

Apparatus and method for forming semi-clathrate hydratesTechnical Field

The present invention relates to an apparatus for forming semi-clathrate hydrates (SCH),
5 and a method for forming SCH.

Background

The demand for cooling has been increasing rapidly, for example in space cooling, industrial process cooling, food preservation, cold chain transportation, etc. Cooling is one of the major contributors to electricity consumption, especially in tropics. There is a
10 need to improve the efficiency of cooling systems to save energy and reduce carbon emission. A common practice currently used is to use chilled water to deliver cold energy from source to user end. However, due to the limited cooling capacity of water, a large amount of chilled water may be required to supply particular cooling loads, thus leading to high pumping energy consumption.

15 Due to the high latent heat associated with solid-liquid phase change as compared with the sensible heat of a single-phase material, phase change materials (PCMs) have been considered for use as thermal energy carriers to replace chilled water in cooling systems. Ice slurries, micro-encapsulated phase change material slurries and semi-clathrate hydrates are some examples which have been considered as being favourable for
20 cooling applications. However, there are many limitations for their use. For example, semi-clathrate hydrates have not commonly been used in commercial cooling systems due to the lack of efficient generation methods of semi-clathrate hydrates and poor rheological performance.

There is therefore a need for an improved cooling system which is more energy efficient
25 and scalable for use in various applications.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved method for forming semi-clathrate hydrates (SCH). There is also provided an apparatus for forming the semi-clathrate hydrates.

30 According to a first aspect, there is provided an apparatus for forming SCH, the apparatus comprising:

- a first storage tank for storing a semi-clathrate based solution;
- a heat exchanger in fluid connection with the first storage tank for enabling formation of SCH from the semi-clathrate based solution, wherein an inner surface of the heat exchanger is coated with a hydrophobic coating;
- 5 - a cooling unit connected to the heat exchanger for providing cooling to the heat exchanger; and
- a second storage tank for collecting and/or storing the formed SCH.

The apparatus may be connected to a system for transporting the formed SCH for use
10 as a thermal energy carrier.

According to a particular aspect, the hydrophobic coating comprises a polymer. The polymer may be any suitable polymer. For example, the coating may comprise a polymer which may be, but not limited to, perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), or a combination thereof.

- 15 The coating may be of a suitable thickness. For example, the coating may have a thickness of 10-80 μm .

The heat exchanger may be any suitable heat exchanger. For example, the heat exchanger may be, but not limited to, a tube and shell type heat exchanger, a plate heat exchanger, tube-in-tube heat exchanger, or a combination thereof.

- 20 According to a particular aspect, the apparatus may further comprise an electrical resistivity sensor in fluid connection with the heat exchanger for measuring the electrical resistivity of slurry comprised in the heat exchanger.

According to a second aspect, there is provided a method of forming semi-clathrate hydrates (SCH), the method comprising:

- 25 - feeding a semi-clathrate based solution into a heat exchanger, wherein an inner surface of the heat exchanger is coated with a hydrophobic coating; and
- cooling the heat exchanger to enable formation of SCH from the semi-clathrate based solution.

- 30 According to a particular aspect, the hydrophobic coating may be any suitable coating. For example, the hydrophobic coating may comprise a polymer. The polymer may be

any suitable polymer. For example, the polymer may be, but not limited to, perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), or a combination thereof.

The hydrophobic coating may have a suitable thickness. For example, the hydrophobic coating may have a thickness of 10-80 μm .

The heat exchanger may be any suitable heat exchanger. For example, the heat exchanger may be a tube and shell type heat exchanger, a plate heat exchanger, tube-in-tube heat exchanger, or a combination thereof.

According to a particular aspect, the semi-clathrate based solution may comprise an additive for increasing SCH formation kinetics and reducing viscosity. For example, the additive may comprise, but is not limited to: semi-clathrate hydrate seed crystal, an amino acid, an anti-agglomerant (AA), or a combination thereof.

The method may further comprise measuring the electrical resistivity of slurry comprised in the heat exchanger during the formation of the SCH to enable measuring weight fraction of SCH in the slurry.

According to a particular aspect, the method may further comprise adding pre-formed SCH as seed crystals to a slurry comprising SCH formed following the cooling.

According to a particular aspect, the method may further comprise transporting the formed SCH for use as a thermal energy carrier. In particular, the method may comprise adding a viscosity-reducing additive to the formed SCH prior to the transporting. The viscosity-reducing additive may be any suitable viscosity-reducing additive. For example, the viscosity-reducing additive may comprise, but is not limited to: an amino acid, an anti-agglomerant (AA), or a combination thereof.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic representation of an apparatus for forming SCH according to one embodiment;

Figure 2 shows a schematic representation of an apparatus for forming SCH according to one embodiment;

Figure 3 shows a schematic representation of an apparatus for forming SCH according to one embodiment;

5 Figure 4 shows temperature and electrical resistivity changes during SCH formation;

Figure 5 shows the cooling performance between different cooling medium;

Figure 6 shows the cooling capacity of SCH slurry formed from tetra-n-butylammonium bromide (TBAB) having hydrate fraction of 0.32 at 8°C and of chilled water at 8°C for cooling hot air at 35°C;

10 Figure 7 shows the hydrate fraction determined by the lever rule and the electrical resistivity-based method according to one embodiment;

Figure 8 shows the electrical resistivity and hydrate fraction of SCH at 3°C according to one embodiment;

Figure 9 shows the kinetics of SCH formation according to one embodiment; and

15 Figure 10 shows the final hydrate fraction formed according to one embodiment.

Detailed Description

As explained above, there is a need for an improved cooling system, particularly one which uses semi-clathrate hydrates (SCH) as thermal energy carriers.

In general terms, the present invention provides an apparatus to generate SCH, and
20 subsequently transport these to end users via pipelines. The apparatus may comprise a heat exchanger with a coating for efficient SCH generation. There is also provided a method of forming the SCH, particularly by using cold energy from suitable sources, such as LNG re-gasification. In particular, the integration of cold energy eliminates the need for conventional refrigeration cooling loop which utilise chillers and cooling towers. In this
25 way, a vast amount of energy and space occupied is saved. The method may also comprise a seed-induced generation method to enhance the SCH formation kinetics, as well as to reduce viscosity of the formed SCH so that the pumping power required for transporting the SCH via pipelines is reduced.

In particular, SCH are made from water and quaternary ammonium salts. The SCH have a high enthalpy of dissociation (~200 kJ/kg) due to the extensive hydrogen bonding framework similar to structure of ice. Its advantages include suitable phase change temperatures (0-27°C) for cooling applications, high thermal density compared to chilled
5 water, well-controlled solid fraction in slurry and high stability during cycling operation.

According to a first aspect, there is provided an apparatus for forming SCH, the apparatus comprising:

- a first storage tank for storing a semi-clathrate based solution;
- a heat exchanger in fluid connection with the first storage tank for enabling
10 formation of SCH from the semi-clathrate based solution, wherein an inner surface of the heat exchanger is coated with a hydrophobic coating;
- a cooling unit connected to the heat exchanger for providing cooling to the heat exchanger; and
- a second storage tank for collecting and/or storing the formed SCH.

15

The apparatus may be connected to a system for transporting the formed SCH for use as a thermal energy carrier.

The hydrophobic coating may be any suitable coating. According to a particular aspect, the hydrophobic coating may be a polymer-based coating. In particular, the hydrophobic
20 coating may comprise a polymer. The polymer may be any suitable polymer. For example, the hydrophobic coating may comprise, but is not limited to, perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), or a combination thereof.

The hydrophobic coating may be of a suitable thickness. For example, the hydrophobic
25 coating may have a thickness of 10-80 µm. In particular, the thickness may be 15-75 µm, 20-70 µm, 25-65 µm, 30-60 µm, 35-55 µm, 40-50 µm, 45-47 µm. Even more in particular, the thickness may be 35-45 µm, preferably about 40 µm.

The heat exchanger may be any suitable heat exchanger. For example, the heat exchanger may be, but not limited to, a tube and shell type heat exchanger, a plate heat
30 exchanger, tube-in-tube heat exchanger, or a combination thereof.

According to a particular aspect, the apparatus may further comprise an electrical resistivity sensor in fluid connection with the heat exchanger for measuring the electrical resistivity of slurry comprised in the heat exchanger.

Having now generally described the apparatus, the same will be more readily understood
5 through reference to the following examples which are provided by way of illustration, and are not intended to be limiting.

Apparatus comprising a continuous plate heat exchanger

A schematic representation of one embodiment of the apparatus comprising a continuous plate heat exchanger is as shown in Figure 1. The apparatus comprises a
10 plate heat exchanger, pumps, solution and slurry storage tanks, a chiller, an electrical resistivity sensor, a fan coil or air handling unit and pressure and temperature sensors.

The plate heat exchanger (PHE) is coated with a hydrophobic material which prevents adhesion or deposition of the formed hydrate crystals on the walls of the heat exchanger. A chiller may be connected to the PHE to provide the necessary cooling. The chiller may
15 be replaced with waste LNG cold energy from LNG regassification. An electrical resistivity sensor may be placed between the PHE and hydrate slurry tank to measure the electrical resistivity of the hydrate slurry. The hydrate weight fraction in the slurry may be determined from the measured electrical resistivity, as explained in detail below in relation to the second aspect.

20 The semi-clathrate based solution from the solution tank may be pumped using a pump P2 to cool to the desired temperature via the PHE. As the solution cools below the semi-clathrate phase equilibrium temperature, SCH crystals start forming. For faster and consistent formation of hydrate slurry, tiny amount of pre-produced crystals may be injected into supercooled solution as a nucleating agent (seed) via syringe pump. The
25 seed crystals may be injected after the supercooled solution leaves the PHE.

The electrical resistivity of the solution/slurry may be measured to check whether desired hydrate fraction has been achieved. If desired hydrate fraction has not been achieved, the cooled solution/slurry may be circulated using 3-way valves via PHE to achieve desired hydrate fraction. Once the desired hydrate fraction has been achieved, the slurry
30 may be collected in the slurry storage tank. This process may form the generation cycle. The slurry may be pumped to the fan coil unit (FCU) or air handling unit (AHU) using a

pump P1. In the FCU or AHU, the SCH in the slurry melt as it gets heated by the incoming air. The incoming air gets cooled due to melting of SCH since melting is an endothermic process. The flow rate of the slurry is achieved using a PID controller to achieve the desired air temperature. The solution from the AHU or FCU is sent back to the solution tank. This process forms the utilization cycle. With optimized flow rate of the solution/slurry, we can operate this process in continuous mode.

Apparatus comprising a tube and shell heat exchanger

A schematic representation of one embodiment of the apparatus comprising a tube and shell heat exchanger is as shown in Figure 2. The apparatus comprises a chiller, two semi-clathrate slurry/solution tanks, a tube and shell heat exchanger, pump, electrical resistivity sensor, AHU or FCU and pressure and temperature sensors.

For this embodiment, the tube and shell heat exchanger has one shell and multiple tubes. However, the heat exchanger may be any suitable tube and shell heat exchanger. The storage tank comprising the semi-clathrate solution acts as the shell. The tubes carry the coolant required to cool the semi-clathrate solution in the storage tank. The outer layer of the tubes may be coated with a hydrophobic coating as described above to prevent deposition of SCH crystals on to them. A vibrator may be added to the tubes which may aid in preventing deposition of SCH as well. An electrical resistivity sensor may measure the electrical resistivity of the solution/slurry to determine the hydrate weight fraction in the slurry.

The operation of the prototype may be as follows: the semi-clathrate solution in storage tank 1 may be cooled to the determined temperature to achieve desired hydrate weight fraction. At the initial stage, a tiny amount of hydrate seed may be injected into the storage tank 1 to make the hydrate slurry. Once the desired weight fraction is achieved, the slurry from the tank 1 may be pumped to the AHU or FCU to cool the incoming air. The solution from the AHU or FCU may be collected in storage tank 2. Meanwhile, the flow of coolant may be diverted to cool the solution in the storage tank 2 to produce hydrate slurry in tank 2. The storage tanks operate in series and parallel to make the process of production of slurry continuous. The switching of flow of slurry and coolant to different tank may be achieved using a PID controller and control valves (V1 to V4 as shown in Figure 2).

Apparatus comprising a plate heat exchanger

A schematic representation of one embodiment of the apparatus comprising a plate heat exchanger is as shown in Figure 3. The apparatus as shown in Figure 3 integrates the hydrate generation and utilization. Efficient hydrate generation method, as well as environmentally benign promoters were used. The generation section of the apparatus may comprise a temperature control system, a plate heat exchanger, a centrifugal pump (Pump 1) and three tanks. During semi-clathrate slurry generation, warm liquid TBAB solution may be pumped from Tank 1, pass through the plate heat exchanger and returned to Tank 1. The other side of the heat exchanger may be cooled by cold ethylene glycol stream mimicking the cold energy source. Once all the TBAB solution in Tank 1 is cooled to a suitable temperature, semi-clathrate hydrates may be generated.

The utilization section consists of a slurry pump (Pump 2), a fan, a heater, and an air handling unit (AHU). TBAB semi-clathrate slurry may be pumped from Tank 1 into the AHU to deliver cold energy. On the other side, hot air may be circulated by the fan and cooled by the AHU heat exchanger. The heater can generate heat at a heating load up to 10 kW mimicking the heat source at data racks. After cooling the hot air, TBAB semi-clathrate slurry may melt and become liquid solution again, and may be collected in Tank 2. During the utilization cycle of the semi-clathrate slurry in Tank 1, Tank 3 may undergo the generation cycle, which makes the overall generation and utilization processes continuous.

A control and data acquisition program may optionally be used for controlling the temperature control system settings to mimic various conditions at the cold energy source side. The flow rate of pump 1 and pump 2 as well as the speed of the fan may be controlled manually or by proportional integral derivative (PID). The on/off of the 14 digital control valves may be controlled via the interface. A total of 15 temperature measurement points, 7 pressure measurement points, 4 electrical conductivity measurement points, 3 liquid level measurement points, 3 flow rate measurement points, and 1 air flow speed measurement point may be recorded at the same time. However, it would be clear to a skilled person that variations are possible.

Use of the apparatus of Figure 3 has been demonstrated. In particular, TBAB semi-clathrate slurry was formed using the apparatus of Figure 3 from 500 kg of 20 wt % TBAB solution.

Figure 4 shows the temperature and electrical resistivity curves during one generation run operated at around 8°C. It took around 60 min to cool the TBAB solution from 20°C to 8°C. Subsequently, around 40 mL of TBAB SCH seeds were injected into the solution, after which a temperature spike was observed indicating hydrate nucleation. Meanwhile, the electrical resistivity increased due to the decrease of temperature during the first hour and generation of non-conductive hydrates after the one hour. At the end of the generation cycle (~ 280 min), it was estimated that 32% of the solution had converted to SCH. The generation of massive SCH was confirmed by visual observation.

Once a sufficient amount of SCH was generated, the slurry was pumped to the AHU at different flow rates to test its performance on cooling the hot air at 35°C with the heater tuned off. Figure 5 presents a comparison on cooling performance between TBAB semi-clathrate slurry and TBAB aqueous solution at 8°C. As can be seen from Figure 5, at the same flow rate, TBAB semi-clathrate slurry could cool the hot air from 35°C to below 20°C at a much faster pace. The cooling speed of TBAB hydrate slurry was more than double that of TBAB solution. Furthermore, even when the flow rate of TBAB solution was increased from 400 kg/h to 800 kg/h, its cooling performance was still much worse than that of TBAB semi-clathrate hydrate slurry at 400 kg/h.

The cooling performance of TBAB semi-clathrate hydrate slurry was also compared with chilled water and shown in Figure 6. In this case, both cold energy carriers were pumped into the AHU to cool hot air at 35°C with the heater on, and the maximum cooling capacities that each energy carrier could achieve at certain flow rates were measured. The cooling capacity of TBAB hydrate slurry was higher than that of chiller water, and its superiority was more significant when the flow rate was high, e.g., at 400 kg/h, the cooling capacity of TBAB hydrate slurry was more than 60% higher than that of chilled water.

According to a second aspect, there is provided a method of forming semi-clathrate hydrates (SCH), the method comprising:

- feeding a semi-clathrate based solution into a heat exchanger, wherein an inner surface of the heat exchanger is coated with a hydrophobic coating; and
- cooling the heat exchanger to enable formation of SCH from the semi-clathrate based solution.

The hydrophobic coating may be any suitable coating. According to a particular aspect, the hydrophobic coating may be a polymer-based coating. In particular, the hydrophobic coating may comprise a polymer. The polymer may be any suitable polymer. For example, the hydrophobic coating may comprise, but is not limited to, perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), or a combination thereof.

The hydrophobic coating may be of a suitable thickness. For example, the hydrophobic coating may have a thickness of 10-80 μm . In particular, the thickness may be 15-75 μm , 20-70 μm , 25-65 μm , 30-60 μm , 35-55 μm , 40-50 μm , 45-47 μm . Even more in particular, the thickness may be 35-45 μm , preferably about 40 μm .

The heat exchanger may be any suitable heat exchanger. For example, the heat exchanger may be, but not limited to, a tube and shell type heat exchanger, a plate heat exchanger, tube-in-tube heat exchanger, or a combination thereof.

The semi-clathrate based solution may be any suitable solution. For example, the semi-clathrate based solution may comprise, but is not limited to, an additive for increasing SCH formation kinetics and reducing viscosity. According to a particular aspect, the additive may comprise, but is not limited to: semi-clathrate hydrate seed crystal, an amino acid, an anti-agglomerant (AA), or a combination thereof.

The semi-clathrate based solution may comprise a suitable amount of semi-clathrate hydrate formers. In particular, the amount of semi-clathrate hydrate formers comprised in the semi-clathrate based solution may range from 10-60 wt %, preferably 10-40 wt %. In particular, the semi-clathrate based solution may comprise 15-35 wt %, 20-30 wt %, 25-27 wt % semi-clathrate hydrate formers based on the total weight of the semi-clathrate based solution.

The semi-clathrate hydrate formers may be any suitable semi-clathrate hydrate former. For example, the semi-clathrate hydrate former may comprise, but is not limited to, tetra-n-butylammonium bromide (TBAB), tetra-n-butylammonium fluoride (TBAF), tetra-n-butylammonium chloride (TBAC), tetra-n-butylammonium acetate (TBAAce), tetra-n-butylammonium acrylate (TBAAcr), tetra-n-butylammonium propionate (TBAPro), tetra-n-butylammonium butyrate (TBABut), tetra-n-butylammonium 2-hydroxybutyrate (TBA2HB), tetra-n-butylammonium 3-hydroxybutyrate (TBA3HB), tetra-n-butylammonium 2-ethylbutyrate (TBA2EB), tetra-n-butylammonium lactate (TBALac),

tetra-n-butylphosphonium bromide (TBPB), tetra-n-butylphosphonium chloride (TBPC), tetra-n-butylphosphonium acetate (TBPAce), tetra-n-butylphosphonium acrylate (TBPAcr), tetra-n-butylphosphonium propionate (TBPPro), tetra-n-butylphosphonium butyrate (TBPBut), tetra-n-butylphosphonium lactate (TBPLac), or a combination thereof.

The fraction of solid SCH formed in the formed SCH slurry during the generation cycle may depend on the desired cooling load. For the purposes of the present application, reference to slurry refers to a mixture of the formed SCH in the semi-clathrate based solution. For example, the SCH slurry formed may comprise 5-60 wt % solid SCH based on the total weight of the semi-clathrate based solution. This refers to 5-60 wt % of the semi-clathrate based solution may be converted to SCH. In particular, the SCH slurry formed may comprise 10-55 wt %, 15-50 wt %, 20-45 wt %, 25-40 wt %, 30-35 wt % SCH based on the total weight of the semi-clathrate based solution. According to a particular embodiment, for a cooling load of 10 kW, the feed may comprise of 40 wt % hydrate fraction of type B semi-clathrate hydrate formed from an initial TBAB concentration of 40 wt % and flowing at a rate of 340.38 kg/h.

According to a particular aspect, the method may further comprise adding pre-formed SCH as SCH seed crystals to a slurry comprising SCH formed following the cooling. As explained above, the slurry comprises a mixture of SCH formed following the cooling in the semi-clathrate based solution. The pre-formed SCH as a seed crystal may comprise any suitable SCH. In particular, the pre-formed SCH may comprise, but is not limited to, tetra-n-butylammonium bromide (TBAB) hydrate, tetra-n-butylammonium fluoride (TBAF) hydrate, tetra-n-butylammonium chloride (TBAC) hydrate, tetra-n-butylammonium acetate (TBAAce) hydrate, tetra-n-butylammonium acrylate (TBAAcr) hydrate, tetra-n-butylammonium propionate (TBAPro) hydrate, tetra-n-butylammonium butyrate (TBABut) hydrate, tetra-n-butylammonium 2-hydroxybutyrate (TBA2HB) hydrate, tetra-n-butylammonium 3-hydroxybutyrate (TBA3HB) hydrate, tetra-n-butylammonium 2-ethylbutyrate (TBA2EB) hydrate, tetra-n-butylammonium lactate (TBALac) hydrate, tetra-n-butylphosphonium bromide (TBPB) hydrate, tetra-n-butylphosphonium chloride (TBPC) hydrate, tetra-n-butylphosphonium acetate (TBPAce) hydrate, tetra-n-butylphosphonium acrylate (TBPAcr) hydrate, tetra-n-butylphosphonium propionate (TBPPro) hydrate, tetra-n-butylphosphonium butyrate (TBPBut) hydrate, tetra-n-butylphosphonium lactate (TBPLac) hydrate, or a combination thereof.

The amino acid which may be added as an additive may be any suitable amino acid. For example, the amino acid may comprise, but is not limited to, alanine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, valine, or a combination thereof.

The anti-agglomerant (AA) may be any suitable AA. For example, the AA may comprise, but is not limited to, cyclodextrin, rhamnolipids, sorbitan fatty acid esters, amine oxides, or a combination thereof.

The method may further comprise measuring the electrical resistivity of slurry comprised in the heat exchanger during the formation of the SCH to enable measuring weight fraction of SCH in the slurry. The measuring may be by any suitable method. For example, the method may comprise, but is not limited to, using a LCR meter with two or four probes, integrated electrical resistivity or conductivity sensors.

According to a particular aspect, the method may further comprise transporting the formed SCH slurry for use as a thermal energy carrier. In particular, the method may comprise adding a viscosity-reducing additive to the formed SCH slurry prior to the transporting. The viscosity-reducing additive may be any suitable viscosity-reducing additive. For example, the viscosity-reducing additive may comprise, but is not limited to: an amino acid, an anti-agglomerant (AA), or a combination thereof. Each of the amino acid and AA may be as described above.

Having now generally described the method, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting.

Monitoring system of hydrate fraction using electrical resistivity

The mass fraction of hydrate in a hydrate slurry, called the hydrate fraction, may be the key factor to determine the cooling capacity and flow properties of SCH slurry. Currently available methods only provide estimates of the hydrate fraction at the equilibrium point based on the equilibrium temperature, salt concentration in the liquid solution and hydrate phases. However, in this way, only the hydrate fraction at equilibrium point and not in the non-equilibrium state may be determined. Therefore, most of kinetic

experiments of semi-clathrate hydrate do not disclose the hydrate fraction trend (non-equilibrium state) due to lack of suitable method.

For typical gas hydrate systems, the hydrate growth kinetics (including non-equilibrium state) may be reliably evaluated via the pressure drop of gas phase in the system. On the other hand, for systems comprising SCH, since there is no gas involved, there is difficulty in determining the detailed kinetic data during the hydrate formation. Thus, there is no reliable and straightforward method to quantitatively observe the hydrate formation kinetics. Based on the method of the present invention, there is provided an accurate and straightforward method to quantify the SCH fraction in slurry based on in-situ electrical resistivity measurement.

It was first confirmed if an electrical resistivity method may predict the hydrate fraction in semi-clathrate hydrate slurry at equilibrium conditions by comparing the results from lever rule (common method described above as currently used at equilibrium conditions). As shown in Figure 7, the hydrate fraction calculated using the lever rule and electrical resistivity methods were in good agreement.

It was observed that when the conductive electrolyte solution converted to non-conductive hydrates, the electrical resistivity of hydrate slurry changed by the amount of hydrate (e.g., hydrate fraction in slurry), which allows analysis of the hydrate growth kinetics. Figure 8 shows the electrical resistivity and estimated hydrate fraction in TBAB SCH slurry during hydrate formation (non-equilibrium state) by the method of the present invention. The electrical resistivity of a hydrate slurry increased with the formation and growth of hydrate.

Interestingly, in the case of TBAB hydrates formed from 20 wt % TBAB solution, electrical resistivity showed a two-step change, which indicated a two-stage hydrate growth (see Figure 8). This may be related to formation of two types of TBAB hydrates, namely, type A and type B with different hydration numbers and crystalline structures. The hydration number of type A and type B TBAB hydrates is 26 and 38, which means the hydrate fraction for type B is typically higher than for type A at the same temperature. The first growth stage indicated formation of type A hydrates and the second growth stage indicated conversion of type A hydrates to type B hydrate, which led to an increase in hydrate fraction.

Method of forming SCH

Key challenges in SCH formation include the high subcooling degree and long induction time required for nucleation. Generally, a lower formation temperature (high subcooling) may be employed to reduce induction and enhance hydrate formation kinetics. However, a lower formation temperature may require more energy and make a large solid fraction, which can lead to bad flowability.

As seen in Figure 8, type A TBAB hydrate formed first and converted to type B hydrate in the end. However, the conversion from type A to type B is unpredictable, thereby leading to yet another challenge in the practical use of SCH in cooling processes.

Accordingly, the method according to one embodiment utilised pre-produced seed with type A and type B separately. It should be noted that each type of pre-produced seed may be made from stoichiometric concentrations (for example, 40.8 wt % for type A and 32.0 wt % for type B) with the flowable slurry state under near the equilibrium temperature, for example, 11.5°C for type A and 9.5°C for type B. It was observed that the SCH was immediately produced within a few minutes right after adding the tiny amount of seed (less than 0.1 wt % in total solution) into the subcooled TBAB solution.

Figure 9 shows the kinetic behaviour of TBAB hydrate formation in the absence and presence of pre-produced seeds. Interestingly, the initial formed type of hydrate was dependent on the type of pre-produced seed provided. For example, Type A pre-produced seed formed type A TBAB hydrates with needle-like morphology and no phase transition observed for 12 hrs, which was similar to hydrates formed from absence of seed. On the other hand, the addition of type B seed directly formed type B TBAB hydrates with irregular shaped morphology with higher final hydrate fraction than type A seed (Figure 10). It is worth noting that this method is straight forward and able to quickly produce hydrates without adding any additional compounds.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Based on the above, it can be seen that the apparatus and method of the present invention provide a simple and scalable way of forming SCH which may then be used for various applications, particularly cooling applications. Use of SCH for cooling applications provides a more efficient method of cooling as compared to current methods using chilled water.

Claims

1. An apparatus for forming semi-clathrate hydrates (SCH), the apparatus comprising:
- a first storage tank for storing a semi-clathrate based solution;
 - 5 - a heat exchanger in fluid connection with the first storage tank for enabling formation of SCH from the semi-clathrate based solution, wherein an inner surface of the heat exchanger is coated with a hydrophobic coating;
 - a cooling unit connected to the heat exchanger for providing cooling to the heat exchanger; and
 - 10 - a second storage tank for collecting and/or storing the formed SCH.
2. The apparatus according to claim 1, wherein the hydrophobic coating comprises a polymer.
- 15 3. The apparatus according to claim 1 or 2, wherein the hydrophobic coating comprises: perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), or a combination thereof.
4. The apparatus according to any preceding claim, wherein the hydrophobic coating has a thickness of 10-80 μm .
- 20 5. The apparatus according to any preceding claim, wherein the heat exchanger is a tube and shell type heat exchanger, a plate heat exchanger, tube-in-tube heat exchanger, or a combination thereof.
- 25 6. The apparatus according to any preceding claim, wherein the apparatus further comprises an electrical resistivity sensor in fluid connection with the heat exchanger for measuring the electrical resistivity of slurry comprised in the heat exchanger.
- 30 7. The apparatus according to any preceding claim, wherein the apparatus is connected to a system for transporting the formed SCH for use as a thermal energy carrier.
8. A method of forming semi-clathrate hydrates (SCH), the method comprising:

- feeding a semi-clathrate based solution into a heat exchanger, wherein an inner surface of the heat exchanger is coated with a hydrophobic coating; and
- cooling the heat exchanger to enable formation of SCH from the semi-clathrate based solution.

9. The method according to claim 8, wherein the hydrophobic coating comprises a polymer.

10. The method according to claim 8 or 9, wherein the hydrophobic coating comprises: perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), or a combination thereof.

11. The method according to any of claims 8 to 10, wherein the hydrophobic coating has a thickness of 10-80 μm .

12. The method according to any of claims 8 to 11, wherein the heat exchanger is a tube and shell type heat exchanger, a plate heat exchanger, tube-in-tube heat exchanger, or a combination thereof.

13. The method according to any of claims 8 to 12, wherein the method further comprises measuring the electrical resistivity of slurry comprised in the heat exchanger during the formation of the SCH to enable measuring weight fraction of SCH in the slurry.

14. The method according to any of claims 8 to 13, wherein the method further comprises adding pre-formed SCH as seed crystals to a slurry comprising SCH formed following the cooling.

15. The method according to any of claims 8 to 14, wherein the semi-clathrate based solution comprises an additive for increasing SCH formation kinetics and reducing viscosity.

16. The method according to claim 15, wherein the additive comprises: semi-clathrate hydrate seed crystal, an amino acid, an anti-agglomerant (AA), or a combination thereof.

17. The method according to any of claims 8 to 16, wherein the method further comprises transporting the formed SCH for use as a thermal energy carrier.

5 18. The method according to claim 17, wherein the method further comprises adding a viscosity-reducing additive to the formed SCH prior to the transporting.

19. The method according to claim 18, wherein the viscosity-reducing additive comprises: an amino acid, an anti-agglomerant (AA), or a combination thereof.