

A comprehensive review on sub-zero temperature cold thermal energy storage materials, technologies, and applications: State of the art and recent developments

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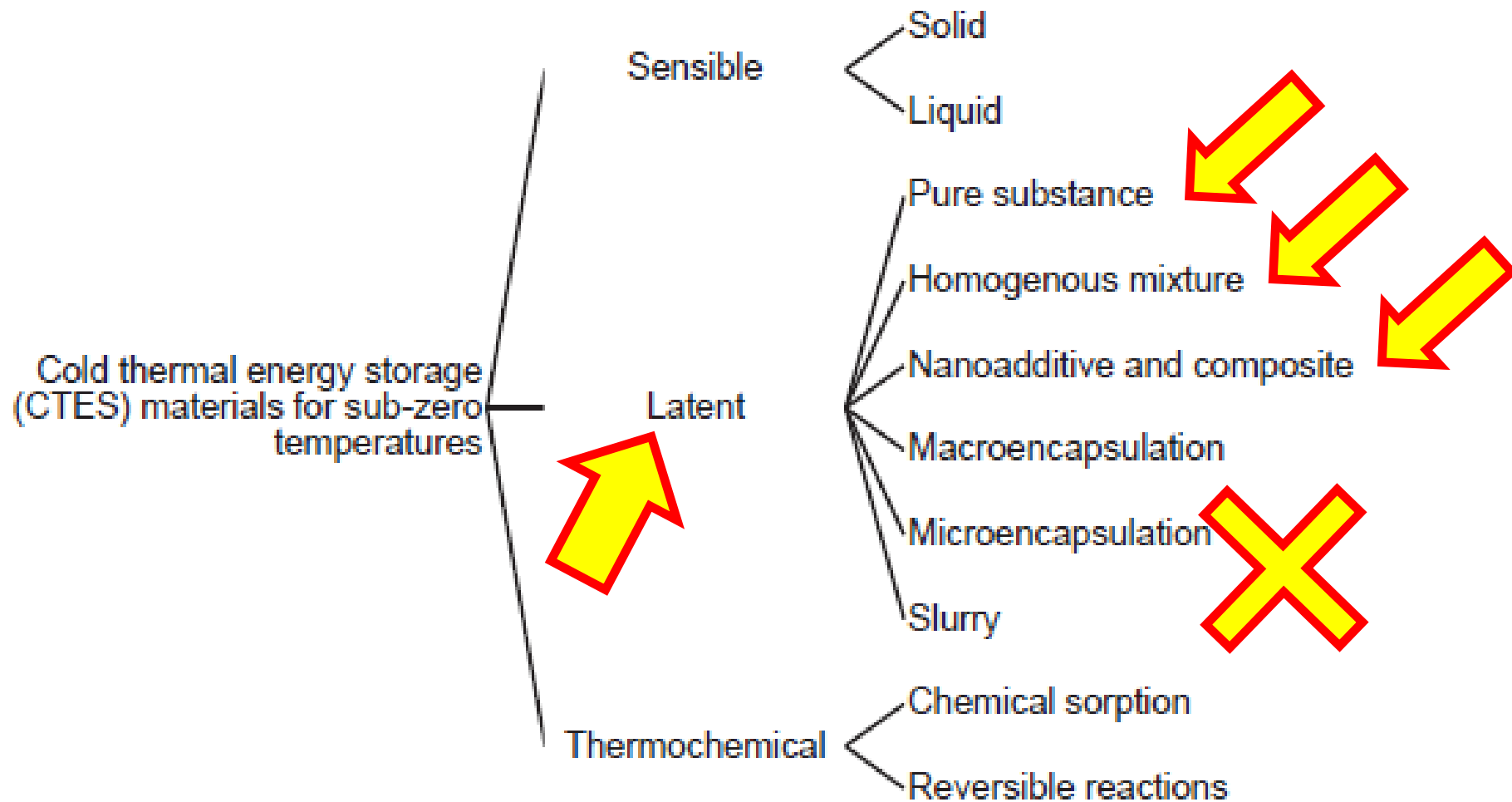
## ABSTRACT

The energy industry needs to take action against climate change by improving efficiency and increasing the share of renewable sources in the energy mix. On top of that, refrigeration, air-conditioning, and heat pump equipment account for 25–30% of the global electricity consumption and will increase dramatically in the next decades. However, some waste cold energy sources have not been fully used. These challenges triggered an interest in developing the concept of cold thermal energy storage, which can be used to recover the waste cold energy, enhance the performance of refrigeration systems, and improve renewable energy integration. This paper comprehensively reviews the research activities about cold thermal energy storage technologies at sub-zero temperatures (from around  $-270\text{ }^{\circ}\text{C}$  to below  $0\text{ }^{\circ}\text{C}$ ). A wide range of existing and potential storage materials are tabulated with their properties. Numerical and experimental work conducted for different storage types is systematically summarized. Current and potential applications of cold thermal energy storage are analyzed with their suitable materials and compatible storage types. Selection criteria of materials and storage types are also presented. This review aims to provide a quick reference for researchers and industry experts in designing cold thermal energy systems. Moreover, by identifying the research gaps where further efforts are needed, the review also outlines the progress and potential development directions of cold thermal energy storage technologies.

## HIGHLIGHTS

- Summarizes a wide temperature range of Cold Thermal Energy Storage materials.
- Phase change material thermal properties deteriorate significantly with temperature.
- Simulation methods and experimental results analyzed with details.
- Future studies need to focus on heat transfer enhancement and mechanical design.
- Analyzes applications with technology readiness and more should be explored.

## Classification:

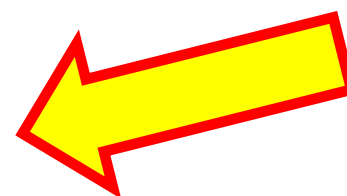


## Pure substances:

Existing and potential pure substance PCMs for sub-zero temperatures.

Material	Density (kg/m <sup>3</sup> )	Transition Temperature (°C)	Specific heat Capacity (J/(g·K))	Thermal Conductivity (W/(m·K))	Latent heat (J/g)	Phase
Butyric acid (C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )	959 (l) (20 °C)	−5.4	1.46–1.82 (s) (−73 °C to −5 °C) 1.91 (l) (−3 °C)	0.154 (l) (−3 °C)	131.55	Solid-liquid
n-Tridecane (C <sub>13</sub> H <sub>28</sub> )	775–770 (l) (−8 °C to 0 °C)	−5.15	1.31–1.75 (s) (−73 °C to −23 °C) 2.15 (l) (−3 °C)	0.143 (l) (−5.3 °C)	156.76	Solid-liquid
Caproic acid (C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> )	929 (l) (20 °C)	−4	1.94 (l) (25 °C)	0.15 (l) (0 °C)	146.18	Solid-liquid
5-Nonanone (C <sub>9</sub> H <sub>18</sub> O)	830 (l) (10 °C)	−3.84	2.08 (l) (−3 °C)	0.14 (l) (−3 °C)	175.3	Solid-liquid
Butane (C <sub>4</sub> H <sub>10</sub> )	2.70 (g) (0 °C)	−0.34	1.64 (g) (0 °C)	0.0145 (g) (0 °C)	385.71	Liquid-gas

Caproic acid  
5-Nonanone  
(Butane)



## Homogeneous mixtures and composites:

Existing and potential homogenous mixture/nanoadditive and composite PCMs for sub-zero temperatures.



Composition	Type	Melting Temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity
10 wt% NaCl	Eutectic water-salt solution	-5	289	
12% Ethylene glycol/H <sub>2</sub> O (vol.%)	Multicomponent organic mixture	-4.9	281	0.558 (l)
20.6 wt% NiSO <sub>4</sub>	Eutectic water-salt solution	-4.15	258.61	
Tetradecane/octadecane	Paraffin mixture	-4.02	227.52	
19 wt% MgSO <sub>4</sub>	Eutectic water-salt solution	-3.9	264.42	
12.7 wt% Na <sub>2</sub> SO <sub>4</sub>	Eutectic water-salt solution	-3.55	284.95	
3.9 wt% NaF	Eutectic water-salt solution	-3.5	309.2–314.09	
Corn-oil ester/Tap water (5:95 vol%)	Multicomponent organic mixture	-3.5	227.8	
Propylene glycol/H <sub>2</sub> O (10:90 vol%)	Multicomponent organic mixture	-3		

✓ Higher latent heat and thermal conductivity than 5-Nonanone

# Salt eutectic mixtures, 2018

## Research Article

# Preparation and Thermal Properties of Eutectic Hydrate Salt Phase Change Thermal Energy Storage Material

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In this study, a new cold storage phase change material eutectic hydrate salt ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} - \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} - \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) was prepared, modified, and tested. The modification was performed by adding a nucleating agent and thickener. The physical properties such as viscosity, surface tension, cold storage characteristics, supercooling, and the stability during freeze-thaw cycles were studied. Results show that the use of nucleating agents, such as sodium tetraborate, sodium fluoride, and nanoparticles, are effective. The solidification temperature and latent heat of these materials which was added with 0, 3, and 5 wt% thickeners were  $-11.9$ ,  $-10.6$ , and  $-14.8^\circ\text{C}$  and 127.2, 118.6, 82.56 J/g, respectively. Adding a nucleating agent can effectively improve the nucleation rate and nucleation stability. Furthermore, increasing viscosity has a positive impact on the solidification rate, supercooling, and the stability during freeze-thaw cycles.

# Salt eutectic mixtures, 2018

Experimental materials	Purity	Application
Sodium dihydrogen phosphate dihydrate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ )	AR	Hydrated salt
Sodium alginate	CP	Thickener
Sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )	AR	Hydrated salt
Dipotassium hydrogen phosphate trihydrate phosphate ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ )	AR	Hydrated salt
Nanoactivated carbon (100 nm, heat treatment)	AR	Nucleating agent
Sodium tetraborate	AR	Nucleating agent
Polyethylene glycol 400	AR	Dispersant
Sodium fluoride	AR	Nucleating agent

✓ They are necessary for temperatures below  $\sim -10\text{ }^\circ\text{C}$



# NaCl-H<sub>2</sub>O, Eurosun 2010

## SALT-WATER SOLUTIONS AS PCM FOR COOLING APPLICATIONS

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### Abstract

The objective of the paper is for experimentally studying and analysing aqueous salt solutions of sodium chloride (NaCl) and potassium chloride (KCl) that could be candidates of phase change materials (PCM) for the cooling applications and cold storage systems. These salts were selected because of their easy availability at low cost. Total 16 aqueous salt solutions of 8 different concentrations each of the NaCl and KCl were prepared and analysed by cyclation and corrosion tests. Cyclation tests were performed in temperature range of -24 °C to -10 °C to check feasibility of their use for cooling applications. KCl-H<sub>2</sub>O mixtures were analysed with 1% glycerine to avoid volume expansion. Results showed that KCl-H<sub>2</sub>O has more phase segregation than NaCl-H<sub>2</sub>O. Overall, melting-freezing temperature ranges of these mixtures are from -20 °C to -3 °C, which is feasible for the cold storage. However, all the 16 solutions showed subcooling. Corrosion tests were performed during 1 week and 1 month using 5 different common metals (Aluminium, Stainless steel, Laminated black steel, Copper and Galvanized steel) immersed in these 16 aqueous salt solutions to check their long term compatibility and corrosion rate of the metal-PCM pairs. 1 week results showed that 5% KCl with copper and galvanized steel and 21% NaCl with galvanized steel have highest corrosivity, while during 1 month, galvanized steel gave high corrosivity with 15% KCl and 21% NaCl.

# NaCl-H<sub>2</sub>O, Eurosun 2010

Table 2. Freezing-melting temperature range and subcooling for aqueous NaCl and KCl solutions

Solutions	Subcooling [°C]	Freezing temperature [°C]	Melting temperature [°C]	Δ (Freezing point depression) <sup>[11]</sup>
5% NaCl	3.87	-3.87/-4.27	-4.87/-3.18	3.04
10% NaCl	6.28	-7.60/-7.70	-7.80/-6.10	6.56
5% KCl	1.59	-3.38/-3.58	-3.28/-2.08	2.32
10% KCl	7.48	-6.60/-7.10	-11.79/-6.00	4.80

- ✓ Water/NaCl is enough for -3 °C
- ✓ Water/Glycol or Water/NaCl/Glycol are also good options

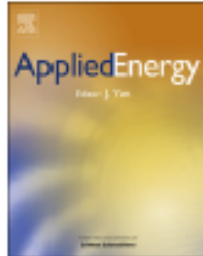




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## Characterization and experimental investigation of phase change materials for chilled food refrigerated cabinet applications



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### H I G H L I G H T S

- ▶ Water based PCMs without nucleate agent have high supercooling degree.
- ▶ Water based PCMs with nucleate agent can be frozen and melted completely within 1.5 °C temperature difference.
- ▶ Water/glycol gel needs 2.5 °C temperature difference to start freezing in dynamic cooling conditions.
- ▶ Paraffin has neglectable supercooling but worst heat transfer performance.

✓ Water/Glycol with AgI



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## Short Communication

# Development of salt hydrate eutectics as latent heat storage for air conditioning and cooling



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## ABSTRACT

Sustainable air conditioning systems require heat reservoirs that operate between 4 and 20 °C. A systematic search for binary and ternary eutectics of inorganic salts and salt hydrates with melting temperatures in this temperature regime and with high enthalpies of fusion has been performed by means of differential scanning calorimetry (DSC). Promising results were obtained for the pseudo-ternary system  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{KNO}_3$  with the melting temperature range 18–21 °C and the enthalpy of fusion of about 110 kJ kg<sup>-1</sup>. Suitable nucleating and thickening agents have been found and tested to prevent the mixture from supercooling and phase separation.

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# Efimova, 2014

As an example of the development of a pseudo-ternary PCM system, the combination of zinc nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , manganese nitrate tetrahydrate,  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and potassium nitrate,  $\text{KNO}_3$  (saltpeter), is presented. The melting temperatures of the pure substances are about  $36^\circ\text{C}$ ,  $37^\circ\text{C}$  and  $334^\circ\text{C}$  for given sequence. At almost equal mass fractions of the components the ternary system forms its eutectic mixture with a melting temperature range from  $18^\circ\text{C}$  (onset) to  $21^\circ\text{C}$  (endset).

The freezing temperature of the pure mixture is about  $-4^\circ\text{C}$ , measured with heating/cooling rate of  $0.5 \text{ K min}^{-1}$  (Fig. 1a). Thus, the average supercooling for the ternary system is 21 K. To prevent this effect, suitable nucleating agent has been tested. The agent manganese nitrate hexahydrate,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used in amounts of 2–3% related to the total mass of the system. It reduces supercooling to 4 K and has no measurable influence on the value of the enthalpy of fusion. The resulting DSC measurements with same heating rate and significantly reduced supercooling are shown in Fig. 1b.