction time and formation time in CO$_2$–TBAB hydrate formation with different promoters](image)

Figure 5.20 shows the supercooling degree and equilibrium temperature of CO$_2$–TBAB hydrate with various promoters. The addition of TBAF increases both the formation and the dissociation temperature while SDS and TiO$_2$ nanoparticles reduce the formation and dissociation temperature. Due to the hysteresis, the formation temperature is not equal to the dissociation temperature. TBAF reduces the discrepancy between the formation and the dissociation temperature, especially at large mass fractions; while SDS and TiO$_2$ nanoparticles both tend to enlarge this discrepancy. The supercooling degree seems to be reduced by SDS, TiO$_2$ nanoparticles, and TBAF at the mass fraction less than 0.5 wt%.
The formation of CO$_2$–TBPB semi-clathrate hydrate aided by different secondary promoters was conducted in the same way. In the 30 g sample of 20 wt% TBPB solution, TBAF was added at the mass fraction of 0.1, 0.5, 2.0 and 3.5 wt%; SDS was at the mass fraction of 0.1, 0.3 and 0.5 wt%; and TiO$_2$ nanoparticles were adopted at the same mass fraction of 0.1 wt% but in different particle sizes – 20 and 80 nm. All trials were at the same feed pressure (5.0 bar) and HTF temperature (4.0°C).
The temperature variation and pressure drop along each formation process are shown in Figure 5.21. Based on these data, the effect of promoters on CO₂ uptake (Figure 5.22), induction time and formation time (Figure 5.23), equilibrium temperatures and supercooling degree (Figure 5.24) are analysed.
As can be seen in Figure 5.22, CO₂ uptake is increased by TBAF at high mass fractions (2.0 and 3.5 wt%) but is reduced by TBAF at low mass fractions (0.1 and 0.5 wt%). The CO₂ uptake is enhanced by SDS at all the mass fractions adopted and by TiO₂ nanoparticles in both sizes. Especially, SDS at 0.3 wt% and TiO₂ nanoparticle in 20 nm are both found to result in the largest CO₂ uptake with the value of 0.16 g (the efficiency of 36%).

Figure 5.23 Induction time and formation time in CO₂–TBPB hydrate formation with different promoters
In Figure 5.23, in the presence of different promoters, the induction and formation time of CO$_2$–TBPB hydrate change obviously. TBAF at 0.1 wt% increases the induction time; while both the induction time and the formation time decrease effectively with TBAF at mass fractions higher than 2.0 wt%. Particularly, TBAF at 3.5 wt% demonstrates the best performance among all the samples – it reduces the induction time to 43.6 min (by 66.2%) and the formation time to 81.4 min (32.7%). Moreover, SDS aids to shorten the induction time – the higher the SDS mass fraction, the shorter the induction time becomes. However, it has insignificant effects on the formation time. TiO$_2$ nanoparticle of 20 nm decreases the induction time to 55.2 min (by 57.2%); on the contrary, TiO$_2$ nanoparticle of 80 nm increases the induction time to a large extent.

![Figure 5.24](image)

**Figure 5.24** Equilibrium temperature and supercooling degree in CO$_2$–TBPB hydrate formation with different promoters

The formation temperature is not always equal to the dissociation temperature. Figure 5.24 shows the discrepancy between the formation temperature and dissociation temperature and the supercooling degree of different samples are shown. On the whole, the addition of promoters does not impact greatly on the formation temperature; yet it changes the dissociation temperature to some extent, with the smallest discrepancy between the formation and dissociation temperature occurring in the case of TBAF at 0.1 wt%, which is 2.62°C (reduced by 41.1%). TiO$_2$ nanoparticles of both sizes also decrease the discrepancy to 2.79°C (by 37.5%). In addition, the supercooling degree is reduced slightly by TBAF at high mass fractions (0.5–3.5 wt%) and TiO$_2$ of 80 nm.
5.5.4 Memory effect

Memory effect is reported [132, 133, 248, 263, 265] to reduce the time and save energy during hydrate formation owing to the residual structure of the dissociated hydrate providing a site of mass transfer between the host and guest molecules.

Figure 5.25 Temperature and pressure drop in repeated CO$_2$–TBAB hydrate formation

<table>
<thead>
<tr>
<th>Tests</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st run (fresh)</td>
<td>156.0 min</td>
<td>209.6 min</td>
<td>196.8 min</td>
</tr>
<tr>
<td>2nd run (memory)</td>
<td>110.5 min</td>
<td>122.3 min</td>
<td>121.8 min</td>
</tr>
<tr>
<td>3rd run (memory)</td>
<td>118.1 min</td>
<td>127.1 min</td>
<td>111.9 min</td>
</tr>
</tbody>
</table>

The CO$_2$–TBAB hydrate formation from the 20 wt% TBAB solution was repeated three times at the same feed pressure (5.0 bar) and a constant HTF temperature (5$^\circ$C), shown in Figure 5.25. The temperature peak in the 2nd and 3rd formation occurs earlier than the 1st one. The formation time are 95.6 min in the 1st run and reduce to 95.0 min (by 0.63%) in the 2nd run, and to 88.9 min (by 7.01%) in the 3rd run. Comparing with the formation time, the induction time was affected more greatly by the memory effect; therefore, the memory effect was tested three times on the induction time and the results are shown in Table 5.2. As can be seen, the induction time in the 1st run are always longer than that in the memory runs; in addition, there are big differences in the 1st runs of the three tests revealing that the 1st runs have poor repeatability. In contrast, the memory runs manifest better repeatability.
Table 5.3 Induction time at different testes in CO₂–TBPB hydrate formation

<table>
<thead>
<tr>
<th>Tests</th>
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<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st run (fresh)</td>
<td>179.4 min</td>
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<td>168.8 min</td>
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<td>2nd run (memory)</td>
<td>162.9 min</td>
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<tr>
<td>3rd run (memory)</td>
<td>130.3 min</td>
<td>109.0 min</td>
<td>102.2 min</td>
</tr>
</tbody>
</table>

Figure 5.26 Temperature and pressure drop in repeated CO₂–TBPB hydrate formation

The CO₂–TBPB hydrate formation from the 20 wt% TBPB solution was repeated three times at the same feed pressure (7.0 bar) and a constant HTF temperature (5°C), shown in Figure 5.26. The formation time changes from 112.9 min to 106.3 min (by 5.85%) then to 102.5 min (by 9.21%). The temperature peak in the 2nd and 3rd trials happens earlier than the 1st one. The induction time is 179.4 min in the 1st trial; it reduces to 162.9 min (by 9.20%) in the 2nd trial and drops further to 130.3 min (by 27.4%) in the 3rd trial. Comparing with the formation time, the induction time was affected more greatly by the memory effect. Similarly, the memory effect was tested three times on the induction time and the results are shown in Table 5.3. As can be seen, the induction time in the 1st run is always longer than that in the memory runs. The induction time in the 3rd run is 36.1% in average lower than that in the 1st run.

For both TBAB and TBPB, none of the equilibrium temperature, pressure drop, or supercooling degree changes much in the repeated runs, compared with those in the 1st run.
Table 5.4 Influencing factors on CO\textsubscript{2}–TBAB hydrate formation behaviour

<table>
<thead>
<tr>
<th>CO\textsubscript{2} uptake</th>
<th>Induction time</th>
<th>Formation time</th>
<th>Supercooling degree</th>
<th>Discrepancy between T\textsubscript{form} and T\textsubscript{diss}</th>
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</thead>
<tbody>
<tr>
<td>Feed pressure</td>
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<td>\</td>
<td>\</td>
</tr>
<tr>
<td>HTF temperature</td>
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<td>Decreases with the reduction in the HTF</td>
<td>Increases with the reduction in the HTF</td>
</tr>
<tr>
<td>TBAF</td>
<td>Decreases at all mass fractions</td>
<td>Shortest at 0.5wt%</td>
<td>Decreases at all mass fractions</td>
<td>Decreases at 0.1–0.5 wt%; Increases at 2.0–3.5 wt%</td>
</tr>
<tr>
<td>SDS</td>
<td>Increases at all mass fractions</td>
<td>Decreases at 0.1–0.3 wt%; Increases at 0.3–0.5 wt%</td>
<td>Decreases at all mass fractions</td>
<td>Decreases at all mass fractions</td>
</tr>
<tr>
<td>TiO\textsubscript{2} nanoparticle</td>
<td>Increases with TiO\textsubscript{2} in both sizes</td>
<td>Decreases with TiO\textsubscript{2} in both sizes</td>
<td>Decreases with TiO\textsubscript{2} in both sizes</td>
<td>Decreases with TiO\textsubscript{2} in both sizes</td>
</tr>
<tr>
<td>Memory effect</td>
<td>No obvious effect</td>
<td>Decreases greatly in the repeated runs</td>
<td>Decreases slightly in the repeated runs</td>
<td>No obvious effect</td>
</tr>
</tbody>
</table>

Table 5.5 Influencing factors on CO\textsubscript{2}–TBPB hydrate formation behaviour

<table>
<thead>
<tr>
<th>CO\textsubscript{2} uptake</th>
<th>Induction time</th>
<th>Formation time</th>
<th>Supercooling degree</th>
<th>Discrepancy between T\textsubscript{form} and T\textsubscript{diss}</th>
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</thead>
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<tr>
<td>Feed pressure</td>
<td>Increases with the rise in feed pressure</td>
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</tr>
<tr>
<td>HTF temperature</td>
<td>No obvious effect</td>
<td>Decreases with the reduction in the HTF</td>
<td>Decreases with the reduction in the HTF</td>
<td>Increases with the reduction in the HTF</td>
</tr>
<tr>
<td>TBAF</td>
<td>Decreases at 0.1–0.5 wt%, increases at 2.0–3.5 wt%</td>
<td>Decreases at 2.0–3.5 wt%</td>
<td>Decreases at 0.5–3.5 wt%, increases at 0.1 wt%</td>
<td>Decreases at 0.1–2.0 wt%, increases at 3.5 wt%</td>
</tr>
<tr>
<td>SDS</td>
<td>Increases at all mass fractions</td>
<td>Decreases at all mass fractions</td>
<td>Increases at all mass fractions</td>
<td>No obvious effect</td>
</tr>
<tr>
<td>TiO\textsubscript{2} nanoparticle</td>
<td>Increases with TiO\textsubscript{2} in both sizes</td>
<td>Decreases with 20nm TiO\textsubscript{2}; increases with 80nm TiO\textsubscript{2}</td>
<td>Decreases with 20nm TiO\textsubscript{2}</td>
<td>Decreases with 50nm TiO\textsubscript{2}</td>
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<tr>
<td>Memory effect</td>
<td>No obvious effect</td>
<td>Decreases greatly in the repeated runs</td>
<td>Decreases slightly in the repeated runs</td>
<td>No obvious effect</td>
</tr>
</tbody>
</table>
The above effects on CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrate formation are respectively summarised in Table 5.4 and Table 5.5. It is difficult to quantify the effect of feed pressure on the induction time and supercooling degree. It is known that a larger feed pressure leads to a higher phase equilibrium temperature; therefore, the effect of feed pressure can also be considered as the effect of HTF temperature. However, since we are aware that the HTF temperature does not affect the CO$_2$ uptake, the effect of feed pressure on the CO$_2$ gas uptake can be justified.

5.6 Synergy of secondary promoters in hydrate formation

From the above study on the effect of secondary promoters, for CO$_2$–TBAB hydrates the favourable promoters are TBAF at low mass fractions (0.1–0.5 wt%), SDS at low mass fractions (0.1–0.3 wt%) and TiO$_2$ nanoparticles in large size (80 nm); for CO$_2$–TBPB hydrates the beneficial promoters are TBAF at relatively high mass fractions (2.0–3.5 wt%), SDS at high mass fractions (0.3–0.5 wt%) and TiO$_2$ nanoparticles in small size (20 nm). Within the mass fraction range/size, the promoters are blended in four cases, TBAF + SDS, TBAF + TiO$_2$, SDS + TiO$_2$, and TBAF + SDS + TiO$_2$ (Table 5.6), and the synergy of the combinations is tested in the hydrate system. The formation is conducted at the feed pressure of 8.5 bar and the HTF temperature of 4.5$^\circ$C. The formation temperature, supercooling degree, induction time and CO$_2$ uptake are obtained from the temperature and pressure curve along the formation, and are shown in Figure 5.27.
All the formation temperatures are in a range of 6.5–7.5°C, which is suitable for air conditioning chillers. The minimum supercooling degree is attained in the case of AFST at only 0.69°C; some other combinations also achieve small extents of supercooling, namely 1.23°C for AFS, 1.02°C for AFT, and 1.22°C for PFS. The largest CO₂ uptake quantity is 0.349 g for AFS, followed by 0.348 g for AST and 0.340 g for PFST. The induction time is short and useful for practical cold storage charge process for the case of AFS (26.3 min), AFST (23.9 min), PFS (27.3 min) and PFST (22.3 min). Overall, the best one among the eight candidates is AFS, which offers a large CO₂ uptake, a small supercooling degree and a short formation time. Therefore, the solution of AFS (TBAB 20 wt% + TBAF 0.25 wt% + SDS 0.15 wt%) is the best to be used in the cold storage system to form CO₂ semi-clathrates.
The dissociation temperature of CO$_2$–AFS semi-clathrates was measured at 10.4$^\circ$C, manifesting a difference between the freezing and melting temperature of 3.17$^\circ$C.

5.7 Stability of the selected hydrate

To evaluate the stability of the formation behaviour of CO$_2$–AFS semi-clathrate hydrate for long-term use in a practical cold store, 10 times of formation of this material was conducted with the feed pressure of 8.3 bar and the HTF temperature of 3.0$^\circ$C. The temperature variation along the formation is plotted in Figure 5.28. In the first four runs of formation, the formation temperature was stable at around 6.48$^\circ$C; however, it gradually dropped to 6.25$^\circ$C or so after the fifth formation. The largest deviation occurred in the last one, which is 4.6 % smaller than the first one. This result manifests a good stability of the formation temperature.

![Figure 5.28 Continuous 10 cycles of the CO$_2$–AFS semi-clathrate hydrate formation](image)

The supercooling degree is on average 0.45$^\circ$C throughout the cycles. The smallest occurred in the fifth formation that was 0.15$^\circ$C while the largest was in the eighth formation that was 1.16$^\circ$C. The largest one occurred due to an accidental error of the experimental system.

The induction time is on average 18.7 min with the longest (26.7 min) in the eighth and the shortest (13.9 min) in the fourth. This reveals that in spite of the intrinsic stochastic induction period of gas hydrates, suitable modifications with promoters can lead to a better repeatability in the hydrate formation. Thus, the CO$_2$–AFS semi-clathrate hydrate is believed to be stable for long-term use in a cold storage system.
5.8 Conclusion

A comprehensive study was conducted on the phase equilibrium of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrates. Through experiments in a self-fabricated tube, the hydrate formation behaviour was studied at various salt mass fractions with or without a secondary promoter. The hydrate formula was determined as 2.49CO$_2$·TBAB·38H$_2$O and 2.84CO$_2$·TBPB·32H$_2$O respectively.

At the same pressure, the dissociation temperature increased as the TBAB/TBPB mass fraction rose. High feed pressure favoured CO$_2$ uptake; however, high TBAB/TBPB mass fraction restrained CO$_2$ uptake. HTF adopted at low temperature would shorten the induction time but enlarge the supercooling degree. In addition, the memory effect had a large impact on the induction time but a slight impact on the formation time.

Among the secondary promoters tested, for CO$_2$–TBAB hydrate, TiO$_2$ nanoparticle of 80 nm was the most favourable to increase the CO$_2$ uptake. TBAF at high concentrations was the most effective to reduce the induction and formation time. The supercooling degree was the smallest in the presence of SDS of 0.5 wt% or TiO$_2$ in both sizes. The discrepancy between the formation and dissociation temperature was the smallest with TBAF at high concentrations. For CO$_2$–TBPB hydrate, TBAF at 3.5 wt%, SDS at 0.3 wt% and TiO$_2$ nanoparticle in 20 nm were most favourable to enlarge the CO$_2$ uptake. TBAF at 3.5 wt% and TiO$_2$ in 20 nm performed the best to shorten the induction and formation time. The supercooling degree was reduced mostly by TBAF at 0.5–3.5 wt% and TiO$_2$ nanoparticle in 20 nm. The discrepancy between the formation and dissociation temperature was decreased by TBAF at 0.1 wt% and TiO$_2$ nanoparticle in both sizes.

Different combinations of promotors have been tested on CO$_2$ hydrate formation. It was found that the synergy of TBAB 20 wt% + TBAF 0.25 wt% + SDS 0.15 wt% was the best, which led to the CO$_2$ uptake of 0.349 g, the hydrate formation temperature of 7.23$^\circ$C, the supercooling degree of 1.23$^\circ$C and the induction time of 26.3 min. The usability and stability of this modified material in a CO$_2$ hydrate based cold storage air conditioning system has been confirmed; thus in the next chapter it will be used in a lab-scale demonstration system to evaluate its performance.
Chapter 6

Formation enthalpy of CO$_2$ semi-clathrate hydrates with TBAB and TBPB

A key feature of PCMs is ‘phase change enthalpy’, which is usually defined as the amount of cooling capacity conserved per unit volume of cold store.

Recent results of Mayoufi et al. [262] showed that the dissociation enthalpy of CO$_2$–TBPB hydrate was close to that of ice and higher than that of single TBPB hydrate, over a temperature range of 284.6–289.0 K.

The dissociation enthalpy of CO$_2$–TBAB double hydrate was calculated by Lin et al. [259] as 313.2 kJ·kg$^{-1}$ using a DTA device.

The dissociation enthalpy of CO$_2$–TBAB hydrate with the TBAB mass fraction of 20 wt% was measured in an oil-in-water emulsion by Youssef et al. [266] using a DTA device as well as 338.9±3.4 kJ·kg$^{-1}$. It was also reported that the melting enthalpy of solid compound increased with pressure.

In another work of Lin et al. [218], the dissociation enthalpy of CO$_2$–containing TBAB hydrates, TBPB hydrates and TBAB + TBPB hydrates were determined using a DSC deceive. In the result, CO$_2$–TBPB hydrate at 37 wt% TBPB mass fraction manifested the largest enthalpy of 221 kJ·kg$^{-1}$; CO$_2$–TBAB hydrate at 40 wt% TBAB mass fraction had an enthalpy of 205 kJ·kg$^{-1}$, and CO$_2$–TBAB–TBPB hydrate at 40 wt% mass fraction had an enthalpy in the range of 212–215 kJ·kg$^{-1}$ at various proportions of the two salts.

Also using DSC, Deschamps et al. [109] measured the dissociation enthalpy of 40 wt% TBAB hydrate with CO$_2$ gas at 0.83 MPa. The measured enthalpy was 346.0 kJ·kg$^{-1}$ (water).

These results also reveal a big deviation between different measuring techniques.
The stored cooling capacity in the formation of CO₂ semi-clathrate hydrate in the present study is calculated by the T-history method. The method has already been verified in salt hydrate formation in chapter 4. In this chapter, the method will be adopted to determine the formation enthalpy of CO₂–TBAB and CO₂–TBPB semi-clathrate hydrates under certain pressures based on the hydrate formula. On the other hand, in practical operations at low pressure conditions (the overpressure driving force is low and CO₂ is insufficient compared to water), the amount of gas hydrate formed in the bulk of solution is usually small; thus a low stored cooling capacity for cold storage is achieved.

In this chapter, the stored cooling capacity of different CO₂ hydrate systems at various temperature and pressure conditions is also measured in the reaction tube that is introduced in chapter 5. The effect of TBAB/TBPB mass fraction, feed pressure and secondary promoters on the cooling capacity storage ability of the hydrate formation and the heat capacity of the liquid phase is studies.

6.1 Experimental setup and procedures

In the T-history experimental system (Figure 6.1), the formation enthalpy of CO₂ semi-clathrate hydrate (2.49CO₂·TBAB·38H₂O and 2.84CO₂·TBPB·32H₂O) was studied using 3.0 g TBAB/TBPB solution with an initial pressure of 10.0 bar. This is to ensure that the amount of CO₂ is enough compared to TBAB/TBPB and sufficient overpressure driving force can be maintained throughout the hydrate formation. The reaction tube was placed in a temperature-controlled air chamber. The air temperature in the chamber can be adjusted from 3 to 10⁰C. Air rather than water is used to cool the samples to ensure the Biot number is less than 0.1 so that the T-history method is applicable. The air temperature applied to each salt mass fraction should ensure the CO₂ hydrate could form at the certain pressure while the salt hydrate would not form, i.e. the measured heat only comes from the formation of CO₂–TBAB or CO₂–TBPB hydrates. This experimental system is also different from the one shown in Figure 4.13. The hydrate formation and dissociation occurred in the reaction tube instead of normal glass test tubes so that the enthalpy of CO₂ hydrate formation can be measured in the pressure range of 1–10 bar. TBAB solution at 32 wt% and TBPB solution at 37 wt% mass fraction were used since this fraction corresponded to the stoichiometric ratio of TBAB/TBPB to water according to the hydration number [219, 221, 224, 259, 262]. After a long time of cooling, the salt in the solution is believed to be totally enclathrated in the clathrate hydrate. The number of moles of salt TBAB/TBPB is equal to the number of moles of the corresponding specified hydrate. With the hydrate composition known, the mass of the formed hydrate can be obtained, and thus the formation enthalpy may be calculated.
In addition, to obtain the maximum amount of stored cooling capacity in the formation of a certain composition of CO₂–TBAB/TBPB hydrate at a given pressure, the stored cooling capacity of hydrate formation from a bulk salt solution at the maximum solid fraction was measured. In such a system, the mass of CO₂ is insufficient comparing with the amount of TBAB/TBPB. In this case, the restraints of the hydrate formation are the heat transfer and the CO₂ mass transfer. The TBAB/TBPB solution (20 g) at various mass fractions (with the TBAB mass fraction of 10, 20, 32 wt% and the TBPB mass fraction of 10, 20, 30, 37 wt%) is placed in the tube. The pressure in the tube is varied between 3 and 9 bar. Secondary prompters are also added in the solution (SDS at 0.1, 0.3, 0.5 wt% and TBAF at 0.5, 2.0, 3.5 wt%). Through the above procedures, the effects of mass fraction, feed pressure and secondary promoters on the stored cooling capacity in the hydrate formation and specific heat of the liquid phase can be investigated. The specific heat of the solid phase cannot be measured accurately using the current apparatus since there is still free water in the reaction tube after the completion of hydrate formation.

6.2 Results and discussions

6.2.1 Enthalpy of CO₂–TBAB/TBPB semi-clathrate hydrates

For CO₂–TBAB semi-clathrate hydrate, the amount of CO₂ uptake is calculated as 0.102 g; thus the mass of formed hydrate is 1.029 g. Therefore, using the T-history method, the formation enthalpy of CO₂–TBAB semi-clathrate hydrate is 318.5 kJ·kg⁻¹(hydrate). This calculated formation enthalpy is close to the dissociation enthalpy of CO₂–TBAB hydrate acquired in other studies [259, 266].
For CO$_2$–TBPB semi-clathrate hydrate, the amount of CO$_2$ uptake is 0.107 g so that the mass of formed hydrate is 0.887 g. Therefore, the formation enthalpy of CO$_2$–TBPB semi-clathrate hydrate is 351.7 kJ·kg$^{-1}$ (hydrate).

### 6.2.2 Influencing factor of stored cooling capacity of CO$_2$–TBAB/TBPB hydrate

#### 6.2.2.1 Salt mass fraction

From TBAB and TBPB solutions at various mass fractions, CO$_2$ semi-clathrate hydrates were formed in the experiment at a same feed pressure of 7.0 bar. The stored cooling capacity and specific heat of sample were determined using the T-history method, and the results are shown in Table 6.1 and Figure 6.2 and 6.3.

![Figure 6.2 Stored cooling capacity and specific heat of CO$_2$–TBAB hydrate](image-url)
Figure 6.3 Stored cooling capacity and specific heat of CO₂–TBPB hydrate

With the increase in the mass fraction, the formation temperature rises, such that the area between the temperature curve of hydrate and the ambient temperature curve is enlarged. The larger area leads to the higher stored cooling capacity. The measured specific heat of the liquid phase also followed such a tendency – larger specific heat is obtained at larger mass fraction.

Table 6.1 The stored cooling capacity in the formation of CO₂ semi-clathrate hydrate at different mass fractions

<table>
<thead>
<tr>
<th>Semi-clathrate hydrate</th>
<th>Salt mass fraction / wt%</th>
<th>Stored cooling capacity / kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂–TBAB</td>
<td>10</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>1.39</td>
</tr>
<tr>
<td>CO₂–TBPB</td>
<td>10</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The stored cooling capacity of the sample is larger for higher mass fractions. However, it has been previously found that the CO₂ uptake is less for higher mass fractions. Less CO₂ uptake indicates that a smaller amount of the hydrate structure of 2.49CO₂·TBAB·38H₂O or 2.84CO₂·TBPB·32H₂O has been formed, in which the relative proportion of CO₂, TBAB/TBPB and water molecules is fixed. However, less hydrate being formed does not necessary mean less thermal energy could be
stored. In fact, the clathrate hydrate formation has two exothermic processes – the distortion of hydrogen bonds to cages structures, and the inclusion of gas molecules. The amount of CO\(_2\) uptake is related to the heat released in the second process but it is not much related to the first process of cage forming. The shaping of cages can be favoured by higher mass fraction of TBAB or TBPB in the solution. This is due to that the Br\(^-\) in both TBAB and TBPB can join to the hydrogen bonds in the cages and the TBA\(^+\) and TBP\(^+\) occupy the cages at the same time. Higher mass fractions help to shape and stabilise the cages. As the cages are more stable, more heat can be released in the formation.

6.2.2.2 Feed pressure

The stored cooling capacity of CO\(_2\)-TBAB/TBPB semi-clathrate hydrate affected by various feed pressures is shown in Table 6.2 and Figure 6.4 and 6.5. The solutions were all at the salt mass fraction of 20 wt%.

It was found that, with the rise in the feed pressure, both the stored cooling capacity and the specific heat increased for the case of both TBAB and TBPB. This indicates that at high feed pressures (large overpressure driving force) the hydrate formation is favoured so that more cooling capacity can be stored. In addition, due to the fact that higher feed pressures result in more CO\(_2\) gas dissolved in the water solution during the sensible period, the specific heat of the liquid phase is enlarged.

![Graph showing stored cooling capacity and specific heat of CO\(_2\)-TBAB hydrate under various feed pressures](image-url)
6.2.2.3 Additives

Secondary promoters such as quaternary fluoride salts and surfactants have been found favourable for faster and easier hydrate formation. Whether these additives can also enlarge the stored cooling capacity of CO$_2$ clathrate hydrate can be investigated based on 20 g 20 wt% solutions of TBAB and TBPB. The results are shown in Table 6.3 and Figure 6.6 and 6.7.
Table 6.3 The stored cooling capacity in the formation of CO$_2$ semi-clathrate hydrate in the presence of different additives

<table>
<thead>
<tr>
<th>Semi-clathrate hydrate</th>
<th>Additive mass fraction / wt%</th>
<th>Stored cooling capacity / kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>SDS 0.1</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>SDS 0.3</td>
<td>1.08</td>
</tr>
<tr>
<td>CO$_2$–TBAB</td>
<td>SDS 0.5</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>TBAF 0.5</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>TBAF 2.0</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>TBAF 3.5</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>SDS 0.1</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>SDS 0.3</td>
<td>1.53</td>
</tr>
<tr>
<td>CO$_2$–TBPB</td>
<td>SDS 0.5</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>TBAF 0.5</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>TBAF 2.0</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>TBAF 3.5</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Figure 6.6 Stored cooling capacity of CO$_2$–TBAB hydrate with different additives
Figure 6.7 Stored cooling capacity of CO$_2$–TBPB hydrate with different additives

Comparing with a reference without secondary promoters, samples modified by SDS at the mass fraction of 0.1, 0.3 and 0.5 wt% and TBAF at the mass fraction of 0.5, 2.0 and 3.5 wt% all manifested promotion effects on the storage capacity of the hydrate material. The comparison revealed that, for CO$_2$–TBAB hydrate systems, the stored cooling capacity of the system increased with the growth of the promoter’s mass fraction. For CO$_2$–TBAB hydrate systems, SDS was found to be capable of enhancing the stored cooling capacity; however, the largest stored cooling capacity was achieved with SDS at 0.1 wt% and it decreased with the increase in the mass fraction of SDS. TBAF also enhanced the stored cooling capacity in the hydrate formation and all the mass fractions of TBAF in this test demonstrated a similar extent of enhancement on the stored cooling capacity.

6.3 Conclusion

The commonly used methods to determine the enthalpy of PCMs are DSC and DTA. These methods are disadvantageous since the mass of the samples tested is small and the repeatability is low when analysing heterogeneous samples. Moreover, these methods are usually designed for atmospheric pressure and the installations with pressurisation are high-cost and hard to perform. In contrast, the T-history method offers an easy and cheap way to characterise PCMs.

By the T-history calculation, the formation enthalpy of CO$_2$–TBAB semi-clathrate hydrate is 318.5 kJ·kg$^{-1}$(hydrate) and that of CO$_2$–TBPB semi-clathrate hydrate is 351.7 kJ·kg$^{-1}$(hydrate). The enthalpy of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrates are high compared to other PCMs, such as TBAB salt hydrate (193.2 kJ·kg$^{-1}$) [222], C14–
C18 (158.3 kJ·kg⁻¹) [267, 268], hexadecane-tetradecane (147.7–182.7 kJ·kg⁻¹) [267, 269, 270], and the mixture of capric acid and lauric acid (115.1 kJ·kg⁻¹) [3].

In addition, higher salt mass fraction in the solution and higher feed pressure were favourable for larger stored cooling capacity storage capacity and specific heat of liquid phase when using these semi-clathrates in practical conditions (usually with insufficient CO₂ and overpressure driving force). Adding TBAF and SDS also enlarged the stored cooling capacity of semi-clathrates and their effect with various concentrations is different.
Chapter 7

CO$_2$ semi-clathrate hydrate in an emulated cold storage system

The use of air-conditioning is one of the main reasons for electrical power demand peaks during summer, accounting for as much as half of the power demands during the hot midday hours in some areas when electricity is most expensive [271]. At night, since utilities have spare electrical generating capacity since the demand falls, the wholesale electricity price is lowered as an incentive for consumption. It is therefore financially attractive to operate an electric air conditioning chiller at off-peak times. However, this strategy requires the chillers to shut down during peak-load hours and to have a backup system to provide cooling at those times.

CTES refers to storage approaches that conserve cooling capacity by extracting heat from a storage medium, such as chilled water, ice and PCMs. It has become one of the primary means of addressing the electrical power imbalance between daytime demand and night-time abundance by provide cooling capacity during the day using electricity at night.

CTES is also used in a solar cooling system to store extra cooling capacity produced by solar energy and supply cooling in solar outage to alleviate energy supply intermittency. In particular, it enables solar cooling to be deployed after sunset.

The combination of a heat pump/chiller and a CTES can provide the following benefits [136]:

1. Load levelling of electricity demand for air-conditioning. The CTES system achieves peak shifting and demand management response, thereby improving the annual load factor of electricity-supply facilities. This may enable electricity suppliers to put off capital expenditure in network asset upgrades. At the same time, customers accrue economic advantages with a CTES system when electric power companies provide discount rates for night-time electricity.

2. Efficient operation of the cooling unit. The heat pump operates at night under favourable condensing conditions. This reduces electricity
consumption compared to an equivalent cooling effect produced during the
daytime. Furthermore, heat pump operation may be optimised for a reduced
operating range of evaporating and condensing temperatures, and be more
independent of the cooling load of building.

3. Reduction of heat pump capacity. For the same amount of cooling
load, the longer operating hours of CTES allow for smaller capacity of the
heat pump thus downsizing the heat pump and offsetting the capital cost of
the cooling system.

CTES systems are most likely to be cost effective in situations where:

- A facility’s maximum cooling load is much greater than its average;
- There are higher demand charges for peak demand periods;
- An existing cooling system is being expanded;
- An existing cold storage tank is available;
- Limited on-site electric power is available;
- Backup cooling capacity is desirable;
- Cold air distribution is desirable or advantageous [136].

CTES systems are presently operational in commercial and industrial building in
some countries. As was introduced in previous chapters, CO₂ hydrates offer a large
phase change latent heat that leads to size and weight advantages. CO₂ hydrates
also provide suitable phase change temperatures in the range of 5–12°C, which suits
to the characteristics of conventional air conditioning systems.

From previous studies, CTES systems using CO₂ hydrate as the PCM are
associated with several problems including:

1. Supercooling may take place, which makes the required chilled water
temperature lower to trigger hydrate formation. This reduces the chiller
efficiency;
2. The induction delay in the hydrate formation makes it longer to initiate
and complete the charging process;
3. The means of pressure control of the storage system may be challenging;
4. It is difficult to build a heat exchanger that is capable of dealing with the
agglomeration of hydrate crystals floating in the liquid;
5. The mass and heat transfer in the heat exchanger may cause
agglomeration of the hydrate;
6. The operation cannot be completely reversed due to the low repeatability
of hydrate formation.
In this chapter, a lab-scale demonstration system was built to study the performance of an emulated CTES system using the CO$_2$ hydrate proposed in chapter 6. The hydrate is investigated in both charging and discharging processes.

### 7.1 System configuration

The lab-scale demonstration system of the CO$_2$ semi-clathrate hydrate based CTES system is shown in Figure 7.1. The system is mainly composed of a storage vessel, a crystalliser and a thermostatic bath. Helical coils are located in the vessel and connected to the thermostatic bath; thus the temperature controlled water from the bath provides a cold and heat source to the CTES. The hydrate formation, storage and dissociation all take place within the vessel but outside the helical coils. The crystalliser is used to test the effect of ultrasonic vibration on the hydrate formation.

![Figure 7.1 Schematic diagram of the lab-scale CO$_2$ hydrate cold storage system](image)

The appearance and internal structure of the storage vessel are respectively shown in Figures 7.2 and 7.3. The storage vessel for the cold storage system is based on an internal melt ice-on-coil system. The vessel uses chilled water as both the charging and discharging fluid in a closed loop system, circulating it through the helical coils submerged in the PCM-filled vessel. Water is circulated by a variable-frequency drive (VFD) pump. The vessel is pressurised by CO$_2$ gas. In the horizontal part, pistons on both ends are used to adjust the vessel inner volume. In this way, the inner volume of the vessel can be adjusted from 8.6 to 16.5 L. The vertical part of the vessel is filled with AFS solution (TBAB 20 wt% + TBAF 0.25 wt% + SDS 0.15 wt%) that was described in chapter 5. There are four platinum temperature sensors on the wall of vessel (respectively 80, 180, 280 and 380 mm from the bottom) and two platinum temperature sensors in the inlet and outlet helical coils of the chilled
water. All the sensors have been calibrated. The uncertainty of temperature measurement is ±0.1°C and of pressure measurement is ±0.05 bar.

There are a coolant loop and a hydrate slurry loop in the system. In the coolant loop, chilled water from the thermostatic bath flows in the helical coils to trigger the formation of CO$_2$ semi-clathrate hydrate outside of the coils. The flow rate of the chilled water is 3.6 L·min$^{-1}$. In the slurry loop, the liquid AFS solution containing dissolved CO$_2$ gas and tiny formed hydrate particles in the vertical part are circulated from the bottom of the vessel to the crystalliser, and then pumped back to the top of the vessel through a nozzle. Rather than form hydrate in a quiescent state, the slurry loop can prompt the hydrate formation by enhancing the contact between CO$_2$ gas and AFS solution.

![Figure 7.2 Appearance of the cold storage vessel](image)

![Figure 7.3 Internal structure of the cold storage vessel](image)
For an ice storage system, the secondary coolant is usually ethylene glycol. The ice storage requires the chiller capable of producing charging temperatures in the range from $-6.0$ to $-3.0^\circ C$. In the discharge, ice storage provides sustained discharging temperatures of $2.0$–$3.0^\circ C$, which are dependent on the discharging rate and the amount of ice remaining. This water temperature is too low for conventional space cooling; thus it is usually adjusted by mixing with return water.

For the $\text{CO}_2$ hydrate based CTES system in the present work, the secondary coolant is water, which is typically required to provide a temperature of $7^\circ C$ for charging and $12^\circ C$ for discharging the cold store. The $7^\circ C$ charging temperature is the normal design chilled water temperature for conventional air conditioning systems or air conditioning systems with water storage; thus it would result in minimal extra operating cost for operating the chiller with CTES.

![Figure 7.4 Appearance of the crystalliser of the cold storage system](image)

Figure 7.4 Appearance of the crystalliser of the cold storage system

![Figure 7.5 Appearance of the ultrasonic transducer of the cold storage system](image)

Figure 7.5 Appearance of the ultrasonic transducer of the cold storage system

The crystalliser is fabricated from brass with an inner volume of $0.196$ L. It has a slurry inlet, a slurry outlet and a gas inlet. Both ends are sealed with flanges and O-rings, and the side walls are transparent polycarbonate with white LEDs inlayed at the bottom for a clear view of the inside. A $50$ W $40$ kHz ultrasonic transducer is mounted on the side wall of the crystalliser, in close contact with the wall. The ultrasonic transducer is made to modulate its operating frequency between $19.08$
and 41.66 kHz over a time cycle of several seconds. The side and top view of the crystalliser are shown in Figure 7.4 and the kit of the ultrasonic transducer is shown in Figure 7.5.

### 7.2 Experimental procedure

At the start of the CTES charging process, the pump is turned on and the solution is circulated in the external hydrate slurry loop. Pressure in the vessel is increased by injecting CO$_2$ gas from the gas cylinder (point I to point A in Figure 7.6 (a)). Once the design feed pressure is reached and the pressure is stable, the injection of CO$_2$ is stopped. Then the cooling is started by circulating the chilled water in the helical coils at a constant temperature that is lower than the formation temperature of the hydrate. During charging, three operation modes were conducted:

1. Storage vessel
2. Storage vessel + nozzle
3. Storage vessel + nozzle + crystalliser with ultrasonic vibration.

For the first mode, hydrate slurry loop is not put into use; for the second one, the external slurry loop is used while the crystalliser is bypassed; for the third one, both the external loop and the crystalliser are active, and the ultrasonic transducer is operating.

In Figure 7.6, the hydrate formation and dissociation take place when crossing the liquid water–hydrate–vapour (L$_w$-H-V) equilibrium curve. To the left of the curve the system is in liquid water and hydrate (L$_w$-H); to the right of the curve the system is in liquid water and vapour (L$_w$-V). In Figure 7.6 (a), CO$_2$ and water at point A forms hydrate at point B and C; while in Figure 7.6 (b), the formed hydrate at point A dissociates at point B and C'.

With respect to the control volume, the operation mode of charge can be either ‘constant mass’ or ‘constant pressure’. The former is implemented if the gas inlet valve is closed when the design pressure is reached and the system becomes a closed control volume (point A to B in Figure 7.6 (a)); the latter is conducted if the gas inlet valve remains open to the gas cylinder and the pressure of the system is constant (point A to C in Figure 7.6 (a)). We observe that ‘constant pressure’ has a higher formation temperature, thus the required chilled water temperature to charge the CTES is higher than that for ‘constant mass’.

Discharge is started by raising the chilled water temperature to a temperature that is higher than the hydrate dissociation temperature at the present pressure. The discharge can be operated by two modes as well – ‘unadjusted pressure’ and ‘reduced pressure’. The former is implemented by directly heating the formed
hydrate and keeping the volume and mass of CO\(_2\) unchanged (A to B in Figure 7.6 (b)); the latter is achieved by moving the pistons to increase the vessel’s inner volume or by releasing CO\(_2\) from the relief valve to decrease the pressure before heating the hydrate (A to C then to C’ in Figure 7.6 (b)). Since the dissociation temperature is lower for the lowered pressure case, the CTES delivers chilled water at a lower temperature for the ‘reduced pressure’ than for ‘unadjusted pressure’.

Figure 7.6 P-T correlation of hydrate formation and dissociation under different operation modes

The control of formation and dissociation pressure appears to offer a method to influence the freezing and melting temperature of the hydrate. This feature allows the air conditioning system some flexibility in real time operation. For example, if dehumidification is not required, the chilled water temperature supplied by the CTES may be raised to say 12ºC. Supply and discharge of energy over a tuneable range of temperatures is not offered by PCMs such as paraffins, eutectic salts or conventional ice.
7.3 System performance indicators

Generally, the performance indicators of internal melt PCM cold thermal storage systems are [272]:

- Charged capacity;
- Charging rate and charging temperature (including subcooling effect);
- Discharging rate and discharging temperature;
- Thermal efficiency;
- Ability to meet peak demand.

The designer can manipulate the chiller set point to control the rate of hydrate formation. This formation rate is determined by measuring the rate of heat added to the chilled water flow. However, a compromise must be made between hydrate formation rate and chiller efficiency. The aim is to fully charge storages in the time available, while minimising chiller and auxiliary energy consumption.

To evaluate the usable storage capacity of an internal melt system, it is essential to test the system against the design load profile. As the CTES is discharged against the design load, the amount of discharged capacity is monitored by measuring the cooling capacity added to the chilled water supply before discharging temperature rises above the maximum usable temperature. The discharging rate and discharging temperature profile are generally verified during the test of storage capacity.

The charging rate and discharging rate are calculated using the energy transfer associated with the bath water

\[ Q_C = \dot{m} c_{p,HTF} (T_b - T_a) \]  \hspace{1cm} (7.1)

\[ Q_D = \dot{m} c_{p,HTF} (T_c - T_d) \]  \hspace{1cm} (7.2)

where \(\dot{m}\) is the mass flow rate of the bath water and \(c_{p,HTF}\) is the specific heat of the bath water. \(T_a\) and \(T_b\) are the temperature of the inlet water and outlet water temperature in the charging; \(T_c\) and \(T_d\) are the temperature of the inlet and outlet water temperature in the discharging as shown in Figure 7.7. The instantaneous charging and discharging rate are calculated from Equation (7.1) and (7.2). The charged capacity and discharged capacity are calculated by respectively integrating the instantaneous charging and discharging rate with respect to time.

The cooling capacity storing rate \(\Delta Q\) is the rate net cooling capacity is accumulated in the cold store. It can be calculated from the energy balance equation

\[ Q_C - (Q_D + Q_L) = \Delta Q \]  \hspace{1cm} (7.3)
The energy loss rate (heat gain rate) $Q_L$, which can be improved by using thermal insulation materials, is not analysed in this study.

Figure 7.7 The charging-storing-discharging process in a general CTES system

In this chapter, the instantaneous charging and discharging rate and the charged and discharged cooling capacity will be assessed. Some influencing factors, such as chiller’s set-point, external flow rate and ultrasonic vibration on the charging rate, and cooling load on the discharging rate, will be evaluated. Moreover, CO$_2$ uptake will be calculated using the method introduced in chapter 5 and will be assessed as a performance indicator.

### 7.4 Morphology of charge and discharge

Series of photos was taken along hydrate formation. The top and side photo before the experiment began is shown in Figure 7.8(a) and (b), respectively. The first trial experiment was conducted using the ‘constant mass’ mode. The gas inlet valve was closed after the vessel’s pressure became stable at 5.0 bar. The chilled water at a constant temperature of 7°C was circulated to the vessel. The external slurry loop was operating.
At around 20 min after the start of cooling, a large pressure decrease was detected. A mass of foam of CO$_2$ and water mixture formed on the liquid surface, which could be viewed from the top window of the vessel (Figure 7.9). From the side windows, three layers were seen – on the top was the foam of CO$_2$ and water mixture, in the middle was the bulk of liquid and at the bottom was the formed hydrate solid piling up like snow (Figure 7.10). Foam was also seen from the top of the crystalliser, but this may have been circulated along with the liquid in the external slurry loop (Figure 7.11).
At around 40 min after cooling, it became more obvious to see that small solid chips (hydrate particles) had formed on the top of the liquid surface and sunk down to the bottom hydrate layer (Figure 7.12 (a)). As the hydrate formation proceeded, the top foam layer became thicker and the formed hydrate gathered in large conglomerates. Gradually, large conglomerates of hydrate sunk down from the top, as shown in Figure 7.12 (b). The bottom layer of hydrate became much thicker. The external surface of the coils also gained large adhesions of hydrate, due to the low coil temperature.
Figure 7.12 Enlarged view of the dropping of formed CO$_2$ hydrate

When no further pressure drop was observed, the external pump was turned off and the chilled water was maintained at constant temperature. This was to avoid any blockage at the inlet of the pump as the solid fraction in the solution increased greatly. The formation of the hydrate became very slow due to the low mass transfer of CO$_2$ gas and because the heat transfer between the chilled water and the bulk hydrate was reduced by the thermal resistance of the already formed hydrate on the outer surface of the coils. The formation finally stopped because of the low overpressure driving force (the pressure decreased as the formation proceeded). Finally, the foam on the top became thick and mushy due to the increased fraction of solid hydrate (Figure 7.13).

Figure 7.13 Top view at the end of CO$_2$ hydrate formation

For the purposes of observation, the remaining liquid was drained from the vessel and the coils emerged, as can be seen in Figure 7.14. The agglomeration of solid
hydrate was visible on the surface of coils, and piled hydrate was at the bottom. The appearance of the formed CO$_2$ semi-clathrate hydrate was just like ice.

Figure 7.14 Top view at the end of CO$_2$ hydrate formation after draining remained water solution

The dissociation of the formed hydrate began by increasing the chilled water temperature to $12^\circ$C. As was observed from the top window, the foam gradually disappeared. From the emerged liquid surface, bubbles rose due to the releasing of CO$_2$ gas from the hydrate (Figure 7.15). From the side windows, small solid chips rose from the bottom hydrate layer with bubbles. The hydrate adhering to the external surface of the coils dissociated and the copper coil became visible (Figure 7.16).

Figure 7.15 Top view at the first half of hydrate dissociation
In this run, the pump was off to slow the process of dissociation for better observation. However, in practical discharge of CTES, the rate of dissociation can be adjusted by running the external circulation and changing the flow rate and temperature of the chilled water.

After 1 hour of dissociation, the appearance was as shown in Figures 7.17 and 7.18. Compared to the formation process, the bulk of liquid in the dissociation was much clearer. The hydrate separating from the external surface dropped to the bottom. The ‘snow drift’ of solid hydrate at the bottom of the vessel thickened up. Every now and then, there were small bubbles rising from the bottom.
In another dissociation process with pressure reducing, as the pressure was reduced by moving the pistons and the hydrate was heated by 12°C chilled water, a large quantity of bubbles rose to the surface of liquid, as shown in Figure 7.19. This is in contrast to the slow bubble rise in the ‘unadjusted pressure’ dissociation.

From the side window, it can be seen that liquid gradually formed on the surface of the solid hydrate; meanwhile, bubbles were released from the solid and grew on the surface (Figure 7.20). At half of the time for dissociation, hydrate crystals were observed in coexistence with the melt liquid, as shown in Figure 7.21.
Figure 7.20 Enlarged view of the hydrate crystal with CO\textsubscript{2} bubble releasing

Figure 7.21 Enlarged view of the hydrate crystal during dissociation
7.5 Charge under different operation modes

7.5.1 Different operation modes of charging

This test (constant mass) was to study the effectiveness of charging the cold storage vessel in three operation modes – under static state, with the external loop (driven by the external pump), and with both the external loop and the ultrasonic vibration.

In the beginning, the vertical part of the vessel contained 6.5 L AFS solution and the horizontal part was filled with CO$_2$ gas. The initial pressure of the vessel was 5.5 bar and its temperature at 19.5°C (the current room temperature). The variations of temperature, pressure, CO$_2$ gas uptake and charged capacity are shown in Figure 7.22.

![Figure 7.22 The charging process under different operation modes](image)

In the first stage (static cooling), chilled water at 7.0°C was sent into the helical coils in the vessel to cool the solution. The pressure decreased with the temperature drop. The charged capacity first increased rapidly due to the large temperature difference for sensible heat transfer, and then it grew slowly. When the temperature curves became stable, the charged capacity was constant at 0.15 kWh.

During the static cooling process, no formed solid was visible; also, there was no peak observed in the temperature curve (temperature peak would indicate hydrate formation). Therefore, after 2.0 h in the second stage, the pump was turned on and the AFS solution was circulated out of the vessel through the crystalliser and back to the vessel via the nozzle. The flow rate of the external slurry loop was 2.4 L·min$^{-1}$. 
In the curve of the 1st derivative of pressure, an obvious valley appeared when the external loop started. Meanwhile, a temperature peak and a big pressure drop appeared, indicating the start of CO\textsubscript{2} hydrate formation. The CO\textsubscript{2} uptake rose at the same time to 27.5 g, and it continued to grow gradually during the formation. An obvious increase also occurred in the charged capacity due to the latent heat exchange in hydrate formation.

After 2.0 h, the ultrasonic transducer on the crystalliser was turned on. It can be seen that after the ultrasonic transducer was switched on, the 1st derivative of pressure became scattered due to the vibration. However, nothing changed in the temperature curves or the pressure curve. The rate of charged capacity did not change. Thus, it is believed that ultrasonic vibration does not affect the hydrate formation period once the formation has already started.

7.5.2 Temperature distribution in cold storage vessel

The temperature distributions from the top to the bottom of the vessel are illustrated in Figure 7.23. This test was conducted at constant pressure (5.0 bar). The inlet chilled water temperature was maintained at 7.0°C.

As can be seen, the temperature of the #4 sensor on the top was the highest among all the temperature sensors. This can be attributed to the observation that the CO\textsubscript{2} hydrate was largely forming at the gas/liquid interface near the top where heat was being released. Therefore, it is reliable to use the temperature of #4 (9.25°C) to manifest the formation temperature of the hydrate.
It was also found that the measured formation temperature is higher than that of CO$_2$–AFS semi-clathrate hydrate tested in the T-history tube. This showed again that the mass of the test sample affects the measured formation temperature. The induction time was also read from the temperature curves as 0.29 h (17.4 min). The supercooling degree was 0.42°C. The CO$_2$–AFS semi-clathrate hydrate of large volume in this configuration showed further reduced supercooling degree and rapid formation compared to the small volume studied in the T-history test tubes.

7.5.3 Maximum valid chilled water temperature

The stepwise method was employed again to determine the maximum chilled water temperature that could trigger the hydrate formation under the experimental conditions (defined as the ‘maximum valid chilled water temperature’ in the present study). The maximum valid chilled water temperature could also manifest the minimum supercooling degree of PCM. The results are shown in Figure 7.24.

The pressure was constant at 5.0 bar throughout the experiment. The chilled water temperature was first cooled down to 8.5°C, which was higher than the maximum valid chilled water temperature at such pressure. At about 1.5 h after cooling, with no hydrate formation observed, the chilled water temperature was lowered by 0.5°C. Sequentially, after another 1.5 h, there was still no formed solid or temperature peak or rise in charging rate observed. Therefore, the chilled water temperature was reduced by 0.5°C again.

Figure 7.24 Temperature and charged capacity in the charge using the stepwise method
Immediately after the chilled water temperature reached 7.5°C, a temperature peak occurred and the charging rate increased from 0.01 to 0.04 kW. The charged capacity started to grow rapidly. All these readings indicated that 7.5°C chilled water triggered the hydrate formation; thus it is considered to be the maximum valid chilled water temperature for the formation at constant 5.0 bar. The accuracy can be enhanced by repeating this method with smaller incremental temperature increases (e.g. 0.1°C).

7.5.4 Influencing factors of the charging rate

7.5.4.1 Chiller’s set-point

In the practical operation of a cooling system, the higher the chiller’s set-point, the higher the energy efficiency that can be achieved. Therefore, it is important to know how the chilled water temperature can affect the charging performance of the CTES.

In these experiments, the outlet water temperature from the thermostatic bath was set at 5.0, 6.0 and 7.0°C, respectively, and the chilled water flow rate was constant at 3.6 L·min⁻¹. The flow rate of the external slurry loop was also constant at 2.4 L·min⁻¹. The ‘constant mass’ mode was adopted and the initial pressure was 4.5 bar. The results are shown in Figure 7.25.

![Figure 7.25 Effect of chiller’s set-point on the charging rate](image)

In the temperature curves, the induction times were 0.15, 0.19 and 0.21 h for 5.0, 6.0 and 7.0°C chilled water respectively. It is obvious that the charging rate was the highest for 5.0°C chilled water followed by that for 6.0°C chilled water. The charged capacity finally achieved 0.18, 0.24 and 0.31 kWh for 7.0, 6.0 and 5.0°C chilled water.
chilled water. The discrepancy in the charged cooling capacity mainly resulted from the latent heat storage capacity by means of CO₂ hydrate formation. High driving force of subcooling (difference between the chilled water temperature and the equilibrium temperature of hydrate) greatly increased the charged cooling capacity by enhancing hydrate formation. By comparison, the case of 7.0°C chilled water manifested poor charged cooling capacity due to the low subcooling – the hydrate formation finally ceased at 1.3 h with the charging rate dropping to 0.01 kW and the charged cooling capacity failing to increase any further. Different sensible heat transfers led by various chilled water temperatures also accounted for a part of the discrepancy in the final charged capacity, but it is negligible compared to latent heat transfer.

This trade-off between the charging temperature and charging capacity is an important operational constraint for the gas hydrate CTES.

7.5.4.2 External flow rate

The external slurry loop was found to be of significance to the hydrate formation, as deduced from Figure 7.22. This section describes the study of how the flow rate of the external loop could affect the charging rate of the CTES.

With the chilled water constant at 7.0°C for all cases, the flow rate of the external loop was varied – 1.2, 1.8 and 2.4 L·min⁻¹. The ‘constant mass’ mode was adopted and the initial pressure was 4.5 bar. The results are shown in Figure 7.26.

![Figure 7.26](image_url) Effect of external flow rate on the charging rate

The induction time was 0.20 and 0.37 h respectively for the flow rate of 2.4 and 1.8 L·min⁻¹. However, the induction time cannot be read directly from the temperature...
This is attributed to the fact that, using a high flow rate the nozzle injected the circulated liquid back to the bulk of solution, and thus the convection heat transfer between the outer surface of the helical coil and the bulk of solution was enhanced; using 1.2 L·min⁻¹ flow rate, the convection heat transfer was weak; thus the sensible heat transfer period before hydrate formation was diminished.

The charged capacity was finally 0.13, 0.15 and 0.19 kWh for 1.2, 1.8 and 2.4 L·min⁻¹. This indicates that the flow rate of the external loop played a significant role in the effective charge of the CO₂ hydrate based cold store, since it could improve both the convection heat transfer and the mass transfer between CO₂ gas and AFS solution.

There was an obvious difference between the charged capacity in the result for 2.4 L·min⁻¹ and that in the section 7.5.1 (Figure 7.22). This is owing to the different pressure conditions – ‘constant mass’ mode was adopted in both cases; however, the initial pressure was 5.5 bar in the section 7.5.1 while it was 4.5 bar in this section. This comparison reveals the effect of the overpressure driving force on the charged capacity of a CO₂ hydrate CTES.

### 7.5.4.3 Ultrasonic vibration

The effect of ultrasonic vibration on the charging process is shown in Figure 7.22 – it does not affect the formation period if the hydrate formation has started already. This test examines whether ultrasonic vibration affects the induction period before the formation starts.

![Figure 7.27 Effect of ultrasonic vibration on the charging rate](image-url)
Two trials were carried out under the same conditions – a constant pressure of 5.0 bar and constant chilled water temperature of 7.0°C. From the results shown in Figure 7.27, in the case without ultrasonic vibration, after the large sensible temperature decrease a lag appeared in the charged capacity, before it continued to increase (from 1.3 to 1.8 h). During this period, the charging rate decreased to 0. This lag was not found in the charged capacity of the case with ultrasonic vibration. The charged capacity of both cases was very close in the end. This reveals that the ultrasonic vibration may help to break the metastability and reduce the induction time, and thus accelerate the charging process; however, it does not show a major impact on the formation period and the charged capacity that a CTES can store.

7.5.5 Charge control strategies

There are two control strategies of charging operation – constant mass and constant pressure. The trials are to investigate what charged capacity can be achieved using different control strategies. They were conducted at the same chilled water temperature of 7.0°C. The pressure of ‘constant mass’ was initially 6.1 bar and it was finally decreased to 4.5 bar after the charging process; the pressure of ‘constant pressure’ was maintained at around 5.3 bar (the average pressure of the ‘constant mass’).

As shown in Figure 7.28, the charged capacity increased more slowly in the case of constant mass. The final charged capacity of the ‘constant mass’ case (0.24 kWh) was much smaller than that of the ‘constant pressure’ case (0.31 kWh). The reason for this discrepancy can be found in Figure 7.6 (a). Adopting ‘constant pressure’ can make the required chilled water temperature higher than using ‘constant mass’.

![Figure 7.28 Pressure and charged capacity for ‘constant mass’ or ‘constant pressure’ mode](image)
This test was at the same chilled water temperature, which makes the subcooling driving force larger for the ‘constant pressure’ case than that of the ‘constant mass’ case. Hence, the charged capacity of the ‘constant pressure’ case was larger. This supports using the ‘constant pressure’ operation in practical cold storage systems.

### 7.6 Discharge using different control strategies

Studies on the discharge of the CO\textsubscript{2} hydrate based CTES mainly focus on the discharging rate, peak demand operation of the cold store, and the comparison of discharging control strategies.

#### 7.6.1 Temperature distribution in cold storage vessel

This trial was carried out directly after a charging process, and the water from the thermostatic bath was increased to 17\textdegree C. During the whole discharging process, the temperature at the position of four measuring points, the pressure variation and the discharged capacity variation were plotted, as shown in Figure 7.29.

![Figure 7.29 Temperature distribution, discharging rate and discharged capacity in the discharge](image)

At 0.22 h, the 1\textsuperscript{st} derivative of pressure reached the first peak followed by a valley in the discharging rate, indicating the dissociation point. The dissociation temperature was 10.5\textdegree C, which was 1.25\textdegree C higher than the formation temperature obtained from Figure 7.23. In this system configuration, the difference between the freezing and thawing temperature was smaller than that measured in the T-history rig due to the increased solution volume.
At 0.72 h, the 1st derivative of pressure stabilised at 0, revealing no more obvious changes in the pressure. The discharge reached a stable stage. The discharging rate gradually increased to 0.5 kW and became almost constant, and the discharged capacity increased linearly.

After the temperatures all increased to the bath water temperature, the temperature of #3 and #4 on the top of the vessel became higher than that of #1 and #2 at the bottom of the vessel. This may be caused by the rise of dissociated CO$_2$ bubbles towards the liquid surface, which has a relatively higher temperature than the bulk of liquid and solid.

### 7.6.2 Discharging rate at various chilled water return temperatures

An important feature of CTES is the discharging performance at different water temperature from the terminals in the air conditioning system. This manifests the ability of the CTES to manage the cooling demand.

![Discharging rate and discharged capacity with various chilled water return temperatures](image)

Figure 7.30 Discharging rate and discharged capacity with various chilled water return temperatures

A series of experiments was carried out with the water from the bath at different temperatures (11–18°C) to emulate chilled water return from cooling load. The discharging rate and capacity were obtained from experiments and are plotted in Figure 7.30. In all the cases, the cold storage vessel was charged at 0.30 kWh before discharging. During the discharge, the discharging rate for higher bath water temperatures was obviously higher than that for lower bath water temperatures. With the bath water temperature of 11°C, which is 0.5°C higher than the dissociation temperature, the discharged capacity was only 0.13 kWh after 3.0 h.
With the bath water temperature of 18°C, the discharged capacity achieved 0.21 kWh after 1.6 h. The biggest difference in the discharging rate was found between 14 and 15°C. It is speculated that, similar to subcooling, ‘overheating’ can also be a driving force for more rapid dissociation of CO₂ hydrate.

The ability of the CTES to discharge during time frames associated with an air conditioning load is clearly influenced by the discharge driving force. However, these experiments have not provided evidence to suggest that the total discharge capacity of the CTES over an extended period will be affected by the discharge temperature.

### 7.6.3 Peak demand operation

Sometimes the CTES has to deliver very high cooling capacity at extreme conditions. In this test, the cold storage vessel with a previously charged capacity of 0.20 kWh was discharged with chilled water return at 12, 16, 20, 24 and 28°C to emulate cooling load from low to high temperatures.

![Discharging rate and discharged capacity under peak load](image)

Figure 7.31 Discharging rate and discharged capacity under peak load

Figure 7.31 shows that the discharged capacity decreased from the high bath water temperature to the low, which is the same tendency shown in Figure 7.30. A large cooling demand with the water temperature of 28°C triggered a large discharged capacity of 0.36 kWh in 1.3 h. In some cases, the discharged capacity was higher than the charged capacity. This was because the chilled water return temperature was higher than the initial solution temperature and it led to an amount of sensible discharged capacity. The initial solution temperature was around 18°C. Taking the case of 28°C water return temperature as an example, the specific heat of the liquid...
solution is 4.0 kJ·kg⁻¹·K⁻¹, and thus the extra sensible discharged capacity is 0.075 kWh, which equals to the eventual discharged capacity measured in the experiment, as shown in Figure 7.31.

In Figure 7.32, correspondingly, the temperatures of the chilled water return and chilled water supply of the coils and the temperatures of the AFS solution / hydrate slurry outside the coils were plotted for various inlet water temperatures. The largest temperature difference between chilled water return and chilled water supply for 12, 16, 20, 24 and 28°C inlet water was 0.66, 1.53, 2.65, 2.79 and 3.47°C, respectively. For this specified storage volume with only 6.5 L AFS solution, the time during which the chilled water supply temperature was held below the return temperature was very short. Given that once the temperature difference between the chilled water return and supply is less than 0.5°C, the chilled water supply would lose the ability to deal with the cooling load, for 12°C chilled water return, the storage vessel maintained usable chilled water supply temperature only for 0.07 h; for 16, 20, 24 and 28°C chilled water return, however, it managed to maintain usable chilled water supply temperature for 0.37, 0.38, 0.48 and 0.59 h, respectively. Therefore, even though a high cooling load consumes the discharged capacity rapidly, it can also trigger more effective hydrate dissociation to maintain a reasonable chilled water supply temperature.

![Figure 7.32 Temperatures of chilled water return, chilled water supply and PCM under peak load](image)

7.6.4 Discharge control strategies

As mentioned, there are two control strategies for discharging – ‘unadjusted pressure’ and ‘reduced pressure’. The former is implemented by directly heating the
formed hydrate without changing the volume and mass of CO$_2$ and the latter is conducted by moving the vessel pistons to increase the vessel’s inner volume or release CO$_2$ from the relief valve to reduce the pressure before heating the hydrate.

This test examined the discharging performance of using the both strategies in the CTES vessel. Using ‘reduced pressure’ the vessel’s pressure was decreased from 4.5 to 1.5 bar by releasing CO$_2$ from the relief valve; for ‘unadjusted pressure’ the pressure was 4.5 bar at the start of discharge. The bath water at 12$^\circ$C was adopted to heat the hydrate for both cases.

In Figure 7.33, the discharging rate for ‘reduced pressure’ was 1.49 times of that for ‘unadjusted pressure’ on average. The discharged capacity of the ‘reduced pressure’ case reached 0.22 kWh in 1.5 h with a total pressure increase of 1.4 bar. The discharged capacity of the ‘unadjusted pressure’ case was only 0.14 kWh in 1.5 h with a slightly smaller pressure increase of 1.1 bar.

It is known from the equilibrium diagram (Figure 7.6 (b)) that the required water temperature to dissociate the hydrate is lower when using ‘reduced pressure’ than when using ‘unadjusted pressure’. The same bath water temperature in this test made the ‘overheating’ driving force larger for the ‘reduced pressure’ case than that for the ‘unadjusted pressure’ case. Hence, the discharged capacity of the ‘reduced pressure’ case was larger. Therefore, pressure reduction is favourable for discharging, and the extent of reduction can be determined according to the equilibrium of the hydrate as well as the operating temperature conditions.

Figure 7.33 Discharging rate and discharged capacity using different control strategies
7.7 CO₂ release

CO₂ gas release in the hydrate dissociation can reflect the discharged capacity to some extent. An experiment on the whole charging-discharging process was conducted to investigate the correlation between CO₂ release and the corresponding discharged capacity.

The charge was started by cooling the vessel by 7.0°C chilled water at a constant vessel pressure of 5.5 bar, without using the external slurry loop. The slurry pump was turned on at 1.4 h after the AFS solution reduced to around the chilled water temperature. The hydrate formation immediately started after the external loop was switched on. The formation temperature was 10.2°C at the existing pressure condition. In the ‘constant pressure’ mode, the CO₂ mass was not constant and the gas flow rate from the cylinder was unknown; thus the CO₂ uptake is difficult to quantify in the charge. In this case, the CO₂ release in the discharge was calculated.

At 5.4 h, the discharge was started by closing the gas valve, moving the pistons to increase the volume from 9.6 to 17.5 L (including the volume of the crystalliser and the external loop), and the pressure in the vessel was thus decreased to 1.9 bar. The chilled water then started to supply constant 12°C water to discharge the vessel. The instantaneous CO₂ release during the dissociation could be calculated (also shown in Figure 7.34). The charged capacity was 0.27 kWh and the discharged capacity was 0.18 kW. This discrepancy was caused by the temperature difference between the initial and final temperature of the AFS solution and the heat gain from the ambient during the storage period.

The CO₂ release is in direct proportion to the latent heat from CO₂ hydrate dissociation. It was found in chapter 6 that the formation enthalpy of CO₂–TBAB semi-clathrate hydrate is 318.5 kJ·kg⁻¹ (hydrate). Using this value, the latent heat release from CO₂ hydrate dissociation in the present case was calculated. The ratio of the cooling capacity from CO₂ hydrate dissociation to the total discharged capacity was calculated and shown in Figure 7.35.

It was mentioned in chapter 6 that the hydrate formation has two exothermic processes – the distortion of hydrogen bonds to semi-clathrate structures (cages) and the inclusion of gas molecules in the cages. The CO₂ uptake is related to the second process but is not related to the first process of cage forming. In fact, the process of cages forming and cages being occupied by TBA⁺ can also store cooling capacity. In other words, not only 2.49CO₂·TBAB·38H₂O but also TBAB·38H₂O are formed in the charge of the vessel. This can be justified by the fact that the free dodecahedral cavities in the semi-clathrate structure are not fully occupied by guest gas, and the occupancy factor is affected by the temperature and pressure conditions [273-
Therefore, the discharging process also has two processes that could release cooling capacity – CO$_2$ separating from cages and cages dissociating.

![Figure 7.34 Temperature, cooling capacity, CO$_2$ uptake-release in a charging-discharging process](image)

The first derivative of pressure, temperature, pressure, and charging capacity are plotted over time. The charging rate and CO$_2$ uptake are also shown. The figure illustrates the dynamics of the discharging process.

![Figure 7.35 Discharged capacity of CO$_2$ hydrate dissociation in the total discharged capacity](image)

In Figure 7.35, the ratio of the cooling capacity from CO$_2$ hydrate dissociation to the total discharged capacity decreased from 34% to 6% as the discharge proceeded. This is attributed to the observations that at low pressure conditions (in the beginning of discharge) the first process of CO$_2$ separating from cages is favoured and the process becomes slower as the pressure increases. In contrast, the second...
process of cages dissociating is less dependent on the pressure conditions but more related to the temperature; thus it is steady and can be even enhanced as the discharge proceeds due to the melting of hydrate (thermal resistance) on the coils.

7.8 Repeatability of CO$_2$ hydrate formation

It was discussed before that the formation data of clathrate hydrate usually manifest low repeatability. It imposes a big concern on the stability of the CO$_2$–AFS semi-clathrate in the repeated operations of a practical system. To study the formation repeatability, the charging-discharging process was repeated twenty times using the ‘constant pressure’ operation mode, and the formation temperature under design experimental pressure of 5.0 bar was recorded. However, due to the error of the pressure control system these trials were conducted within the pressure range of 4.8 to 5.3 bar. There was limited ability to tightly control the gas delivery pressure, and this resulted in some scatter in the data.

Results from twenty experiments were plotted – the formation temperature is shown in Figure 7.36 and the induction time is shown in Figure 7.37. The average formation temperature measured was 9.1°C. The error in the measured formation temperatures were in a range of –0.4 to 0.4°C. Despite some scatter, the range of formation temperatures does not pose problems for the operation of a real gas hydrate CTES. The induction times measured were all within 15.5 min, which is acceptable for charging the CTES.

![Fluctuation level in formation temperature](image)

**Figure 7.36 Formation temperature of CO$_2$-AFS semi-clathrate in 20 cycles of cold storage**
7.9 Conclusion

CTES can aid in the efficient deployment of thermal energy whenever there is a mismatch between energy generation and use. Various subsets of CTES processes have been investigated and developed for building cooling systems. In this chapter, a lab-scale emulated cold storage system was built to investigate the performance of formation and dissociation of CO$_2$–AFS semi-clathrate hydrate in realistic CTES cooling system operating conditions.

The effectiveness of charging the CTES was compared in three operation modes. It was found that for the experimental system, the hydrate formation could only proceed effectively when using the external loop with nozzle. Ultrasonic vibration can reduce the induction period. However, it had no obvious effect on the formation period.

Using the stepwise temperature reduction method, 7.5°C was found to be maximum valid chilled water temperature for the CO$_2$–AFS hydrate formation at constant pressure of 5.0 bar.

It was found that substantial subcooling can increase the storage capacity of the hydrate. Also, the external loop flow rate played a significant role in the effective charge of the CTES, since it could improve both the convection heat transfer and the mass transfer between CO$_2$ and water.

Using ‘constant pressure’ in the charge made the required chilled water temperature higher than when using ‘constant mass’. This allows the chiller to operate more
efficiently. Also, the charged capacity of using ‘constant pressure’ was greater than that of using ‘constant mass’. It is suggested that the ‘constant pressure’ operation be adopted in practical cold storage systems.

The chilled water return temperature required to dissociate hydrate by using ‘reduced pressure’ was lower than that by using ‘unadjusted pressure’. Also, the discharged capacity of the ‘reduced pressure’ case was greater. Hence, pressure reduction is favourable for discharging, and the extent of reduction can be determined according to the hydrate equilibrium diagram and the operating temperature conditions.

In this constant pressure configuration, the cold storage media showed further reduced supercooling behaviour, rapid formation and small difference between the freezing and thawing temperature compared to the small volume studied in the T-history test tubes.

For the discharge, even though a high cooling load consumes more discharged capacity, it can also trigger more hydrate dissociation to maintain a reasonable outlet water temperature. This provides a hydrate CTES with a unique ability to deal very well with high peak cooling loads.

The system with 6.5 L AFS solution (containing 1.34 kg TBAB) is able to store 0.41 kWh cooling capacity if all TBAB are enclathrated in 2.49CO₂·TBAB·38H₂O. However, it was found that the storage capacity of the system was only 0.25 kWh on average. Also it was found that in discharge, the ratio of the cooling capacity from CO₂ hydrate dissociation to the total discharged capacity was 6–34%. Thus, it is believed that both 2.49CO₂·TBAB·38H₂O and TBAB·38H₂O have formed in the charge, and since the formation of 2.49CO₂·TBAB·38H₂O was restrained by factors such as CO₂ and water mass transfer and overpressure driving force, the formation of TBAB·38H₂O prevailed.

It is known that the enthalpy of 2.49CO₂·TBAB·38H₂O is much higher than that of TBAB·38H₂O; hence, future studies should focus on improving the formation of 2.49CO₂·TBAB·38H₂O in the CTES under low pressure conditions by optimising the heat exchanger structure, the gas/liquid interface and the operation mode.

Twenty times of repeated experiments showed that the formation temperatures manifested stability for the use in a real CTES; the induction times, although varied to some extent, were all short enough for practical operations. However, a longer experiment of several hundred cycles with tightly fixed conditions should be conducted if time allows. Moreover, the storage capacity of CO₂–AFS semi-clathrate hydrate should be examined as well for it is one of the most important performance indicators of the CTES. Both experiments have been planned by the author and will be conducted in an extended time after this thesis.
Conclusions and future work

Conventional chillers have undergone detailed development such that chiller efficiency is approaching its practical limits. For further improvements in energy efficiency for air conditioning of buildings, we must turn our attention to the whole air conditioning system. This system is comprised of the chiller, its energy supply infrastructure, the cooling distribution system, the building and the building occupants.

Cold thermal energy storage (CTES) provides a means to smooth supply of cooling service and demand of electricity for a building. CTES has other benefits: the chiller capacity can be reduced, thereby saving capital cost to offset the cost of CTES; off-peak electricity rates can be accessed; the chiller efficiency improves through operation overnight in cooler condensing conditions and a degree of resilience is provided to the air conditioning system.

Of the classes of CTES, phase change materials (PCMs) are ideal candidates for air conditioning applications due to their constant temperature freezing property (suits chiller evaporators that also operate a latent heat process), constant temperature melting property (suits air dehumidification) and high energy density.

Of the PCMs, the use of conventional ice is problematic because the chiller must operate its evaporator at much reduced temperature to freeze the water. This is detrimental to its efficiency. Many other PCMs are expensive (paraffins and hydrated salts) and some have cyclic stability problems due to phase segregation (hydrated salts) or have limited heat transfer capability.

In this work, we investigate gas hydrates as an option for CTES in air conditioning applications. Most small and non-polar gas molecules will form gas hydrates with water. We have selected CO\(_2\) hydrate due to its high energy density, low cost, safety and low environmental impact. However not much is known about the suitability of CO\(_2\) gas hydrates in CTES applied to air conditioning applications.
This thesis provides a broad investigation on CO₂ hydrate cold storage air conditioning applications, including a simulation on a CO₂ hydrate based cold storage cooling system driven by PV panels, the characterisation on the thermal properties of CO₂ hydrate, the modification on the formation and dissociation behaviours of CO₂ hydrate under low pressures, and an experimental study on the performance of the modified CO₂ hydrate as a PCM in an emulated cold storage system.

8.1 Main findings

It would be reasonable to expect that a PV powered air conditioner with battery electricity storage would provide a feasible alternative to a grid electricity powered air conditioner with CTES. In chapter 3, the performance of both alternatives was compared by simulation for a residential scale system in three diverse climates. The battery store provided higher primary energy savings compared to the CTES, but at much higher capital cost. Also in this study, a CTES based on CO₂ hydrate was found to be superior to both an ice CTES and a fatty acid base PCM CTES.

Gas hydrates based on CO₂ naturally form at very high pressures (~40 bar). For CO₂ hydrates to be adopted in practical and low cost CTES for air conditioning, the hydrate formation pressure must be reduced substantially. The work in chapter 4 presented an experimental study on the formation behaviour of the hydrate of TBAB, TBAF and TBPB. These quaternary salts reduce the required pressure in the formation of CO₂ semi-clathrate hydrate. It was also found that the formation temperature of the hydrate could be adjusted by changing the proportion of salt in the hydrate forming solution and that the resulting formation temperature range (5-12 °C) was suited to air conditioning system supply temperatures.

Some hydrate formation promoters were tested on these salt hydrates. It was found that surfactant SDS alleviated supercooling and shortened the induction time, while the effect of TiO₂ nanoparticle on these hydrates was less controllable. The memory effect in the repeated formations also reduced the induction time.

The T-history method was applied to salt hydrates to determine their enthalpy and heat capacity. By comparing the results to those from other studies, it was proved that the T-history method was valid and reliable to determine the phase change enthalpy of salt hydrates. Using the enthalpy method, a thermal model of a small cold storage tube was established. Through this model, it was found that the required charging time could be shortened by reducing the HTF temperature, tube size and wall thickness or by increasing the thermal conductivity of the tube wall.
Another outcome of this research is the development of a CO$_2$ hydrate based cold storage material. Leading on from the work on salt hydrates, TBAB and TBPB were selected to aid the formation of CO$_2$ hydrate since they were able to form semi-clathrates with CO$_2$ molecules at desired temperatures under reduced pressures. To study the phase equilibrium of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrate, a reaction tube was fabricated and it was able to work safely at up to 10 bar. Hydrates were formed in the tube at various salt mass fractions under different pressures with or without a secondary promoter.

It was found that under the same pressure, the equilibrium temperature increased as the proportion of salt in the hydrate forming solution rose. High gas feed pressure could also favour CO$_2$ uptake. However, high proportions of salt restrained CO$_2$ uptake to some extent. Low HTF temperatures shortened the induction time. In addition, the memory effect had an obvious impact on the induction time but only a slight impact on the formation time.

The T-history method was applied to the formation of CO$_2$–TBAB and CO$_2$–TBPB semi-clathrate hydrate. This was the first that the T-history method had been adopted to a gas hydrate at elevated pressure. It was found that the enthalpy of CO$_2$–TBAB and CO$_2$–TBPB hydrate were much larger than many other PCMs. The hydrate molecular composition formula was also determined.

Secondary promoters were tested to optimise the formation behaviour of CO$_3$–TBAB and CO$_2$–TBPB semi-clathrates. Best results were obtained with TBAB at 20 wt%, TBAF at 0.25 wt% and SDS at 0.15 wt%. In this way, the gas hydrate manifested a large CO$_2$ uptake, small supercooling degree, short induction time and cyclic stability.

This gas hydrate recipe was then used in a lab-scale emulated cold storage system to evaluate its charging and discharging performance. The experimental system was composed of a cold storage vessel with a maximum inner volume of 16.5 L, an external slurry loop (consisting of a nozzle and a crystalliser with ultrasonic transducer), and a coolant loop.

We found that effective mixing of the gas and salt solution improved hydrate formation by reducing the subcooling metastability and ultrasonic vibration assisted in the hydrate formation rate.

Charging the gas hydrate CTES under ‘constant pressure’ hydrate conditions allows a chiller to charge with elevated evaporator temperatures compared to charging with ‘constant mass’ conditions. Discharging the gas hydrate CTES under ‘reduced pressure’ hydrate conditions allows chilled water to be delivered at a lower temperature compared to discharge without pressure control. These practices are recommended with the CO$_2$ hydrate CTES as they favour chiller energy efficiency.
and CTES energy storage capacity. Furthermore, high discharge rates seemed to exhibit elevated CTES capacity, possibly due to dissociation of salt hydrate in addition to dissociation of the gas hydrate.

8.2 Future work

Chemical models of the nucleation process of CO$_2$ hydrate need to be established to understand how the supercooling degree, induction time and nucleation rate and memory effect are affected by different driving forces. Such models could be based on the model of Kashchiev et al. [152-154], Anklam et al. [155] and Kjamme et al. [156]. Chemical modelling of CO$_2$ hydrate is at an early stage of development.

The enthalpy of 2.49CO$_2$·TBAB·38H$_2$O is much higher than that of TBAB·38H$_2$O; however, in a real cold storage vessel, the formation of 2.49CO$_2$·TBAB·38H$_2$O may be restrained by both mass transfer and heat transfer, thus the charging rate may be constrained. An improved CTES structure can enhance the heat transfer between the HTF and the bulk hydrate solution. The interaction between CO$_2$ gas and water solution can affect the mass transfer. To optimise the CTES, different heat exchanger types and flow arrangements can be tried for a better charging rate.

The CTES capacity and charging rate are affected by operating conditions within the cooling application. These conditions may change with time. The CO$_2$ hydrate CTES is uniquely capable of altering its phase transition temperature by manipulation of the charging rate and hydrate pressure. Development of a control strategy that coordinates the actions of the chiller and CTES in response to a cooling load would enable maximal benefit to be realised for the use of the CTES. Some load forecasting might be beneficial to control strategy.

To assist any CTES control strategy, a means to explicitly measure the CTES state of charge is helpful. Although it is possible to estimate state of charge for the constant mass CTES operation (using gas pressure), a state of charge indicator for constant pressure operation needs to be developed.

Our first experiments with gas hydrates at ANU began in 2007 where we produced hydrates in batches of 1 cm$^3$. In this work, our batch volume has increased firstly to about 100 cm$^3$ (the pressurised test tubes) and then approaching 10,000 cm$^3$ (the vessel). Each new trial has seen the batch volume increase by two orders of magnitude! In each new trial, the apparatus developed in a direction that is heading towards a practical CTES and we have learnt more about the intriguing properties of CO$_2$ gas hydrate. In keeping with our logarithmic batch sizing, we would like now to develop a test system comprised of a real air conditioning chiller (10 kW) and a CTES of 1000 L volume. In this system we would need to overcome further design challenges to demonstrate continuous autonomous operation, coordinated
control with a varying cooling load, and to measure the CTES operating performance.

8.3 Epilogue

The first evidence for the existence of CO\textsubscript{2} hydrates dates back to the year 1882, when Wróblewski [276] reported clathrate formation while studying carbonic acid. He noted that gas hydrate was a white material resembling snow, and could be formed by raising the pressure above a certain limit in his H\textsubscript{2}O–CO\textsubscript{2} system. Over more than a century, the intriguing features of CO\textsubscript{2} hydrate have attracted numerous academics and some of its mysteries have been solved. It is now considered as a useful material for CO\textsubscript{2} capture and sequestration, replacement of CH\textsubscript{4} by CO\textsubscript{2} in naturally occurring hydrates, and for refrigeration processes. This work emphasised the feasibility of CO\textsubscript{2} hydrate in cold storage applications, which can be a promising technology for the utilisation of renewable energy and the load balance on electricity grids in the near future. We have confidence that the work presented in this thesis is of significance for the development of cold storage and air conditioning technology as well as for knowledge on CO\textsubscript{2} gas hydrate.
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Appendix

Abstract of publications

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Clathrate hydrate technology for cold storage in air conditioning systems

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Abstract

Clathrate hydrate is an attractive technology for cold storage applications. It offers a high cold storage density and elevates the phase change temperature compared to water. It offers better heat transfer properties and improved cyclic stability compared to conventional salts. This paper reviews previous work on clathrate hydrates as phase change materials (PCMs) for cold storage air conditioning applications. Three aspects have been focused on: the characteristics of clathrate hydrates, modification of clathrate hydrate properties, and practical utilization of clathrate hydrates as cold storage media. Specifically, refrigerant clathrate hydrates, CO₂ clathrate hydrates, hydrocarbon-clathrate hydrates and multi-component clathrate hydrates are introduced. Technologies to decrease equilibrium pressure, increase dissociation enthalpy, accelerate formation process, decrease supercooling extent and enhance gas solubility are summarized. Clathrate hydrate based cold storage air conditioning systems that transport cooling in a manner of fixed container as well as in hydrate slurry are reviewed, and optimizing methods of system performance are studied. Finally, four features of clathrate hydrates, namely the self-preservation effect, memory effect, gas conversion and hydrate structure transformation are discussed.

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A comparison of battery and phase change cold storage in a PV cooling system under different climates

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Keywords: PV cooling, Battery, Phase change cold storage, Primary energy saving

SUMMARY

Energy storage in PV cooling systems is desirable in supplying on-site loads during solar outages. Current storage methods of such systems typically use battery storage to conserve surplus electricity produced by solar panels, or cold thermal storage to store excess cooling capacity generated by a chiller. This study presents a simulation work using TRNSYS to predict the performance of a PV cooling system, respectively with a battery or a phase change cold storage, for a residential building under different climates - Shanghai, Madrid and Brisbane. A self-programmed cold storage component based on effectiveness-NTU method was adopted. The energy efficiency of both storages was evaluated under variable working conditions. Under different climates, both storage approaches were compared with regard to the energy consumption and primary energy saving ratio (PESR). The results revealed the feasibility of both storage approaches in PV cooling systems with favourable PESR.

1 INTRODUCTION

Building cooling over summer periods has been a major contributing factor to the increasing energy consumption and grid load over the past decades. This is mainly due to the prevalent use of conventional air-conditioning system with mechanical vapour compression refrigeration cycle. To alleviate electricity load, photovoltaic (PV) powered cooling systems have been widely implemented. Such system uses PV array as the primary generation source that converts solar energy into electricity when operated synchronously and in parallel with the electricity grid, hereby drives the chiller to meet the cooling demand and provides an alternative to the grid. To evaluate the energy saving performance, a simulation work on a PV cooling system comparing with a solar thermal cooling system was presented under different climates and cooling loads (Eicker and Colmenar-Santos et al. 2014). The results showed that the energy efficiency was favoured with the PV case, which covered almost half of the energy demand with a consequent primary energy saving of 50%.

Despite the great amount of grid power shouldered by PV arrays, solar energy with intrinsic intermittency will constantly lead to suspensions of energy supply if largely relied on. Energy
Influencing factors on the energy saving performance of battery storage and phase change cold storage in a PV cooling system

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Abstract

Energy storage is desirable in photovoltaic (PV) cooling systems to maintain service during solar outages and to supply peak cooling loads. Energy storage may be supplied using battery storage to conserve surplus electricity produced by solar panels, or cold thermal storage to store excess cooling capacity generated by a chiller. In this study, the energy saving performance of a residential solar cooling system is investigated in three distinct climates (Madrid, Shanghai, and Brisbane). The system is provided with either battery energy storage or cold storage and these cases are compared to the case where no energy storage is provided at all. The investigation is conducted by software modeling in TRNSYS. The cold storage case simulates phase-change energy stores using ice, eutectic of capric acid and lauric acid, and CO₂ clathrate hydrate. The energy saving metric is the primary energy saving ratio (PESR). A sensitivity study is conducted on the effect of the cooling load, chilled water set-point, chiller COP, storage capacity on the PESR of each storage approach. We conclude that the CO₂ clathrate hydrate was the best performing cold store and this approach provided credible savings compared to a system without energy storage. However, in most cases, battery storage provided superior primary energy savings than the cold storage.

1. Introduction

Building cooling over summer periods has been a major contributing factor to the increasing energy consumption and electricity grid load over the past decades. This is mainly due to the prevalent use of conventional air conditioning systems with the mechanical vapour compression refrigeration cycle. To alleviate electricity load, photovoltaic (PV) powered cooling systems are being implemented. PV cooling systems use solar generated electricity as the primary energy source and grid electricity as backup. The near coincidence of building cooling demand and PV sourced electricity assists to soften peak electricity demand from buildings. However, the intrinsic intermittency of PV generation must be addressed if high displacement of grid electricity is to be achieved. For PV cooling systems, current storage methods typically use battery storage to conserve surplus electricity produced by solar panels, or cold thermal storage to store excess cooling capacity generated by a chiller by means of latent heat or sensible heat. Both storage approaches can conserve sufficient energy for later use and potentially deliver higher grid electricity saving by increasing the utilization of available solar energy.

Lu et al. [1] have verified the significance of the PV and battery sizing in reducing the system lifecycle cost of a large scale grid connected PV system with battery storage. A complex algorithm was presented to determine the best manner to schedule charging and discharging the battery. Case studies presented in this paper demonstrate that the PV/battery system is able to alleviate peak grid electricity grid and peak grid electricity cost where the battery and PV system supported local loads.

The use of cold thermal storage has been investigated recently by numerous authors. Using TRNSYS modeling, Molerov-Villar et al. [2] compared a number of system configurations with thermal storage and a grid driven electric chiller as backup. They compared the energy efficiency of a residential cooling system in Spain with thermal storage in two places: first in the heat supply to a solar-thermal driven absorption chiller and second with a chilled water storage. They concluded that the system using cold storage performed better in summer but would have higher capital costs than a system with storage only in the hot water supply. This would generally be correct when the thermal chiller COP is less than about 1.0, notwithstanding increased thermal losses from the high temperature storage tank. In addition to simulation methods, experiments have been reported. Ayegun et al. [3] developed a domestic-scale prototype experimental solar cooling system consisting of evacuated tube solar collectors (12 m²), a LiBr/H₂O absorption chiller (4.5 kW) and a chilled water storage tank (1000 L). In this system,
An experimental study on the formation behavior of single and binary hydrates of TBAB, TBAF and TBPB for cold storage air conditioning applications

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HIGHLIGHTS
- We determine the formation temperature of TBAB, TBAF and TBPB semi-clathrate hydrates.
- We examine the effect of the additives, temperature difference, and memory effect.
- We present sequential images of crystal morphology along the hydrate formation.
- The supercooling and induction time can be modified by SDS and TiO₂ nanoparticles.
- The repeatability can be improved by proper temperature difference driving force.

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ABSTRACT
Thermal storage can be applied to air conditioning systems to shift the demand on electricity grids to decrease the peak load. It is also a feasible backup for solar cooling systems to supply on-site loads during solar outages. Although chilled water has been widely used for thermal storage, phase change materials offer greater energy storage density than chilled water. Semi-clathrate hydrates, having large heat of fusion and phase transition temperatures in the range of 5–10 °C, are proposed for thermal storage in air conditioning applications. This work presents an experimental study on the formation behavior of semi-clathrate hydrates based on tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium fluoride (TBAF) and tetra-n-butylphosphonium bromide (TBPB). The experiments vary the salt mass fraction from 10 wt% to 40 wt%. Single salt hydrates and binary salt mixtures are studied at various proportions. Furthermore, surfactant sodium dodecyl sulfate, 0.05–0.5 wt%) and nanoparticles (TiO₂, 20-80 nm) are employed to aid hydrate formation. The effect of the temperature difference driving force and memory effect on the hydrate formation are examined through consecutive formation and dissociation cycles. The formation temperature, maximum induction temperature and induction time are measured. It is observed that the supercooling and induction time differ for different salt hydrates. Both these parameters can be modified for air conditioning applications by suitable additives and proper operating conditions. Images of crystal morphology indicate that the columnar crystals of TBAB and TBAF are more compact than the hexagonal crystals of TBPB.

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1. Introduction
Air conditioning systems equipped with cold thermal storage offer a means to alleviate the peak load on electricity grids and to utilize power in off-peak periods. Recently, gas hydrates (or clathrate hydrates) have been widely proposed as a suitable phase change material (PCM) in cold thermal storage for the large latent heat storage density. Gas hydrates also offer proper phase transition temperatures that are good for the chiller performance while charging as well as for efficient cooling supply while discharging. However, due to the formation of most natural gas–water hydrates normally requires impractically either low temperatures or high pressures, additives to moderate the formation conditions of natural gas hydrates are of significance. Tetra-n-butylammonium bromide (TBAB) (Ali et al., 2012) has been subjected to the most intensive studies for modifying the phase transition behavior of gas hydrates by forming semi-clathrate hydrates in which TBAB molecules act both as a part of the host (the water cage) and as the guest (the molecules trapped in the water cage). There are still

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Characterisation of thermal properties and charging performance of semi-clathrate hydrates for cold storage applications

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HIGHLIGHTS

• Enthalpy and heat capacity of semi-clathrate hydrates are determined using T-history method.
• The most suitable hydrate is selected from candidates according to the thermal properties.
• A numerical model on hydrate formation in a cold storage tube is built using enthalpy method.
• Influencing factors on hydrate formation in the cold storage tube are studied.

ABSTRACT

Thermal storage for air conditioning applications has potential to flatten peak load on electricity grids and improve energy savings of cooling systems. Phase change materials (PCMs) for thermal storage have much greater energy storage density than sensible thermal storage materials. It is proven that semi-clathrate hydrates of tetra-n-butylammonium fluoride (TBAF) can offer appropriate phase change temperatures and rapid formation rates, thus they are considered favourable for cold storage. To demonstrate the feasibility of TBAF hydrate as a cold storage medium, its thermal properties are determined. TBAF aqueous solutions are tested at a mass fraction range of 15–40 wt% in the presence or absence of another two quaternary ammonium/phosphonium salts – tetra-n-butylammonium bromide (TBAH) and tetra-n-butylphosphonium bromide (TBFP). The T-history method is employed to determine the enthalpy and heat capacity of the material while the heat diffusion equation is used to obtain the material’s thermal conductivity. The material with the highest formation enthalpy was selected for further analysis. For this material, a model of hydrate formation in a cold storage tube is established using the enthalpy method. By this means, the accumulated cooling capacity and charging rate of the tube is predicted, and the influencing factors on the charging performance are studied. The results indicate that careful selection of the heat transfer fluid (HTF) temperature, tube diameter, thermal conductivity and thickness of the tube wall can all potentially shorten the required charging time of the cold storage tube.

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1. Introduction

Air conditioning systems equipped with cold storage provide a means to alleviate the peak load on electricity grids and utilise power in off-peak periods. Cold thermal storage with phase change materials (PCMs) offers large energy storage density so that it can reduce the required space of a cold store relative to a sensible cold store. Furthermore, PCMs can improve the heat transfer effectiveness in discharge because it can maintain adequate heat transfer temperature difference by its constant phase change temperature.

PCMs can also provide a constant-temperature cooling source for dehumidification.

Hydrates of natural gas are potential cold storage media to store cooling capacity with both suitable melting temperatures for building cooling supply and suitable freezing temperatures for efficient operation of the chiller. In recent years, the storage capacity and efficiency of gas hydrates based cold storage systems have been studied and improved in numerous studies [1–6]. However, most applications of natural gas hydrates were dependent on the use of quaternary ammonium/phosphonium salts to form semi-clathrate structures in order to reduce the required formation pressure. For example, tetra-n-butyl ammonium bromide (TBAH) in water forms a semi-clathrate structure, in which TBAH molecules act as both the host and the guest. In such a structure, there are still

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Phase equilibrium and formation behaviour of CO₂-TBAB semi-clathrate hydrate at low pressures for cold storage air conditioning applications

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**HIGHLIGHTS**

- The phase equilibrium of CO₂-TBAB hydrate is studied in the dissociation.
- The formation enthalpy of CO₂-TBAB hydrate is measured using the T-history method.
- The hydrate formation behaviour is investigated at various feed pressures and HTF temperatures.
- The effect of promoters, namely TBAI, SDS and TiO₂ nanoparticles, on the hydrate formation is studied.

**ABSTRACT**

Cold thermal storage has been widely used in air conditioning systems. For electric air conditioning, it helps to shift the peak load on electricity grids; for solar cooling, it enables cooling supply during solar outages. CO₂ hydrate has been proposed as a cold storage medium for its suitable phase change temperature and large latent heat. Tetra-n-butyl ammonium bromide (TBAB) has been studied to moderate the formation pressure of CO₂ hydrate. In this study, formation and dissociation of CO₂-TBAB semi-clathrate hydrate were conducted at low pressures (<10 bar) applicable to the operating conditions of air conditioning systems. The hydrates were formed with the TBAB mass fraction of 10, 20 and 32 wt%. Using the T-history method, the formation enthalpy of CO₂-TBAB semi-clathrate hydrate was measured in a self-fabricated reaction tube. In addition, the formation behaviour of CO₂-TBAB semi-clathrate hydrate, namely the CO₂ gas uptake, the induction time and the supercooling degree, were investigated under various feed pressures and heat transfer fluid (HTF) temperatures. Besides, secondary promoters (tetrabutylammonium fluoride (TBAF) at the mass fraction of 0.1, 0.5, 2.0 and 3.5 wt%, sodium dodecyl sulphate (SDS) at the mass fraction of 0.1, 0.3 and 0.5 wt%, and TiO₂ nanoparticle in 20 and 80 nm) were used to aid the hydrate formation. The aim of this study is to reduce the capital and operating cost of a CO₂ hydrate cold storage system by increasing the gas uptake, decreasing the supercooling degree and shortening the induction time.

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1. Introduction

Power consumption and greenhouse gases emission have been major concerns of the air conditioning industries. To alleviate these issues, cold storage has been applied to air conditioning systems to shift the peak load on electricity grids and to favour the chiller efficiency. The use of CO₂ hydrate as a cold storage medium or a secondary refrigerant is a novel technology (Lin et al., 2013, 2008). In the work of Zhou et al. Zhou et al. (2015), a shell-andtube fluidised bed heat exchanger combined with a storage vessel was designed to generate CO₂ hydrate slurry during the night. The COP (coefficient of performance) of the chiller in such a system was found 23–43% higher than that of conventional systems. With the continuous removal of the formed hydrate slurry, the solid fraction was maintained up to 35%. In addition to the use in space cooling (Sun and Kang, 2015), the CO₂ hydrate technology has also been applied in many other aspects, such as CO₂ gas separation (Kim et al., 2015; Babu et al., 2014; Ho et al., 2013; Park et al., 2006; Lee et al., 2015; Seo et al., 2016; Babu et al., 2015; Linga et al., 2010; Lee et al., 2010; Linga et al., 2007), hydrate-based desalination (Yang et al., 2014; Lee et al., 2011; Choi et al., 2011; Park et al., 2011; Kang et al., 2014) and engine generator (Obara et al., 2011). Therefore, a good understanding of the formation and dissociation mechanism of CO₂ gas hydrate is of great significance.

CO₂ hydrate can be generated by direct CO₂ gas injection in a
Phase Equilibrium and Formation Behavior of the CO$_2$–TBPB Semiclathrate Hydrate for Cold Storage Applications

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ABSTRACT: Cold thermal storage is primarily used for demand management on electricity grids due to air conditioner use. The CO$_2$ hydrate has been widely studied as a cold storage medium for its proper phase equilibrium temperature range and large latent heat. This study presents experimental work on the phase equilibrium behavior of the CO$_2$ hydrate under pressures (<10 bar) for the potential to use in air conditioning systems. The formation of hydrate was accelerated with 1.3-m-butylphosphonium bromide (TBPB) at mass fractions of 10, 20, 30, and 37 wt % to lower the required pressure. Instead of using complex calorimeters, the enthalpy of the CO$_2$–TBPB hydrate was measured using a modified T-history method in a self-fabricated pressure tube. Through this test, the enthalpy of the CO$_2$–TBPB hydrate was found to be much higher than for other normally used phase change materials. However, the hydrate formation was also manifested in a large degree of supercooling and a long induction delay. To reduce them, secondary promoters, namely, sodium dodecyl sulfate and TiO$_2$ nanoparticles, were used. Meanwhile, the effect of feed pressure, heat-transfer fluid temperature, promoter concentration, and the memory effect on CO$_2$–TBPB hydrate formation was investigated. This study provides suggestions for effective and efficient operation of CO$_2$–TBPB hydrate-based cold storage air conditioning systems.

1. INTRODUCTION

To alleviate the energy consumption and greenhouse gas emission caused by space cooling, cold thermal storage has been applied in electric air conditioning systems to shift the peak electricity load. This approach allows customers to realize electricity cost savings and a more energy-efficient provision of cooling service. Furthermore, it is one means of overcoming the intermittency of service for solar cooling systems. As the key in latent thermal energy storage technology, phase change materials (PCMs) and research on them are of chief importance. The use of a CO$_2$ gas hydrate as a PCM for cold thermal storage is a novel technology. Lin et al. provided the phase equilibrium data of a modified CO$_2$ hydrate and found that it could be a feasible cold storage material for its large enthalpy and suitable phase change temperature under moderate pressure.

A big limitation of the use of the CO$_2$ hydrate in cold storage is that its formation requires a pressure that is too high for the safe operation of air conditioning systems. To form the CO$_2$ hydrate at 8 °C, the corresponding formation pressure is more than 3 MPa. This pressure should be lowered since dealing safely with high pressure is costly. Current research mainly involves mitigating the hydrate formation pressure and increasing the formation rate and CO$_2$ gas capacity. For this purpose, semicladrates are proposed to help. The guests in semicladrate structures are peralkylation cations of some organic salts physically trapped in aqueous host cavities, and the anions of the organic salts are inserted into the aqueous host network via hydrogenic interactions. The methods to use tetra-n-butyl ammonium bromide (TIBAB) to form semi-cladrates are relatively mature. Besides, tetra-n-butyl ammonium chloride (TBAC), tetra-n-butyl ammonium fluoride (TBAF), tetra-n-butyl ammonium nitrate (TBANO$_3$), and tetra-n-butylphosphonium bromide (TBPB) have demonstrated their abilities to shape semicladrate structures. Some other additives such as tetrahydrofuran and cyclopentane are also reported to lower the CO$_2$ hydrate formation pressure.

The phase equilibrium data of TBPB semicladrates with CO$_2$, CH$_4$, and N$_2$ were investigated by Imani-Kashkouli et al. in a static high-pressure cell. The equilibrium data were measured at various TBPB mass fractions at temperatures of 279.3–291.4 K and pressures of 1.06–7.79 MPa. The results indicated that TBPB had a promotion effect on pure gas hydrate formation. The recent results of Mayoufi et al. showed that the dissociation enthalpy of the CO$_2$–TBPB hydrate was close to that of ice and higher than that of a single TBPB hydrate. It was believed that the CO$_2$–TBPB mixed hydrate could be used as a phase change material (PCM), which had a suitable temperature range from 284.6 to 289.0 K. In another work by Mayoufi et al., the phase equilibrium behavior of simple and mixed semicladrate hydrates formed from CO$_2$–TBPB water mixtures was studied using a pressure-controlled differential scanning calorimeter (DSC). The test was conducted at a TBPB concentration of 0–0.073 mol % in a pressure range of 0–2.0 MPa. It was found that CO$_2$ insertion had a strong

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