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Review

Clathrate Hydrates for Thermal Energy Storage in Buildings: Overview of Proper Hydrate-Forming Compounds

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Abstract: Increasing energy costs are at the origin of the great progress in the field of phase change materials (PCMs). The present work aims at studying the application of clathrate hydrates as PCMs in buildings. Clathrate hydrates are crystalline structures in which guest molecules are enclosed in the crystal lattice of water molecules. Clathrate hydrates can form also at ambient pressure and present a high latent heat, and for this reason, they are good candidates for being used as PCMs. The parameter that makes a PCM suitable to be used in buildings is, first of all, a melting temperature at about 25 °C. The paper provides an overview of groups of clathrate hydrates, whose physical and chemical characteristics could meet the requirements needed for their application in buildings. Simulations with a dynamic building simulation tool are carried out to evaluate the performance of clathrate hydrates in enhancing thermal comfort through the moderation of summer temperature swings and, therefore, in reducing energy consumption. Simulations suggest that clathrate hydrates have a potential in terms of improvement of indoor thermal comfort and a reduction of energy consumption for cooling. Cooling effects of 0.5 °C and reduced overheating hours of up to 1.1% are predicted.

Keywords: clathrate hydrates; phase change materials; building simulation; thermal storage

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1. Introduction

The building sector is the dominant energy consumer around the world with a total of 30% of the share of the overall energy consumption [1].

Moreover, in recent years, the energy demands for buildings have increased very rapidly due to an increase in the growth rate of the population, an evolving indoor comfort expectation and technological development worldwide. Increasingly, advanced technologies and methodologies have been investigated and developed to cope with the increasing demand of energy and resources [2–4].

Thermal energy storage is an efficient method to improve the energy efficiency of buildings and obtain a significant economic benefit [5].

Thermal energy storage can be accomplished either by using sensible heat storage or latent heat storage [6]. Sensible heat storage has been used for centuries by builders to store/release thermal energy passively, but a much larger volume of material is required to store the same amount of energy in comparison to latent heat storage.

Latent heat storage is a very efficient way of storing thermal energy: unlike sensible heat storage, latent heat storage is characterized by a higher storage density and by a smaller temperature difference between storing and releasing heat [7]. Latent heat storage is achieved using the so-called phase change materials (PCMs).

The principle of using the phase change materials is simple: as the heat is supplied, the material changes its phase from solid to liquid and *vice versa* at a constant temperature, until it completely converts into a solid. Similarly, when heat is released, the material changes phase from liquid to solid, again at a constant temperature, until it solidifies completely [8].

The latent heat storage by using PCMs in buildings is an attractive way to compensate for the small storage capacity of most existing modern buildings. Using PCM material in buildings can decrease the temperature fluctuation, particularly due to incident solar radiation loads, as proven in several numerical studies [9].

In the last 40 years, several materials have been studied, in particular hydrated salts, paraffin waxes, fatty acids and eutectics of organic and non- organic compounds [10–14]. In addition to the mentioned materials, clathrate hydrates show an interesting behavior as a PCM.

Clathrates are crystalline structures in which molecules of one type are enclosed in the crystal lattice of another. Clathrate hydrates have been studied as a technology for gas storage and separation [15,16], but thanks to formation occurring also at ambient pressure and a high latent heat, they are also good candidates for being used as a PCM [17].

Generally, PCMs should meet several requirements, divided into three main groups:

- Physical requirements (high density, high latent heat of fusion for unit mass, high specific heat);
- Chemical requirements (chemical stability, chemical non decomposition, non-corrosiveness with respect to the construction materials, non-toxicity);
- Economic requirements (wide availability of material, low material costs).

The objective of the present work is to provide an overview of groups of clathrate hydrates, whose physical and chemical characteristics meet the requirements needed for their application in buildings.

After a brief description of thermal storage applications for which clathrate hydrates are already used, data on the physical and chemical characteristics of clathrate hydrates for building applications are provided.

Simulations are carried out to evaluate the performance of clathrate hydrates in enhancing thermal comfort through the reduction of summer temperature swings and, therefore, in reducing energy consumption. The effect of clathrate hydrate PCM wallboard on indoor temperatures is examined for a building located in Rome using a dynamic building simulation tool and is compared to commercial wax PCM wallboards.

2. Clathrate Hydrates as Phase Change Materials

An attractive application of clathrate hydrates is thermal storage as a PCM. In general, the use of PCMs depends on their melting temperature: (i) T < 15 °C, they are used for storing coolness in air conditioning applications; (ii) T > 90 °C, they are used for absorption refrigeration; and (iii) 15 °C < T < 90 °C, they are used in solar heating and in heat load leveling applications. Among these uses, residential building applications have been receiving growing attention in the last few years in order to obtain PCMs with the required melting point and thermal properties. Exhaustive surveys on various existing types of PCM can be found in the literature [5,6,11–14,18–27], and data are reported in Table 1. Figure 1 shows the thermal properties of clathrate hydrates with respect to the other existing PCMs.

Figure 1. Melting temperature and fusion heat of existing phase change materials (PCMs), based on [5,6,11–14,18–27].

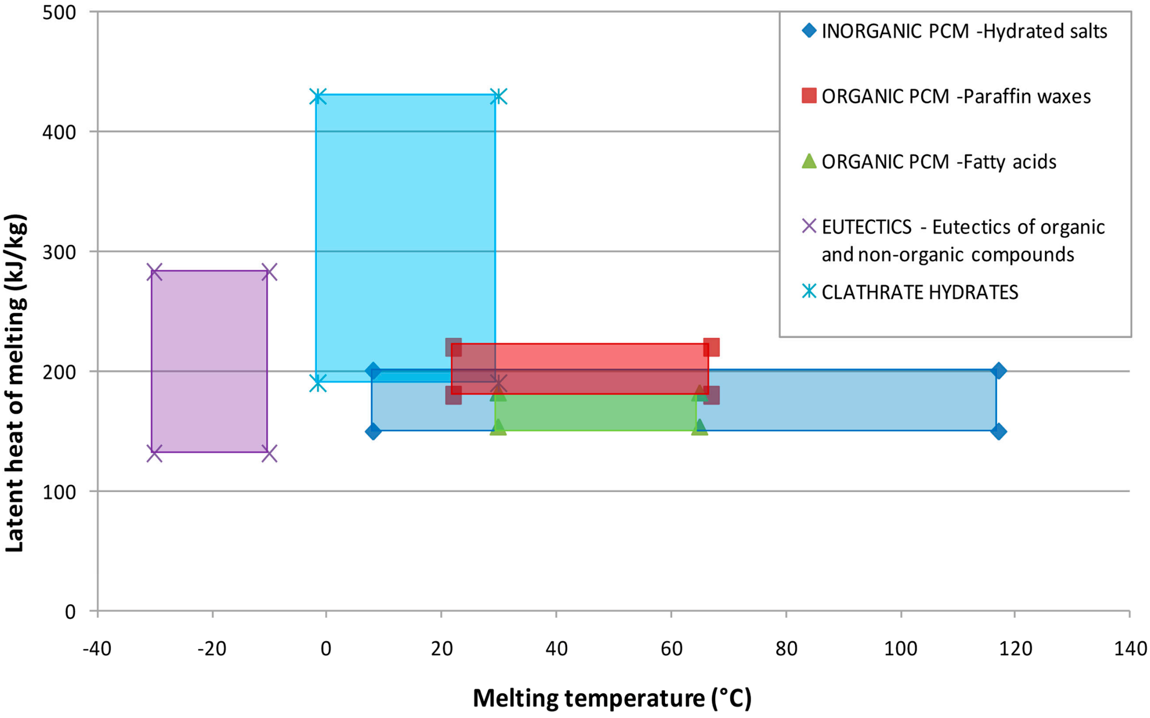


Table 1. PCM classification, based on [5,6,11–14,18–27].

PCMs	Melting Temperature	Latent Heat of Melting	Other Investigated Parameters	Advantages/Disadvantages
Inorganic PCM: Hydrated salts	From ~8 °C to ~117 °C	~150–200 kJ/kg	Thermal conductivity: ~0.5 W/m °C (liquid), ~0.8 W/m °C (solid)	Advantages • High volumetric latent heat storage capacity • Availability and low cost • Sharp melting point • High thermal conductivity • High heat of fusion • Non-flammable Disadvantages • Change of volume is very high • Super cooling is a major problem in the solid-liquid transition • Nucleating agents are needed, and they often become inoperative after repeated cycling
Organic PCM: Paraffin waxes	From ~22 °C to ~67 °C commercial waxes	~200 kJ/kg	Thermal conductivity: ~ 0.2 W/m °C	Advantages • Crystallize without much supercooling • Ability to melt congruently • Self-nucleating properties • Compatibility with conventional material of construction • No segregation • Chemically stable • High heat of fusion • Safe and non-reactive • Recyclable Disadvantages • Low thermal conductivity in their solid state • Low volumetric latent heat storage capacity • Flammable • High costs
Organic PCM: Fatty acids	From ~30 °C to ~65 °C.	From ~153 kJ/kg to ~182 kJ/kg	Thermal conductivity: ~ 0.15 W/m °C	
Eutectics of organic and non-organic compounds	From ~–30 °C to ~–10 °C	From ~131 kJ/kg To ~283 kJ/kg	*Density*: ~1283 to ~1126 (liquid), ~1251 to ~1105 (solid)	Advantages • Eutectics have a melting point similar to the pure substance • Volumetric storage density is slightly above organic compounds Disadvantages • Only limited data is available on the thermo-physical properties, as the use of these materials is relatively new to thermal storage applications

Clathrate hydrates as PCMs have been mostly studied for cold storage in air conditioning systems [28–30]. Since this type of novel cold storage medium was first proposed, research activities have obtained outstanding achievements [31–36].

Clathrate hydrates used in cold storage applications are formed by hydrofluorocarbon (HFC), CO_2, tetra-n-butylammonium bromide (TBAB), Tetrabutyl ammonium chloride (TBAC) and tetrahydrofuran (THF).

Most refrigerant hydrates can be formed under low pressure (below 1 MPa) with a suitable phase change temperature for air-conditioning and large fusion heat (270–430 kJ/kg). Refrigerant hydrates have a larger fusion heat than eutectic salts, paraffin waxes and fatty acids.

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) hydrates, such as CFC-11, CFC-12, HCFC-21, HCFC-22 and HCFC-141b hydrates, were first studied, but have been gradually prohibited, because of their environmental impact. Hydrofluorocarbon (HFC) hydrates instead were studied by [32,35,37,38].

Mixtures of solid CO_2 hydrate crystal and liquid aqueous solution are produced by non-mechanical generation processes, with a higher heat of fusion than that of ice. The production conditions can change melting the point of CO_2 hydrate slurries and their content of solid crystals, so that they can release plentiful latent heat in delayed time [39].

Furthermore, TBAB, TBAC and THF are characterized by rapid hydrate formation [40–47]. TBAC hydrates have a melting point of 15.0 °C and a latent heat of 200.7 kJ/kg [44,45], while THF hydrates have a melting point of 4.4 °C and a latent heat of 260 kJ/kg [46,47].

TBAB hydrates are the most studied as phase change materials. They have a melting temperature of 12 °C, good fluidity and a large cold storage density, which is about 2–4 times of that of chilled water. Researchers have conducted many investigations on the crystallization characteristics of TBAB hydrate crystals and their practical applications. The thermal and thermodynamic properties of TBAB semiclathrate hydrates, including their phase diagram [40,48,49], have been measured, and some data are presented in Table 2.

Real-sized prototypes have been implemented and studied [50]. A compression cycle refrigeration unit (with a condenser installed outside the building) allowed, via a scraped surface heat exchanger (cooled down by the evaporator), the creation of TBAB hydrates slurries, which were stored in a tank during the night [36].

Since 2005, the JFE Engineering Corporation (Japan) has shown the feasibility of the large-scale utilization of clathrate hydrate slurry for air conditioning [43]. The experiments demonstrated the feasibility of an air-conditioning system using TBAB hydrate slurry as a secondary refrigerant, with some technological problems to be solved, but different solutions have been proposed and tested.

Table 2. Thermal properties of tetra-n-butylammonium bromide (TBAB) hydrates.

Guest	Hydration number	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Heat capacity (kJ/(kg·K))	Thermal conductivity (W/(m·K))
TBAB hydrate crystal	Type A 26	12.0 [40], 12.3 [41], 11.8 [37,38]	193.2 [40], 210 [48]	1080 [51]	2.22–2.61 [51], 1.859–2.605 [40]	0.42 [51]
	Type B 36/38	9.9 [40], 9.6 [41]	199.6 [40], 205 [42,43], 224 [48]	1030 [51]	2.00–2.54 [51] 2.5 (5 °C) [48] 1.995–2.541 [40]	
TBAB clathrate hydrate slurry (5–30 wt%)	-			1015.69–1015.56 [51]	4.001–3.667 [51]	0.469–0.485 [51]

Clathrate Hydrates of Organic Compounds

Another potential application of clathrate hydrates as PCMs is in buildings to deliver possible energy savings and peak load time shift. During the last few decades, clathrate hydrates of organic compounds have been characterized in terms of molecular structure, enthalpy of formation and melting temperatures. Among several hydrate-forming molecules, there are some that have the required thermodynamic features: (i) a fairly high melting point, which can also be near or equal to room temperature; (ii) the formation by cooling their aqueous solutions at atmospheric pressure; and (iii) a very wide concentration range from which the hydrate is separated out [44].

Studies on clathrate hydrates of quaternary ammonium halides, quaternary ammonium fluorides, bolaform salts, tetrabutylammonium carboxylates and tetrabutylammonium alkane-sulfonates are available in the literature.

The thermal properties of clathrate hydrates of quaternary ammonium fluorides $(n\text{-}C_4H_9)_3RNF$ were investigated in [49]: depending significantly on the type of the alkyl group (R: CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $i\text{-}C_5H_{11}$, $C_6H_5CH_2$), the melting temperature varies from −1.5 °C to 28.3 °C. In Table 3, data on the physical and chemical properties of four quaternary ammonium halide clathrate hydrates ($(n\text{-}C_4H_9)_4NF{\cdot}30H_2O$; $(n\text{-}C_4H_9)_4NCl{\cdot}30H_2O$, $(i\text{-}C_5H_{11})_4NF{\cdot}39H_2O$, $(i\text{-}C_5H_{11})_4NCl{\cdot}39H_2O$) are reported.

Table 3. Quaternary ammonium halide clathrate hydrates [39].

Guest	Hydration number	Melting temperature (°C)	Heat of fusion (kJ/mol)	Density (kg/m^3)
$(n\text{-}C_4H_9)_4NF$	30 [44], 30 [52], 32 [53], 28 [53]	28.3 [44], 25 [52], 27.2 [53], 27.4 [49]	184 [44], 197 [52], 204 [54], 177 [54]	1057 [44]
$(n\text{-}C_4H_9)_4NCl$	30 [44]	15.0 [44]	156 [44]	1026 [44]
$(i\text{-}C_5H_{11})_4NF$	39 [44], 28 [49]	31.5 [44], 26.4 [49]	256 [44]	
$(i\text{-}C_5H_{11})_4NCl$	39 [44]	29.6 [44]	283 [44]	

The clathrate hydrate of bolaform salts $[(C_4H_9)_3N(CH_2)_n(C_4H_9)_3]F_2$ may be regarded as extended hydrates that have a large guest molecule. From the solid-liquid phase diagrams [55] of mixtures of water, all salts appear to form hydrates that melt congruently and have large hydration numbers. The melting temperatures ranges from −3.1 to 20.4 °C, not suitable for building applications.

Clathrate hydrates of tetraisopentylammonium alkanoates, $[(i\text{-}C_5H_{11})_4N]C_nH_{2n+1}COO$ ($n = 0$–9), instead present fairly high melting points between 10 and 28 °C [56], but to the extent of our knowledge, there are no data about their latent heat.

3. Clathrate Hydrates for Building Applications: Thermal Comfort Evaluation

The effect of quaternary ammonium halide clathrate hydrates $(n\text{-}C_4H_9)_4NF{\cdot}30H_2O$ incorporated into the wallboard of the building envelope was examined using the PCM Express Building Simulation tool, for a building located in Rome, Italy.

PCM Express, developed by Valentin Energy Software, in collaboration with the Fraunhofer Institute for Solar Energy (ISE), is a simulation software for evaluating the effect of phase change materials in building. The effectiveness of the PCM boards was evaluated in terms of indoor thermal comfort, indoor temperature leveling and the increase in free cooling.

PCM Express was used to carry out simulations for three types of PCM: paraffin waxes Micronal® with operating temperature of 23 °C and 26 °C (Case 1 and Case 2 in Table 4) and the selected clathrate hydrate with an operating temperature of 25 °C (Case 3 in Table 4).

Simulations were carried out considering a one-room structure with a length of 5 m, a width of 5 m and a height of 3 m. The building model had one south-facing window of 2 m^2 with double thermal-insulating glass. The stratigraphy of the envelope is shown in Table 4.

Table 4. Envelope features.

	Envelope	**Layers**	**Material thickness (mm)**	**Thermal conductivity (W/(m·K))**
Base Case	Floor/Ceiling	Gypsum	15	0.2
		Concrete	250	1.6
		Polyurethane	20	0.025
		Cement floating screed	30	1.6
	Walls	Gypsum (Internal)	15	0.2
		Full brick masonry	300	0.6
		Expanded polystyrene	80	0.04
		Mineral (External)	10	0.8
	Envelope	**Layers**	**Material thickness (mm)**	**Thermal conductivity (W/(m·K))**
Case 1	Floor/Ceiling	Gypsum	15	0.2
		Concrete	250	1.6
		Polyurethane	20	0.025
		Cement floating screed	30	1.6
	Walls	Micronal PCM 23	15	0.196
		Full brick masonry	300	0.6
		Expanded polystyrene	80	0.04
		Mineral (External)	10	0.8

Table 4. *Cont.*

	Envelope	**Layers**	**Material thickness (mm)**	**Thermal conductivity (W/(m·K))**
Case 2	Floor/Ceiling	Gypsum	15	0.2
		Concrete	250	1.6
		Polyurethane	20	0.025
		Cement floating screed	30	1.6
	Walls	Micronal PCM 26	15	0.196
		Full brick masonry	300	0.6
		Expanded polystyrene	80	0.04
		Mineral (External)	10	0.8
	Envelope	**Layers**	**Material thickness (mm)**	**Thermal conductivity (W/(m·K))**
Case 3	Floor/Ceiling	Gypsum	15	0.2
		Concrete	250	1.6
		Polyurethane	20	0.025
		Cement floating screed	30	1.6
	Walls	$(n\text{-}C_4H_9)_4NF \cdot 30H_2O$	15	0.4
		Full brick masonry	300	0.6
		Expanded polystyrene	80	0.04
		Mineral (External)	10	0.8

The thermo-physical properties of the clathrate hydrate used in the simulation are shown in Table 5.

Table 5. Thermo-physical properties of clathrate hydrates $(n\text{-}C_4H_9)_4NF \cdot 30H_2O$.

Guest	**Hydration number**	**Melting temperature (°C)**	**Heat of fusion (kJ/mol)**	**Density (kg/m^3)**	**Heat capacity (kJ/(kg·K))**	**Thermal conductivity (W/(m·K))**
$(n\text{-}C_4H_9)_4NF$	30 [44]	25 [52]	197 [52]	1.057 [44]	3.6 [57]	0.4 [58]

Micronal® PCMs are microencapsulated. Clathrate hydrates are assumed to be stored in a wallboard of the same thickness. PCM wallboards were compared to the base case, *i.e.*, a structure with ordinary gypsum wallboards. A heating system output of 50 W/m^2 is assumed during a heating period from October 15 to March 31, with a heating threshold temperature of 20 °C. A heat recovery and ventilation system operates with an efficiency of 85%, typical of passive house constructions [59].

Results and Discussion

Table 6 summarizes the results obtained for the three PCM used in a building located in Rome, Italy.

Results show that in all cases, PCMs improve the indoor comfort in terms of a reduction of hours in which the indoor temperature exceeds the comfort range. This means that, with respect to the base case, all PCMs provide free cooling. It is noteworthy that clathrate hydrates theoretically provide freer cooling that wax PCMs. Figure 2 shows that the effect of all PCMs is to increase the number of times in which temperatures are in the range from 20 °C to 26 °C. The frequency of the room's temperature being inside the comfort range is higher in the case of clathrate hydrates (Case 3) than in the case of waxes (Case 1 and Case 2). On the other hand, clathrate hydrates shift room temperatures towards 26 °C and 27 °C, but the effect is negligible (0.1%).

Table 6. Results: the number of hours in which indoor temperature exceeds the comfort range (>26 °C).

Case Study	No. of hours with temperature exceeding comfort range (>26 °C) (h)	Time with temperature exceeding comfort range (>26 °C) (%)
Base Case	552	6.3
Case 1, Micronal 23	543	6.2
Case 2, Micronal 26	499	5.7
Case 3, $(n\text{-}C_4H_9)_4NF{\cdot}30H_2O$	456	5.2

Figure 2. Distribution of room temperatures.

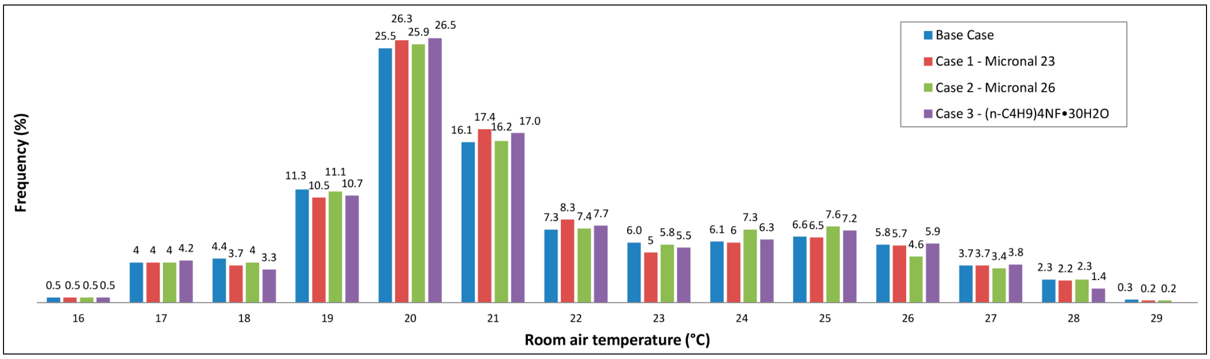
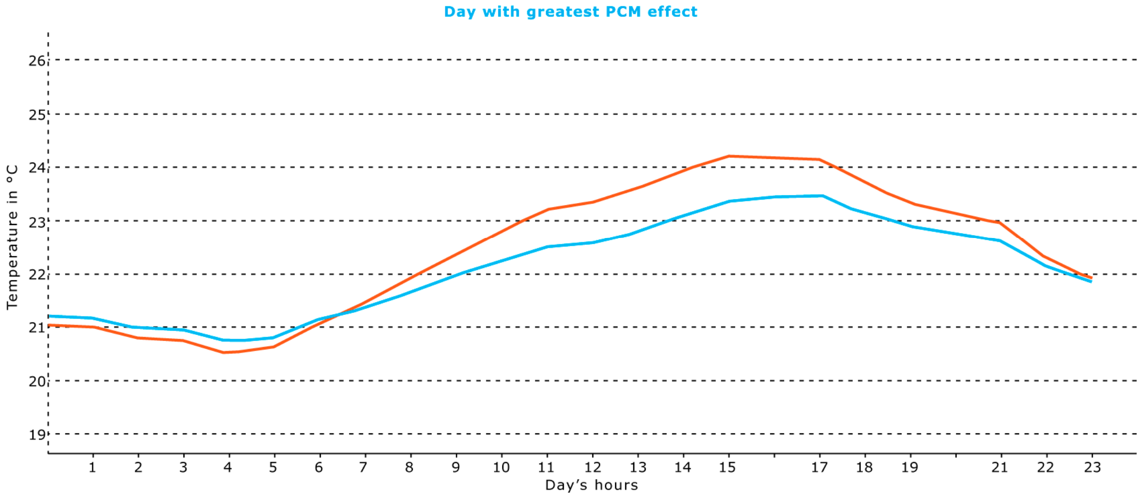


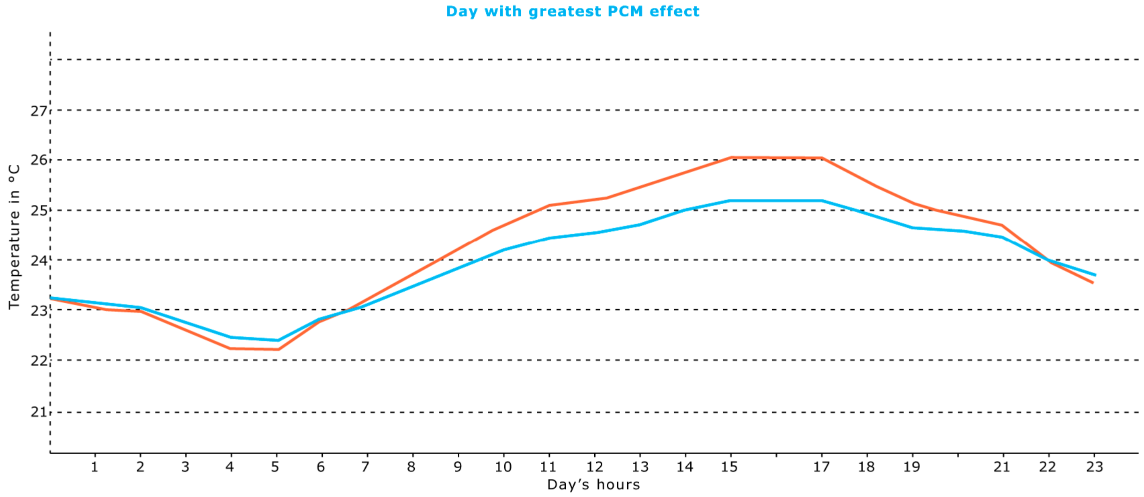
Figure 3 shows temperature profiles during the days with the best PCM effect. The largest free cooling is obtained in Case 1 and Case 2 with a reduction of 1 °C in room temperature during the daytime, while clathrate hydrates in Case 3 allow one to obtain a reduction of 0.5 °C. Anyway, the damping effect of clathrate hydrates is comparable to that of commercial PCM.

Figure 3. The day with the greatest PCM effect (PCM internal temperature in blue, conventional system internal temperature in red).

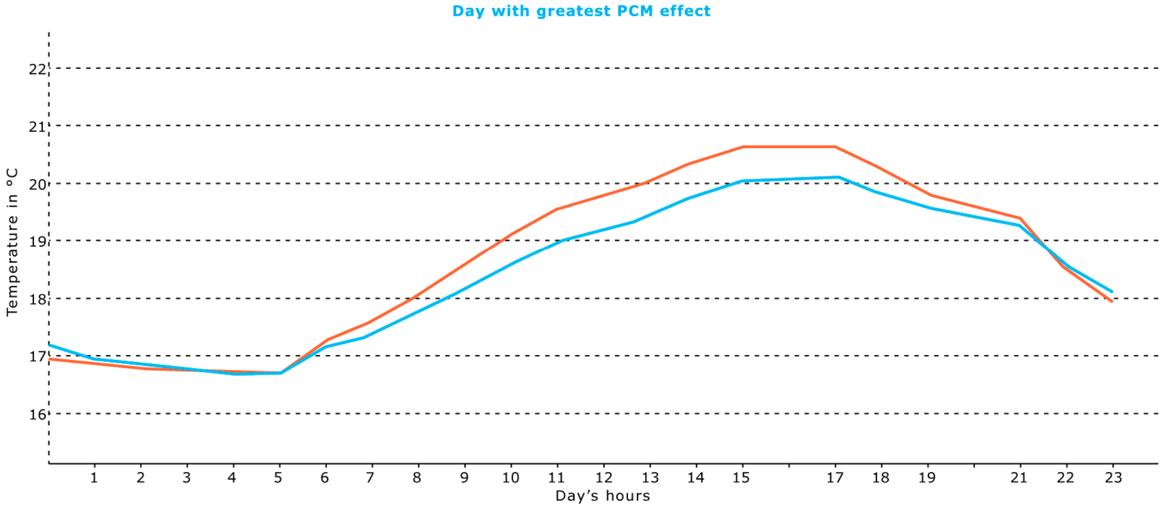


Case 1, Micronal 23 (8 June 2014)

Figure 3. *Cont.*



Case 2, Micronal 26 (14 June 2014)



Case 3, $(n\text{-}C_4H_9)_4NF \cdot 30H_2O$ (6 May 2014)

4. Conclusions

Clathrate hydrates have been suggested as a potential group of PCMs. The performed overview on the thermo-physical characteristics of different clathrate hydrates allows one to assess which of them are suitable for PCM applications in buildings.

The effect of quaternary ammonium halide clathrate hydrates incorporated into the wallboard of the building envelope was examined using the PCM Express Building Simulation program, for a building located in Rome, Italy.

Simulations suggest that clathrate hydrates have a potential in terms of the improvement of indoor thermal comfort and a reduction of energy consumption for cooling. Cooling effects of 0.5 °C and reduced overheating hours of up to 1.1% are predicted. Therefore, there is an argument for the experimental investigation of clathrate hydrates in building applications.

Anyway, further experimental work is necessary to better comprehend the kinetic and chemical properties of clathrate hydrates and to assess if they meet the needed chemical and economical requirements.

Kinetic properties, such as a high nucleation rate and little or no supercooling of the liquid phase and a high rate of crystallization, and chemical properties, such as completely reversible melt/crystallize cycles, long-term chemical stability and no degradation after a large number of melt/crystallize cycles, non-corrosiveness and compatibility with construction materials, non-toxic, non-flammable and non-explosive, as well as economic properties, such as abundance, availability and cost effectiveness, should be investigated. Properties, such as low embodied energy, separation facility from the other materials and recycling potential, low environmental impact and non-polluting, are environmentally requested. Studies on methods of micro- or macro-encapsulation should be also carried out.

The effectiveness of the wallboard is climate dependent, and care must be taken to choose the most appropriate phase change temperature [59].

Since melting temperature and melting enthalpy depend on molecular effects and properties, such as different chain lengths, ions, crystal structure and the position of the chain of anions, future activities should focus on modifying molecular structures and synthesizing original molecules starting from the selected clathrate-forming molecules. The objective is to obtain hydrate-forming compounds with proper phase change temperatures and a high formation enthalpy.

Author Contributions

All authors contributed extensively to the work presented in this paper. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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