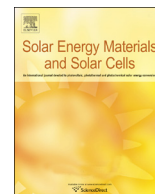




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## Review

# Salt hydrates as latent heat storage materials: Thermophysical properties and costs



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## ABSTRACT

Thermal energy storage is considered as one of the most perspective technologies for increasing the efficiency of energy conversion processes and effective utilization of available sources of heat. Advantages and technical attractiveness of the thermal energy storing have resulted in continuously increasing numbers of research activities, especially in the last four decades. Among various applications of thermal energy storage, the heat or cold accumulation in the temperature range from  $-50\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$  has a greater market potential and this can be carried out using a wide range of phase change latent heat materials. Among these materials the salt hydrates deserve a special attention and currently a large number of phase change compositions based on salt hydrates are produced commercially and available on the market. However, reliable data on thermophysical properties as well as their thermal stability over their lifetime is required to build effective storage systems. Currently this data is insufficient and is scattered across numerous sources that are often difficult to access for potential consumers. This paper summarises practically all available original experimental data on the phase change diagram of salt-water systems, melting temperatures, heat of fusion, specific heat, density, thermal conductivity, and thermal diffusivity in solid and liquid states and viscosity in the liquid state for 18 salt hydrates. The above information is provided for major market products on the basis of the salt hydrates for latent heat storage. The wholesale prices for pure salt, salt hydrates, and salt hydrate heat storage compositions are also additionally discussed.

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## 1. Introduction

The first systematic investigations of salt hydrates as perspective phase change materials for thermal energy storage were carried out by Telkes [1–11]. However, in the period preceding the World Energy Crisis in 1973–1974 a number of such investigations were very small. During the first decade following the Energy Crisis there was a sharp rise in research activities on studying physical and chemical properties of salt hydrates and on the development of phase change materials with improved properties on their basis. The most salt hydrates are known to undergo the change in the stoichiometric composition in heating and cooling processes. Another significant shortcoming of salt hydrates is supercooling during their solidification. Since salt hydrates were not widely used as the working agent in thermal storage devices

then their thermophysical properties have not been sufficiently studied.

For efficient application of salt hydrates as the working agent in systems for thermal energy storage, the reliable data on thermophysical and chemical properties together with knowledge of maintaining these properties during the system's lifetime was required. In the period from 1970 to present the main effort of researchers was focused on the development of new phase change materials with a high stable composition and reduced degree of supercooling. However, the advances in the development of PCMs for thermal energy storage were not always accompanied by relevant investigations on thermophysical properties and long-term performance of pure compounds and commercial phase change compositions based on these compounds. For instance, the thermophysical properties of salt hydrates were considered in numerous review papers on phase change materials and based on

**Table 1**

The most cited values of thermal properties of some salt hydrates to be used as latent heat storage materials.

	$T_m$ (°C)	$\Delta H_m$ (J/g)	$\rho$ (g/cm <sup>3</sup> )		$C_p$ (J/g °C)		$k$ (W/m °C)		Ref.
			solid	liquid	solid	liquid	solid	liquid	
Lithium chlorate trihydrate	8.1	253	1.72 <sup>8,1a</sup>	1.53 <sup>8,1</sup>					Schröder and Gawron [10]
Potassium fluoride dihydrate	18.5	231	1.447 <sup>18,5</sup>	1.455 <sup>20</sup>	1.84 <sup>18,5</sup>	2.39 <sup>18,5</sup>			Lane [14]
Manganese nitrate hexahydrate	26.0	140							Telkes [10]
Calcium chloride hexahydrate	29.5	170	1.68		1.42	2.30			Telkes [10]
	29.6	191	1.802 <sup>24</sup>	1.562 <sup>32</sup>	1.42 <sup>16</sup>	2.10 <sup>48</sup>	1.088 <sup>23</sup>	0.540 <sup>39</sup>	Lane [14]
Lithium nitrate trihydrate	30.0	125							Telkes [10]
	29.9	296							Lane [14]
Sodium sulphate decahydrate	32.4	251							Telkes [10]
Sodium carbonate decahydrate	34.0	251	1.44		1.88	3.35			Telkes [10]
	33.0	247	1.460						Lane [14]
Calcium bromide hexahydrate	34.3	116	2.194 <sup>24</sup>	1.956 <sup>35</sup>					Lane [14]
Zinc nitrate hexahydrate	36.4	130	2.07		1.34	2.26			Telkes [10]
Disodium hydrophosphate dodecahydrate	36.5	264	1.52		1.55	3.18			Telkes [10]
Calcium nitrate tetrahydrate	35.2–44.6	280	1.52	1.442	1.70	1.95	0.514	0.476	Lane [14]
	42.6	140	1.82		1.46				Telkes [10]
	42.7	142							Guion [15]
Sodium thiosulfate pentahydrate	49.0		1.69	1.66	1.46	2.38			Telkes [10]
	48.5–55.2	201	1.750 <sup>25</sup>	1.67					Lane [14]
	48.0	200							Guion [15]
Sodium acetate trihydrate	58.0	180	1.45		1.97	3.35			Telkes [10]
	58.0	289							Guion [15]
Cadmium nitrate tetrahydrate	59.5	106	2.45		1.09				Telkes [10]
Sodium hydroxide monohydrate	64.0	272							Telkes [10]
Barium hydroxide octahydrate	78.0	301	2.18		1.17				Telkes [10]
	78.0	266							[10]
	78.0	295							Lane [14]
									Guion [15]
Magnesium nitrate hexahydrate	90.0	160	1.46		2.26	3.68	0.669 <sup>56</sup>	0.490 <sup>95</sup>	Telkes [10]
	89.9	163	1.636 <sup>25</sup>	1.550 <sup>94</sup>	1.81 <sup>41</sup>	2.48 <sup>98</sup>			Lane [14]
Ammonium alum	94.0	269	1.65		1.71 <sup>82,3</sup>	3.05 <sup>95,9</sup>			Lane [14]
Magnesium chloride hexahydrate	117.0	172	1.56		1.59	2.85			Telkes [10]
	116.7	169	1.57 <sup>20</sup>	1.45 <sup>120</sup>	2.25 <sup>100</sup>	2.61 <sup>120</sup>	0.704 <sup>110</sup>	0.570 <sup>120</sup>	Lane [13]

<sup>a</sup> The temperatures at which the properties were determined.

data obtained by Telkes [10], Schröder and Gawron [12], Lane [13,14] and Guion [15]. Table 1 presents thermophysical properties of the most studied salt hydrates cited by many researchers. As it can be seen in this Table, some thermal properties of pure substances are not known. The thermal properties of patented PCMs for latent heat storage and commercially produced heat storage products have not been investigated in detail.

The purpose of present paper is to analyse the original investigations of the phase diagram of salt–water systems, melting temperature and heat of fusion, specific heat, thermal conductivity and development of phase change compositions for latent heat storage on the basis of considered salt hydrates. Safety issues in handling and that of corrosion are of a paramount importance in designing the storage systems with salt hydrates. However, these issues were not considered in this work and could be a topic for a separate and dedicated investigative study to analyse the large volume of accumulated relevant data.

## 2. Salt hydrates for latent heat storage

There is a big number of available salt hydrates and they melt congruently, semi-congruently or incongruently. The most valuable ones are salt hydrates which melt congruently, abundant and have a low cost. However, the number of such salt hydrates is very limited. Information on some hydrates, which partially meet the above criteria is presented below.

### 2.1. Lithium chlorate trihydrate (LCT – $\text{LiClO}_3 \cdot 3\text{H}_2\text{O}$ )

The molecular weight of lithium chlorate trihydrate is 140.44 g/mol. The weight proportions of salt and water are 62.58% and 37.42% and it occurs as shining transparent crystals. The phase diagram of the lithium chlorate–water system, created using experimental data by Kraus and Burgless [16], Berg [17] and Campbell and Griffiths [18], is shown in Fig. 1. It can be seen in this figure that the system consists of a compound with congruent melting and two eutectic compositions.

#### 2.1.1. The melting temperature and other thermophysical properties

Melting temperatures were measured by Kraus and Burgless [16], Berg [17] and Campbell and Griffiths [18] in the process of studying the phase diagram and are 8.0 °C, 8.1 °C and 8.1 °C, respectively. There is no information on thermophysical properties of LCT except that reported by Schröder and Gawron in [12], see Table 1.

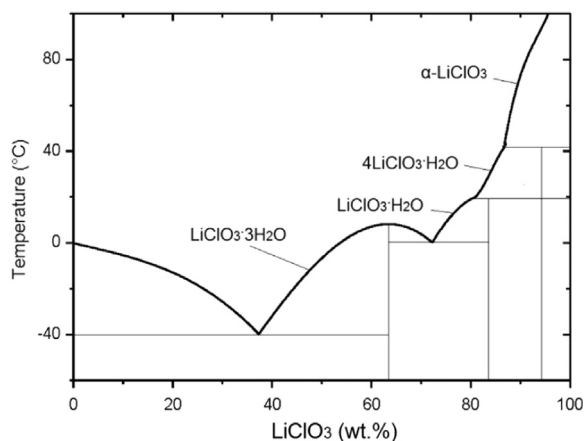


Fig. 1. Phase diagram of lithium chlorate–water system.

#### 2.1.2. LCT as phase change latent heat storage material

Taking into account the congruent character of melting of lithium chlorate trihydrate, Schröder and Gawron [19] developed the phase change material based on LCT. In order to decrease the supercooling degree they used additives in the form of  $\text{KClO}_4$ ,  $\text{Na}_2\text{SiF}_6$  and  $\text{BaSiF}_6$ . No reports have been found on the LCT application for the thermal storage purposes in practice.

### 2.2. Potassium fluoride tetrahydrate (PFT – $\text{KF} \cdot 4\text{H}_2\text{O}$ )

The molecular weight of PFT is 130.158 g/mol. The weight proportions of salt and water are 44.64% and 55.36%, respectively, and it occurs as colourless monocline crystals. PFT is produced as result of reaction of potassium carbonate and water solution of fluoric acid. The phase diagram of fluoric potassium and water, created using data compiled by Zdanovskii et al. [20], is shown in Fig. 2. It can be seen in this figure that the  $\text{KF} \cdot 4\text{H}_2\text{O}$  compound melts congruently. Information available on its physical properties is very limited.

#### 2.2.1. The melting temperature and heat of fusion

Data reported in the open literature on the melting temperature and heat of fusion is presented in Table 2. The published values of the melting point are in good agreement but there are discrepancies in information on the heat of fusion. Information reported by de Forcrand [21], Counioux and Cohen-Adad [22] and Gawron and Schröder [23,24] is almost identical. The lowest value was obtained by Reznitskii and Fillipova [25] using the DSC technique while Shamberger and Reid [26] reported the highest value of the melting enthalpy. Unfortunately, no sufficient information was provided to pinpoint the reason for such the difference in published data.

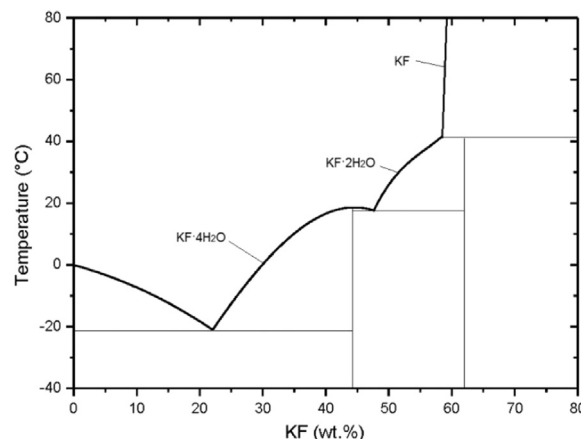


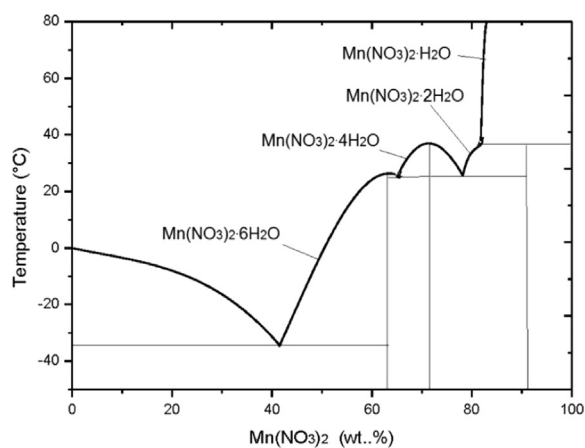
Fig. 2. Phase diagram of potassium fluoride–water system.

Table 2  
Melting temperature and heat of fusion of potassium fluoride tetrahydrate.

Melting temperature (°C)	Heat of fusion (J/g °C)	Ref.
18.8	232	de Forcrand [21]
18.7	231	Counioux and Cohen-Adad [22]
18.5	231	Gawron and Schröder [23,24]
18.5	201	Reznitskii and Fillipova [25]
18.4	246	Shamberger and Reid [26]

**Table 3**  
Thermophysical properties determined by Shamberger and Reid [26].

Property	Temperature (°C)										
	–30	–20	–10	0	10	20	30	40	50	60	70
Density (g/cm <sup>3</sup> )						1.456	1.452	1.448	1.444	1.440	1.335
Specific heat (J/g °C)	1.41	1.45	1.49	1.56				2.47	2.47	2.47	2.48
Thermal conductivity (W/m °C)		0.672	0.654	0.632	0.608		0.484	0.489	0.493		
Thermal diffusivity (10 <sup>8</sup> m <sup>2</sup> /s)		32.1	30.5	28.1	26.1		12.6	12.7	12.8		
Absolute viscosity (mPa s)							3.83	3.07	2.61	2.13	1.85



**Fig. 3.** Phase diagram of manganese nitrate–water system.

### 2.2.2. Other thermophysical properties

There is only one work by Shamberger and Reid [26], in which a set of thermophysical properties of potassium fluoride tetrahydrate were studied, see Table 3.

### 2.2.3. PFT as phase change latent heat storage material

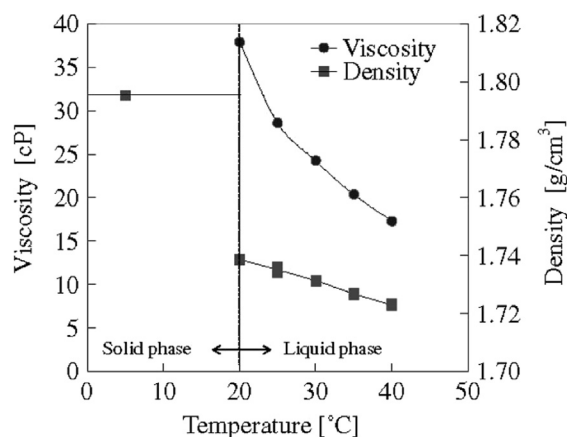
Only few thermophysical properties of potassium fluoride tetrahydrate were investigated by Schröder and Gawron [12,23,24] and Reznizkii and Phillipova [25] with a purpose of using it as a latent heat storage material. Currently PFT is not used for accumulation of heat because of its toxicity.

## 2.3. Manganese nitrate hexahydrate (MnNH – Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O)

Molecular weight of manganese nitrate hexahydrate is 288.977 g/mol. The weight proportions of salt and water are 62.37% and 37.66%, respectively. MnNH occurs as pale rose cubic crystals. It is highly soluble in water (102 g of anhydrous in 100 ml of water at 0 °C and 137.1 g at 25 °C). The phase diagram of manganese nitrate built using experimental data by Funk [27] and Ewing and Rasmussen [28] is shown in Fig. 3. It can be seen that there are two hydrated compounds which melt congruently.

### 2.3.1. The melting temperature and heat of fusion

The melting temperature of 26 °C was reported by Telkes in [10] and this was based on measurements of the melting point which had been carried out by Funk in [27]. The melting temperatures of manganese nitrate hexahydrate and tetrahydrate are 25.8 °C and 34 °C, respectively. The similar measurements were made by Ewing and Rasmussen [28] in their study of the solubility of manganese nitrate in water producing the corresponding values of 25.3 °C and 37.1 °C. Nagano with colleagues [29] reported that MnNH melts at 25.3 °C. All reported cases are in a very good agreement with each other. Currently, the value of 25.3 °C is



**Fig. 4.** Viscosity and density of the mixture of Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 3.5 wt% of MnCl<sub>2</sub>·4H<sub>2</sub>O [29].

recommended to be used as the melting temperature of MnNH but this can be refined in future by using more finer measurements.

The heat of fusion for this substance was determined in papers by Riesenfeld and Milchsack [30] as 120 J/g and by Nagano et al. [29] as 126 J/g. It can be seen that the above reported values are sufficiently close to each other.

### 2.3.2. Other thermophysical properties

Thermophysical properties of manganese nitrate hexahydrate are practically not investigated. There is only one paper by Nagano et al. [29] in which the results of measurements of viscosity and density are reported. Experimental data obtained in the above measurements is presented in Fig. 4.

### 2.3.3. MnNH as phase change latent heat storage material

Nagano et al. in [29] consider manganese nitrate hexahydrate as having a good potential as a phase change material for application in cooling systems. They studied the effect of a number of additives on minimising the supercooling effect. It was reported that adding 1 wt% of chlorides, nitrates, sulphates, fine powders and solvents practically did not improve the supercooling performance of MnNH since the supercooling temperature values varied between 45.3 °C and 7.5 °C. It was found that the adding up to 10 wt% of MnCl<sub>2</sub>·4H<sub>2</sub>O does not effects the value of the heat of fusion.

## 2.4. Calcium chloride hexahydrate (CCH – CaCl<sub>2</sub>·6H<sub>2</sub>O)

The molecular weight of this substance is 219.08 g/mol and the weight proportions of salt and water are 50.66% and 49.34%, respectively. Calcium chloride hexahydrate crystallises from a water solution at the room temperature creating the super-saturated solutions. When the temperature slightly exceeds the melting temperature of 27.7 °C, the more thermodynamically

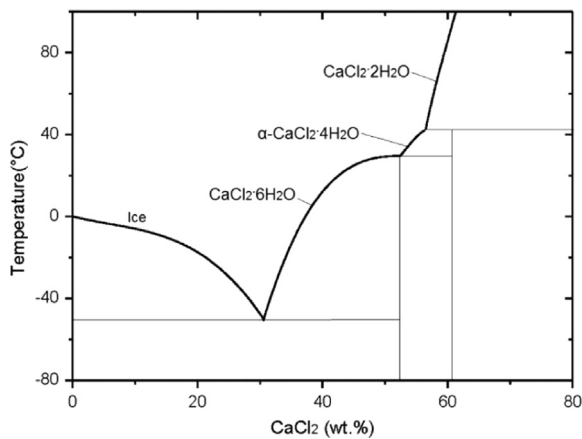


Fig. 5. Phase diagram of calcium chloride–water system.

Table 4

Melting temperature and heat of fusion of calcium chloride hexahydrate.

Melting temperature (°C)	Heat of fusion (J/g °C)	Ref.
29.8		Bakhuis Rooseboom [35,36]
29.3	160	Abhat et al. [37]
29.0	160	Abhat and Malatidis [38]
29.5		Lannung [39]
29.5		Carlsson et al. [32]
29.5	198	Meisingset and Grønvold [40]
29.3	209	Feilchenfeld et al. [41]

stable tetrahydrate is formed. CCH is produced as a waste co-product in many chemical processes including production of soda ash. The pure CCH is produced by dissolving limestone in hydrochloric acid. The part of the simplified phase diagram of  $\text{CaCl}_2\text{-H}_2\text{O}$  system has been built using compiled data by Zdanovskii et al. [31] and shown in Fig. 5. More detailed information regarding the chemical behaviour of CCH can be found in Lane [13], Carlsson et al. [32], Carlsson and Wettermark [33] and Carlsson [34].

#### 2.4.1. The melting temperature and heat of fusion

A very detailed investigation of the binary calcium chloride–water system was carried out by Bakhuis Rooseboom in [35,36]. Fig. 5 shows diagrams obtained by the authors of this review paper by processing experimental results presented in [35,36]. The melting point of CCH and peritectic point ( $\text{CaCl}_2 \cdot 6.1\text{H}_2\text{O}$ ) has the same value of 29.8 °C. The measurements of the melting temperature carried out by Abhat et al. using the DSC produced the values of 29.3 °C [37] and 29.0 °C [38]. It should be highlighted that the melting of CCH observed in [38] took place in the temperature range between 28.5 °C and 30.2 °C. Table 4 presents the results of original measurements of the melting temperature and heat of fusion, which were carried out by a number of researchers. It can be seen in the table that information obtained is in a good agreement. It is recommended by authors of this paper to use the value of 29.5 °C for the CCH melting point.

The heat of fusion of CCH has been measured in four original research studies. The significant differences between data presented in [37,38] and in [40,41] cannot be explained by measurement errors only. The fact that the non-equilibrium solidification of CCH resulted in production of some amount of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and that it was only observed during the partial phase transition was underlined by a number of scholars. The similar effect can be observed in experiments by Abhat et al. [37]. The traditional calorimetric measurements by Meisingset and

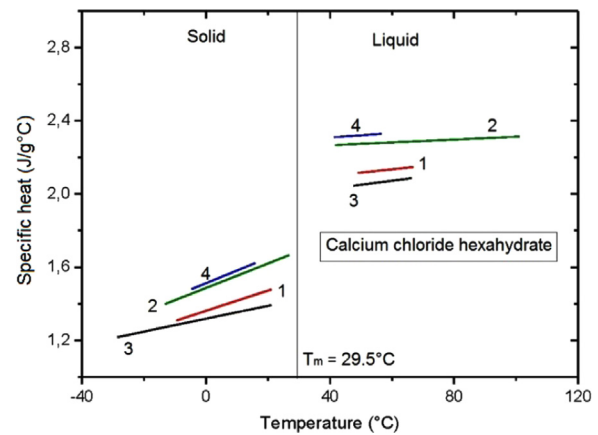


Fig. 6. Specific heat of calcium chloride hexahydrate vs. temperature: 1 – Lane [42]; 2 – Meisingset and Grønvold [40]; 3 – Lane [14]; 4 – Malatidis and Abhat [43].

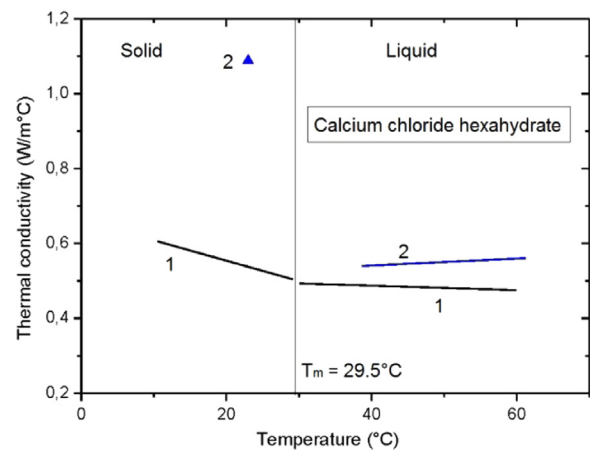


Fig. 7. Variation of the thermal conductivity of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  with, temperature: 1 – Nikolić and Tripković [44]; 2 – Lane [14].

Grønvold [40] and Feilchenfeld et al. [41] produced the values that are close to each other. Meisingset and Grønvold [40] used in their experiments a high precision adiabatic calorimeter. Therefore, it is recommended by authors of this paper to use the value of 198 J/g as the heat of fusion for calcium chloride hexahydrate.

#### 2.4.2. Density

Information on measurements of the temperature dependence of the CCH density in solid and liquid state has not been found in the open literature.

#### 2.4.3. Specific heat

The specific heat of CCH was measured by in [14] and [41] using the DSC technique. It can be seen in Fig. 6 that results of both measurements are very close to each other. Measurements by Abhat and his co-workers [37] were also carried out using a differential scanning calorimeter. Experiments by Meisingset and Grønvold [40] were carried out using an adiabatic calorimeter. The values obtained by Meisingset and Grønvold [40] and Abhat et al. [37] are practically identical. As the measurement technique used by Meisingset and Grønvold are more accurate, then their data are recommended to be used as a reference.

#### 2.4.4. Thermal conductivity

The thermal conductivities of CCH for the solid and molten states were investigated by Lane [14] and Nikolić et al. [44]. The results of the above measurements are presented in Fig. 7. In the

liquid state, the values obtained in the both measurements are in a good agreement whilst for the solid state the obtained values are very different and deviations exceed the normal range of measurement errors. Therefore, further accurate measurements are required to obtain the refined values of the coefficient of thermal conductivity for both the solid and liquid states.

#### 2.4.5. CCH as a phase change latent heat storage material

The low cost and abundance of CCH make it attractive as a phase change latent heat storage material [40–81]. The tendency to supercooling and formation of tetrahydrate in the process of the CCH crystallisation prevented its application as a latent heat storage material but, as a result of numerous detailed investigations, several compositions were developed which are suitable for latent heat storage applications. For example, Kimura and Kai [68] observed that the  $\text{CaCl}_2 \cdot 6.11\text{H}_2\text{O}$  composition, containing the amount of water which slightly exceeds that in the stoichiometric composition of CCH but less than in the peritectic composition ( $\text{H}_2\text{O}=6.12$ ), has a higher stability than that of calcium chloride hexahydrate. Introduction of sodium, potassium and rubidium chlorides and fluorides additives into this composition in small amounts (up to 1 wt%) made it possible to carry out more than 1000 thermal cycles of melting and crystallisation without noticeable changes in thermal characteristics. The heat of fusion for CCH was determined using the DSC technique and was reported to be equal to 180 J/g. The high level of stability of the PCM on the basis of CCH, created by Lane and Rossow [73] (Dow Chemical), was demonstrated by Porisini [75] by performing tests with more than 5000 thermal cycles of melting and freezing.

Tyagi et al. [77] experimentally investigated the performance of the PCM based on CCH with the melting temperature of 23.26 °C and heat of fusion equal to 125 J/g. The DSC Q-100 was used for measurements of its thermal properties during 1000 thermal cycles. The samples have been tested with the temperature change rate of 7° per minute in the temperature range from –10 °C to +60 °C. The test results are presented in Table 5. As it can be seen, no noticeable changes in the melting temperature or heat of fusion were recorded.

### 2.5. Lithium nitrate trihydrate (LNT- $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ )

Its molecular weight is 122.99 g/mol and the weight proportions of salt and water are 56.05% and 43.95%, respectively.  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  occurs as orthorhombic crystals in the lithium nitrate–water system. LNT is produced as the result of reaction of nitric acid and lithium carbonate. The phase diagram of the lithium nitrate–water system which is built using data published in [82–86] is shown in Fig. 8. In this system, there is only one compound,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , which melts congruently.

#### 2.5.1. Melting temperature and heat of fusion

The literature analysis carried out in the current study indicates that thermo-physical properties of this salt hydrate were not sufficiently studied. The most referenced value of the melting point for LNT is 29.88 °C, which had been obtained by Donnan and Burt [82] when they studied the solubility of lithium nitrate in water. Campbell and Bailey [83] observed the congruent melting of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  at 29.6 °C during their study of the lithium nitrate–ethanol–water

system. The values of the experimentally determined melting point and heat of fusion for this substance are summarised in Table 6. The value of 29.88 °C was obtained by Donnan and Burt using the LNT crystals which had been preliminary purified by multi-recrystallisation. The temperature in their experiments was measured using a special thermometer calibrated against a Travers' hydrogen thermometer. The melting temperatures reported by Koski [87], Shamberger and Reid [86] were obtained using calorimetric measurements. Therefore the above reported results are noticeably differ in values.

The heat of fusion of LNT was determined first by Livingstone et al. [76,77] in solubility experiments taking into account that the melting point is 29.88 °C and the measured value was 295 J/g. Data reported by Nedeljković [78] was also obtained using solubility measurements. In measurements by Koski [73] and Shamberger and Reid [74], the DSC technique was used. Unlike the case of the melting point values, all reported information on the heat of fusion for lithium nitrate trihydrate are in a very good agreement and small differences can be explained by the equipment accuracy limits in measuring experimental parameters.

#### 2.5.2. Density

The first density measurements of LNT were performed by Zavodnaya and Vorob'ev [91] and Mashovets et al. [92]. Shamberger and Reid [86] investigated the density of LNT along with its other thermophysical properties. Experimental data obtained by above authors is shown in Fig. 9. Results produced by Shamberger and Reid for the solid phase were calculated using available

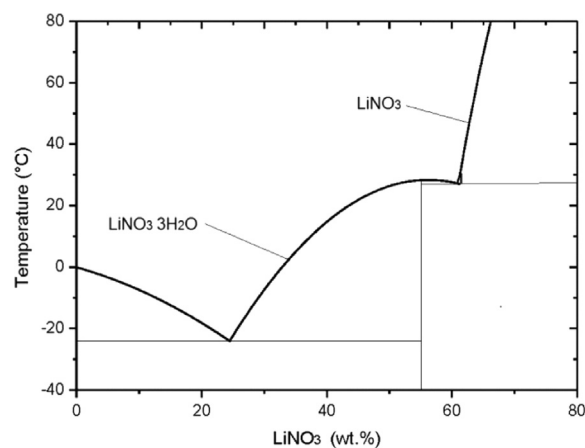


Fig. 8. Phase diagram of lithium nitrate–water system.

Table 6

Melting temperature and heat of fusion of lithium nitrate trihydrate.

Melting temperature (°C)	Heat of fusion (J/g °C)	Ref.
29.88		Donnan and Burt [82]
29.6		Campbell and Bailey [83]
	295	Livingstone et al. [88,89]
	283	Nedeljković [90]
31.1	290	Koski [87]
31.1	287	Shamberger and Reid [86]

Table 5

Influence of thermal cycling on thermal properties of the composition containing CCH [65].

Number of cycles	1	10	100	200	300	400	500	600	700	800	900	1000
$T_m$ (°C)	23.26	26.85	27.14	24.62	24.79	24.34	24.54	24.41	24.26	24.15	23.95	23.26
$\Delta H_m$ (J/g)	125.4	138.1	117.9	130.3	130.0	135.3	130.1	127.1	129.5	129.6	122.3	125.4

diffraction data in the open literature. As it can be seen, for the liquid phase all experimental data obtained is in a very agreement with each other. The above results were interpolated in this work as:

for the solid state

$$\rho_s (\text{g/cm}^3) = 1.5799 - 3.75 \times 10^{-4} t \text{ when } 16^\circ\text{C} \leq t \leq 28^\circ\text{C}$$

and for the liquid and supercooled states

$$\rho_l (\text{g/cm}^3) = 1.4599 - 0.001 t \text{ when } 25^\circ\text{C} \leq t \leq 80^\circ\text{C}$$

### 2.5.3. Other thermophysical properties

In general, thermophysical properties of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  are not sufficiently studied. There is only one study by Shamberger and Reid [86] which reports on results of comprehensive investigations of LNT thermophysical properties. Experimental data obtained in the above study is summarised in Table 7. The specific heat of LNT in the temperature range from 24.5 °C to 41 °C was also determined by Koski [87]. Experimental data on specific heat obtained in [86,87] is presented in Fig. 10.

### 2.5.4. LNT as phase change latent heat storage material

Its high heat of fusion and the melting point makes LNT a convenient material for a wide range of practical applications and a number of studies were performed to develop phase change compositions based on LNT. Examples of such compositions are shown in Table 8. The practical application of LNT and its blends is however very limited at present due to a high cost of lithium salts and particularly LNT whilst the cost of calcium chloride hexahydrate with similar properties is substantially lower.

### 2.6. Sodium sulphate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ Glauber's salt – SSD)

The molecular weight of sodium sulphate decahydrate is 322 g/mol. The weight proportions of salt and water are 44.09%

and 55.91%, respectively. Disodium sulphate is produced in water solutions below 32.38 °C in the form of colourless layered monocline prismatic crystals of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . In dry air this is rapidly

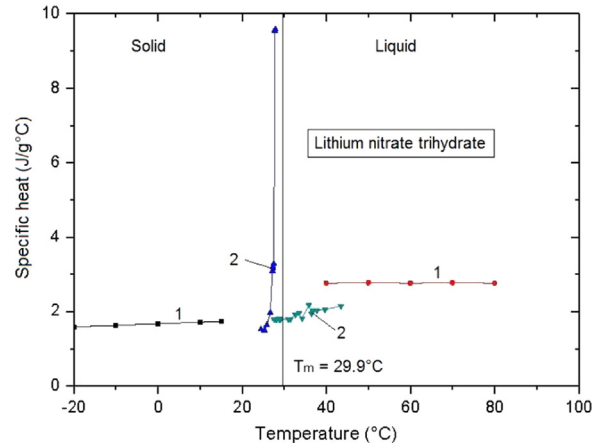


Fig. 10. Specific heat of lithium nitrate trihydrate: 1 – Shamberger and Reid [86]; 2 – Koski [87].

Table 8

Heat storage media on the basis of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ .

Latent heat storage composition (wt%)	$T_m$ (°C)	$\Delta H_m$ (J/g)	Ref.
(45–52) $\text{LiNO}_3 \cdot 3\text{H}_2\text{O} + (48–55)$ Zn ( $\text{NO}_3$ ) <sub>2</sub> · 6H <sub>2</sub> O	17.2	220 ± 5	Danilin et al. [93]
(55–65) $\text{LiNO}_3 \cdot 3\text{H}_2\text{O} + (35–45)$ Ni ( $\text{NO}_3$ ) <sub>2</sub> · 6H <sub>2</sub> O	24.2	230 ± 5	Danilin et al. [94]
(47.3–52.2) $\text{LiNO}_3 \cdot 3\text{H}_2\text{O} + (41.5–42.5)$ Co( $\text{NO}_3$ ) <sub>2</sub> · 6H <sub>2</sub> O + (5.8–9.7) H <sub>2</sub> O	22.3	265	Danilin et al. [95]
(50–55) $\text{LiNO}_3 + (7–9)$ NaNO <sub>3</sub> + (34–43) H <sub>2</sub> O	27		Neuschütz et al. [96]

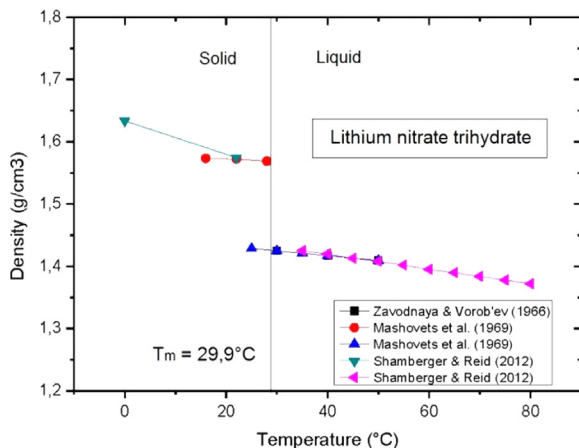


Fig. 9. Temperature dependence of lithium nitrate trihydrate density.

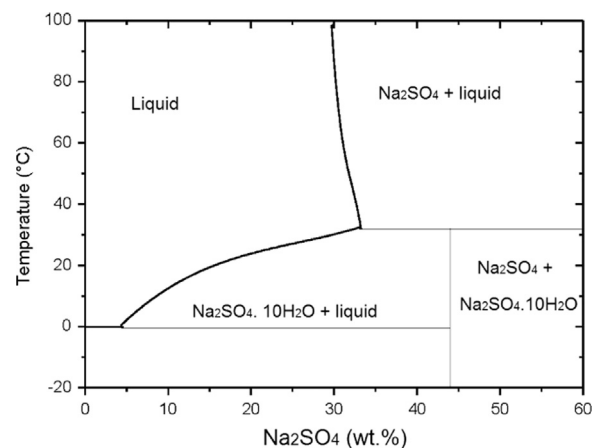


Fig. 11. Partial phase diagram of the sodium sulphate–water system.

Table 7

Thermophysical properties of lithium nitrate trihydrate determined by Shamberger and Reid [86].

Property	Temperature (°C)										
	–20	–10	0	10	20	30	40	50	60	70	80
Specific heat (J/g °C)	1.59	1.63	1.67	1.71			2.76	2.77	2.76	2.77	2.76
Thermal conductivity (W/m °C)	0.760	0.740	0.770	0.740	0.750	0.770	0.581	0.583	0.588	0.588	0.611
Thermal diffusivity (10 <sup>8</sup> m <sup>2</sup> /s)	30	29	29	28	27		14.0	14.1	14.2	14.2	14.5
Absolute viscosity (mPa s)							4.80	3.96	3.31	2.84	2.46



dehydrated. When heated above 32.4 °C, crystals melt in own water (see Fig. 11) forming salt anhydrous. In the nature,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  can be found as a mirabilit mineral. It can be seen in Fig. 11 that the melting of the Glauber's salt has a peritectic feature.

### 2.6.1. Melting temperature

The melting temperature for  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  listed in Table 1 was presented by Telkes in [10] but originally had been obtained in measurements by Richards [97] and Richards and Wells [98]. Sodium sulphate decahydrate is considered to be a perspective material for applications in the temperature range between the ice melting point and water boiling point. Its melting temperature was determined to be 32.38 °C using sufficiently accurate methods. Later, this value was confirmed in the investigations conducted by Dickinson and Mueller [99] with a deployment of a high accuracy technique. The melting temperature with the value of 32.37 °C was obtained by Magin et al. [100]

### 2.6.2. Density

The literature search conducted by authors of the current work indicated that there have been no experimental investigations conducted on determination of the temperature dependence of the density of Glauber's salt in the solid and molten states.

### 2.6.3. Specific heat and heat of fusion

The first measurement of the specific heat of molten sodium sulphate decahydrate was conducted by Kobe and Anderson [101]. There are three studies, namely by Pitzer and Coulter [102], Brodale and Giaque [103] and Grønvold and Meisingset [104], in which investigations of the temperature dependence of the specific heat of Glauber's salt were carried out using adiabatic calorimeters. Data obtained in above investigations is presented in Fig. 12. As expected, values obtained using adiabatic calorimeters are close to each other. The values of the heat of fusion determined by Cohen [105] and Leehardt and Boutaric [106] are 214 J/g and 239 J/g, respectively.

The melting enthalpy measured by Kobe and Anderson [101] was 243 J/g. The most accurate measurements were made with the use of adiabatic calorimeters [103,104] and these produced values for heat of fusion equal to 242 J/g and 245 J/g. Telkes also described in his paper [10] some studies which had reported measurements of the heat of fusion of molten sodium sulphate decahydrate (see Table 1) but original sources of data could not be found by authors of this review paper.

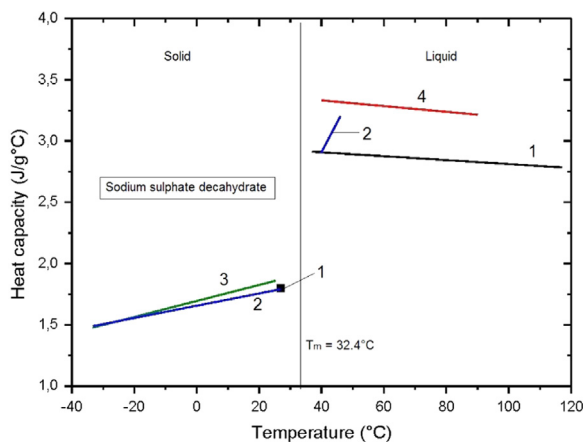


Fig. 12. Temperature dependence of sodium sulphate decahydrate specific heat: 1 – Grønvold and Meisingset [104]; 2 – Brodale and Giaque [103]; 3 – Pitzer and Coulter [102]; 4 – Kobe and Anderson [101].

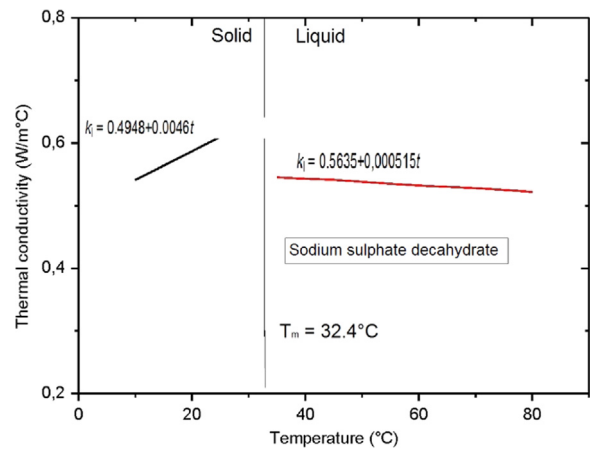


Fig. 13. Temperature dependence of sodium sulphate decahydrate thermal conductivity.

### 2.6.4. Thermal conductivity

There is only one study in which the temperature dependence of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  was investigated, namely by Nie et al. [94]. Data from this work originally presented in the table form is shown as liner functions in Fig. 13.

### 2.6.5. SSD as the phase change latent heat storage material

Due to its low cost, SSD is very attractive as heat storage material and first studies in this area were carried out by Telkes [108,109]. The main shortcoming of this crystal hydrate is its tendency to supercooling and separation of phases. The investigations of Telkes and then other researchers were directed on minimising effects of the above shortcomings. A number of improvements in SSD characteristics were achieved by Marks [111–113], Herrick et al. [114,115] and others [110,116–126,128,129]. Because of these improvements it became possible for phase change materials on the basis of SSD to maintain their characteristics up to 1000 thermal cycles and heat of fusion on the level of 220 J/g. However, in general, thermophysical properties of commercially produced phase change materials on the basis of SSD have not been investigated in detail.

## 2.7. Sodium carbonate decahydrate (SCD – $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ )

The molecular weight of SCD is 286.14 g/mol. The weight proportions of salt and water are 37.04% and 62.94%, respectively. The sodium carbonate crystals occur in various forms: the colourless  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  monoclinic crystals above 32 °C transform into colourless rhombic crystals of  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ . The latter, when heated above 35.37 °C, transforms into colourless crystalline  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . SCD crystallises from water solutions of sodium carbonate at the temperatures below 33 °C. The phase diagram of the sodium carbonate–water system which is built by authors of this study using results of investigations by Kobe and Sheehy [130] and compiled data by Zdanovskii et al. [20] are presented in Fig. 14. As it can be seen in this figure, sodium carbonate decahydrate melts incongruently.

### 2.7.1. Melting temperature and heat of fusion

The melting temperature referenced by Telkes [10] (see Table 1) appear to be based on the study by Kobe and Sheehy [130]. The first preliminary determination of the melting point for a set of salt hydrated crystals was carried out by Richards and Churchill [131]. In their experiments the melting temperature of SCD was found to be 35.2 °C. As the experiments of Wells and McAdam [132] demonstrated, this temperature corresponds to the

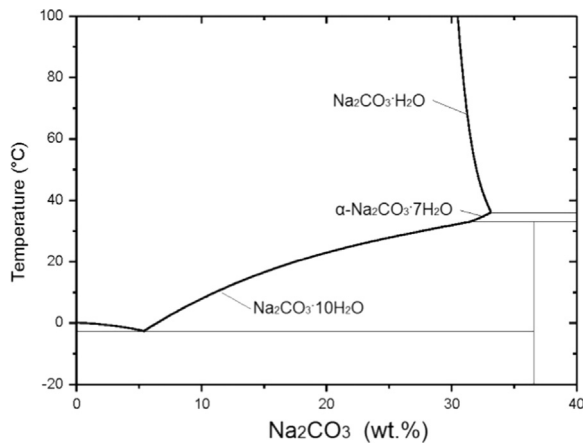


Fig. 14. Phase diagram of disodium carbonate–water system.

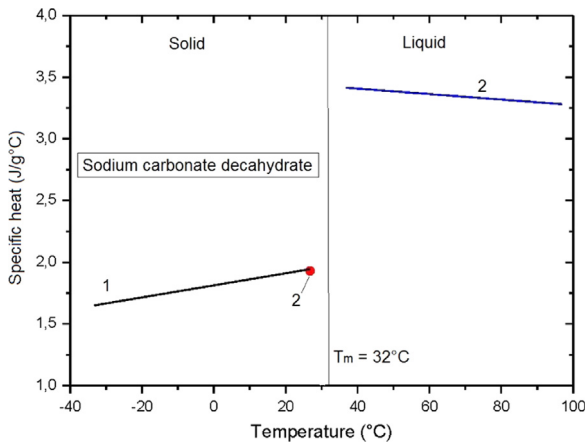


Fig. 15. Specific heat of sodium carbonate decahydrate vs temperature: 1 – Waterfield et al. [135]; 2 – Grønvold and Meisingset [134].

equilibrium temperature between heptahydrate and monohydrate forms of sodium carbonate. Their measurement of this equilibrium temperature produced the value of 35.37 °C. The melting point of SCD found by Wells and McAdam [132] was 32.00 °C. The accurate measurement of the melting point by Richards and Fiske [133] using samples of SCD obtained by multi-recrystallisation and high precision Beckmann thermometers produced the value of 32.017 °C. Grønvold and Meisingset [134] using calorimetric measurements established that SCD melts at the temperature of 32.0 °C. Thus, the recommended value of the melting temperature for sodium carbonate decahydrate is 32.0 °C.

Telkes [10] referenced several studies which produced the value of the heat of fusion. However, the authors of this review paper were not able to access original publications. There is only a single work of Grønvold and Meisingset [134] in which the heat of fusion was determined using an adiabatic calorimeter and this value was found to be 235 J/g.

#### 2.7.2. Density

The literature search conducted by authors of this work indicates that there have been no experimental investigations conducted on determination of the temperature dependence of the density of sodium carbonate hexahydrate in the solid and molten states.

#### 2.7.3. Specific heat

There are two original studies on the measurement of the specific heat with the use of adiabatic calorimeters. The results of these measurements are presented in Fig. 15. As it can be seen in

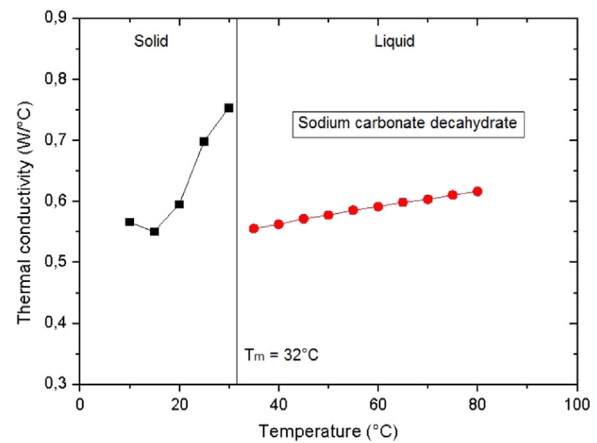


Fig. 16. Temperature dependence of SCD thermal conductivity.

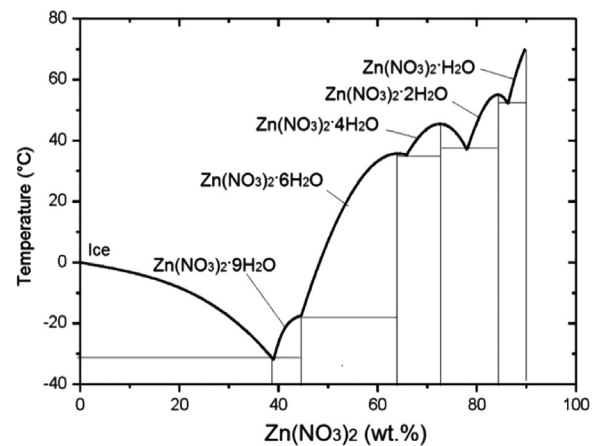


Fig. 17. Phase diagram of zinc nitrate–water system.

this figure, Waterfield et al. [135] measured the specific heat only in the solid phase and Grønvold and Meisingset [134] conducted measurements predominantly in the liquid phase. The specific heat measured for the temperatures lower than the melting point coincides with values provided by Waterfield et al. [135].

#### 2.7.4. Thermal conductivity

The temperature dependence of the thermal conductivity of SCD measured by Nie et al. [107] is presented in Fig. 16. Behaviour of SCD in the solid phase is unusual in comparison with other salt hydrates. At the same time, the behaviour in the liquid phase is similar to behaviour of other salts hydrates.

#### 2.7.5. SCD as phase change latent heat storage material

According to Fig. 14, sodium carbonate decahydrate has incongruent character of melting and it decomposes into sodium carbonate heptahydrate and water. The last two factors present barriers to application of SCD as a PCM. In addition, it has tendency to supercooling. In accordance with Chen [119], to avoid supercooling, the temperature of SCD should be maintained below 38 °C. Currently, SCD is considered to be less attractive as a potential latent heat storage material in comparison with Glauber's salt or calcium chloride hexahydrate. Alexandrov and Sobolev [137] recommended the eutectic mixture on the basis of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  to use as a latent heat storage material.

## 2.8. Zinc nitrate hexahydrate (ZNH – $Zn(NO_3)_2 \cdot 6H_2O$ )

The molecular weight of ZNH is 297.49 g/mol. The weight proportions of salt and water are 63.67% and 36.33%, respectively. ZNH is formed as colourless rhombic crystals which grow from the zinc nitrate water solution when the temperature exceeds  $-17.6^\circ\text{C}$ . At temperatures above  $105^\circ\text{C}$ , it is fully dehydrated.  $Zn(NO_3)_2$  is produced in the reaction of nitric acid with zinc or zinc oxide (carbonate). The phase diagram of zinc nitrate–water system is shown in Fig. 17 and it is based on experimental data by Funk [27], Ewing et al. [138] and Sieverts and Petzold [139]. It can be seen in this diagram that a number of zinc nitrate hydrates including  $Zn(NO_3)_2 \cdot 6H_2O$  is produced.

### 2.8.1. Melting temperature and heat of fusion

The first study on the melting point for some nitrate water compounds was carried out by Ordway [140] and the melting temperature of ZNH has been reported by him to be  $36.388^\circ\text{C}$ . Later Funk [27] investigated the solubility of metal nitrates and reported the melting temperature of zinc nitrate hexahydrate equal to  $36.4^\circ\text{C}$ . The lower melting temperature of  $36.1^\circ\text{C}$  was observed by Ewing et al. [138] for the composition with the lower zinc nitrate content (63.4 wt%). Jain [141] studied the density of molten ZNH and found that its melting temperature was  $36.9^\circ\text{C}$ . No other investigations on the ZNH melting point have been found in this review work.

The value of the heat of fusion equal to 130 J/g was cited by Telkes (see Table 1) based on the work of Riesenfeld and Milchsack [30] who had experimentally determined this value using a bomb calorimeter. Abhat et al. [142] reported the different values of the heat of fusion, namely 147 J/g. The conclusion can be made that the latter value was obtained with the use of the DSC technique.

### 2.8.2. Density

The density of molten ZNH was measured by Jain [141], Ramana et al. [143] and Sharma et al. [144]. All reported experimental data is in a good agreement and this information was interpolated by authors of the current work as the following linear function:

$$\rho_l(\text{g}/\text{cm}^3) = 1.8689 - 1.13 \times 10^{-3} t(^{\circ}\text{C}) \quad 39^\circ\text{C} \leq t \leq 80^\circ\text{C}$$

### 2.8.3. Specific heat

The specific heat of ZNH was measured by Abhat et al. [37] and Aboul-Enein and Ramadan [145] as a function of the temperature in the solid and liquid states using the DSC technique. Data obtained is presented in Fig. 18. It can be observed in this figure

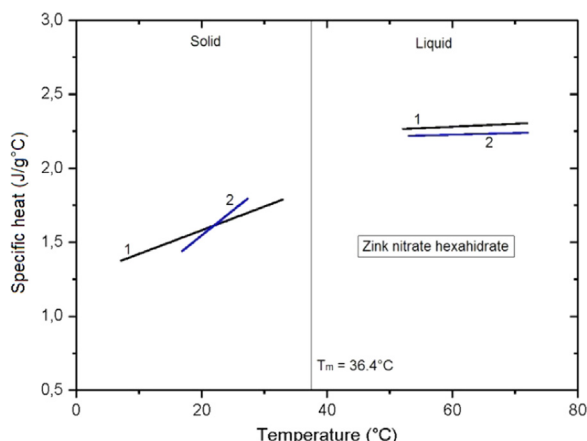


Fig. 18. Specific heat of zinc nitrate hexahydrate: 1 – Abhat et al. [37]; 2 – Aboul-Enein et al. [145].

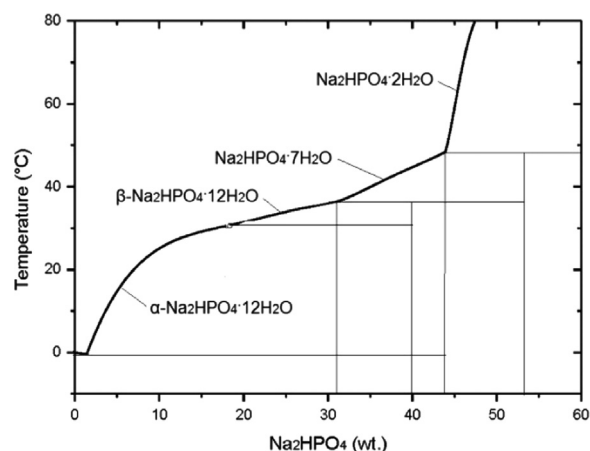


Fig. 19. Phase diagram of sodium hydrogen phosphate–water system.

that the measured values for the liquid phase are in a good agreement whilst there is a difference in the trend for the values determined for the solid phase.

### 2.8.4. ZNH as phase change latent heat storage material

The congruent character of melting makes ZNH very attractive for developing PCMs on its basis. Danilin et al. [146–148] developed the phase change composition on the basis of ZNH and used additives to decrease supercooling to  $5^\circ\text{C}$ . The latent heat storage composition melts at the temperature of  $36.4 \pm 0.1^\circ\text{C}$ .

## 2.9. Disodium hydrogenphosphate dodecahydrate (DHPD – $Na_2HPO_4 \cdot 12H_2O$ )

The molecular weight of DHPD is 358.14 g/mol. The weight proportions of salt and water are 39.64% and 60.36%, respectively. DHPD is formed as colourless monocline platelets, which dry in air with the water loss. The phase diagram of  $Na_2HPO_4$ – $H_2O$  system in Fig. 19 is drawn using data by Zdanovskii et al. [31]. The first  $\alpha$ -phase of DHPD PD is stable up to  $29.6^\circ\text{C}$  and the second  $\beta$ -phase undergoes the peritectic reaction at  $35.2^\circ\text{C}$  with forming heptahydrate of disodium hydrogen phosphate and the liquid phase containing anhydrous. Since there is only small difference between stoichiometric and peritectic compositions then this crystal hydrate has tendency to decomposition and when heated up to  $95^\circ\text{C}$  it losses 12 molecules of water.

### 2.9.1. Melting temperature and heat of fusion

The melting temperature of  $36.45^\circ\text{C}$  cited by Telkes in [10] is based on data of Shiomi [149]. This temperature was obtained when Shiomi investigated the phase diagram of sodium hydrogen phosphate–water binary system. Later Hammick with colleagues [150] studied the same binary system and as a result of a number of tests found that the average value for the melting temperature of DHPD was  $35.1^\circ\text{C}$  but recommendation was made to use the value for melting point as  $35^\circ\text{C}$ . The Japanese scientists Hirano and Saitoh [152], Hirano et al. [151] carried out investigations on several thermophysical properties of DHPD and observed that it melted at the temperature of  $35.54^\circ\text{C}$ . The measurements of Specific heat by Lan et al. [153] and Nicolici et al. [154] produced the temperature of melting of  $35.2^\circ\text{C}$  and  $34.9^\circ\text{C}$ , respectively. The recommended melting point for DHPD is  $35.2^\circ\text{C}$ .

The original research, outcomes of which were cited by Telkes [10] (see Table 1), could not be identified by authors of this review article. Only two original works were found in which the heat of fusion of DHPD was measured. The melting enthalpy measured by Hirano et al. [151,152] using the DSC technique was  $256.6\text{ J/g}$ . The

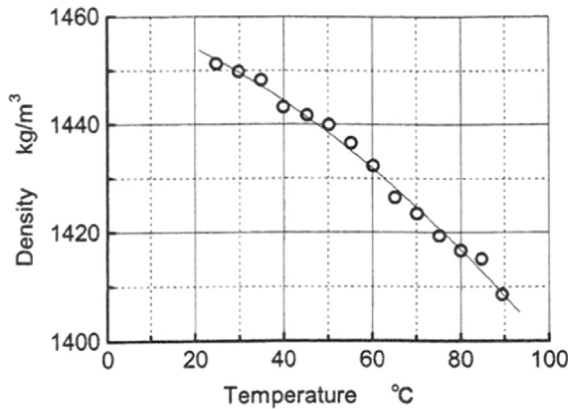


Fig. 20. Density of SHPD vs temperature Hirano and Saitoh [151,152].

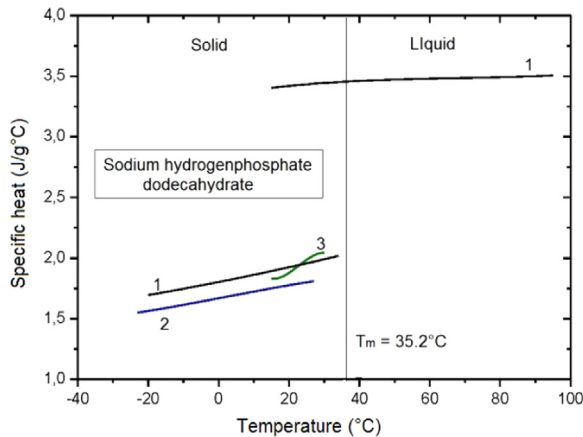


Fig. 21. Specific heat of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ : 1 – Hirano et al. [151,152]; 2 – Waterfield and Staveley [155]; 3 – Lan et al. [153].

measurement errors were estimated to be in the  $\pm 3.7$  J/g range. The measurements performed by Garay Ramirez et al. [127] with using an adiabatic calorimeter produce the value equal to 181 J/g. As it can be seen, there is a significant discrepancy in the above measurements and this cannot be explained by measurement errors only. Therefore, the additional measurements are required for this property.

### 2.9.2. Density

The experimental data on DHPD in the liquid and supercooled phase were obtained by Hirano and Saitoh [151,152] and can be described as the following function:

$$\rho_l(\text{g/cm}^3) = 1.461 - 2.93 \cdot 10^{-4}t - 3.289 \cdot 10^{-6}t^2 \quad \text{for } 25^\circ\text{C} \leq t \leq 90^\circ\text{C}$$

The trend in the temperature variation of density is shown in Fig. 20. The solid state density measured by the above authors is  $1.52 \text{ g/cm}^3$  (corresponding temperature were not reported). The measurement errors were estimated to be in the  $\pm 0.006 \text{ g/cm}^3$  range.

### 2.9.3. Specific heat

Waterfield and Staveley [155] measured the specific heat of DHPD for the temperature range from 10 K to 300 K using an adiabatic calorimeter. The same technique was deployed by Lan et al. [153] in the narrow temperature range from 288 K to 303.7 K. In measurements of Hirano and Saitoh [151,152], the DSC technique was used for determination the specific heat in the solid and liquid states. The diagram with experimental data obtained in the above studies is shown in Fig. 21. As it can be seen, all

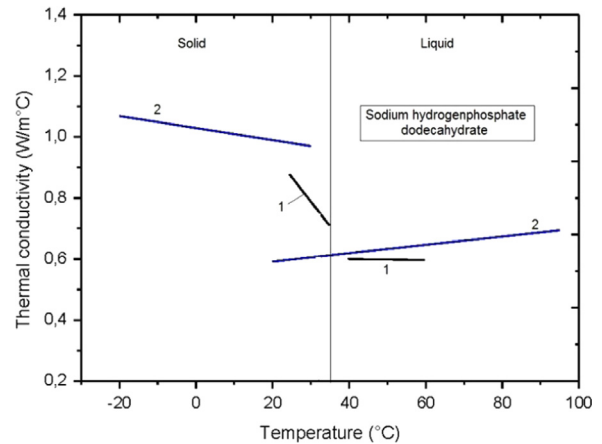


Fig. 22. Thermal conductivity of disodium hydrophosphate dodecahydrate: 1 – Nikolić et al. [154]; 2 – Hirano et al. [151,152].

Table 9

Heat storage compositions on the basis of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

Heat storage composition content	Ref.
$\text{Na}_2\text{HPO}_4$ (35 wt%) + water (65 wt%) + glass wool (1 vol%)	Telkes [156]
$\text{Na}_2\text{HPO}_4$ (100 w.p.) <sup>a</sup> + water (150–260 w.p.) + sharcoal (0.1–50 w.p.) + $\text{Na}_3\text{PO}_4$ (11.0–46.2 w.p.)	Broadley and Town-end [157]
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ + water (0.5–5 wt%) + urea (0.1–2.0 wt%)	Fridrichs and Friedrichs-Weinle [158]

<sup>a</sup> w.p. – weight part.

experimental data in the solid state is in good agreement whilst for the liquid phase there is only data obtained by Japanese researchers. Experimental data in Fig. 21 can be described by the following equations:

$$C_{ps}(\text{J/g}^\circ\text{C}) = 1.803 + 5.736 \times 10^{-3}t + 1.739 \times 10^{-5}t^2 \quad \text{for } -20^\circ\text{C} \leq t \leq 34^\circ\text{C}$$

and

$$C_{pl}(\text{J/g}^\circ\text{C}) = 3.34 + 5.17 \times 10^{-3}t - 6.68 \times 10^{-5}t^2 + 3.23 \times 10^{-7}t^3 \quad \text{for } 15^\circ\text{C} \leq t \leq 100^\circ\text{C}.$$

### 2.9.4. Thermal conductivity

The steady-state method of co-axial cylinders was used by Nikolić et al. [154] for determination of thermal conductivity of solid and liquid  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  in the temperature range from 297 K to 333 K. In their work the copper cylinders coated by nickel were used. The reproducibility of measurement is estimated to be  $\pm 0.7\%$ .

Hirano and Saitoh [151,152] studied the thermal conductivity by using the transient plane source (TPS) technique. The results of these measurements are shown in Fig. 22. As the TPS technique accuracy is noticeably higher than the accuracy of the technique based on the steady-state method and therefore data of these Japanese researchers can be considered to be more reliable. Experimental data obtained by Hirano et al. can be presented by the following equation:

$$k_s(\text{W/m}^\circ\text{C}) = 1.079 - 1.973 \cdot 10^{-3}t \quad \text{for } -20^\circ\text{C} \leq t \leq 32^\circ\text{C}$$

and

$$k_l(\text{W/m}^\circ\text{C}) = 0.564 + 1.37 \times 10^{-3}t \quad \text{for } 20^\circ\text{C} \leq t \leq 95^\circ\text{C}.$$

### 2.9.5. DHPD as phase change latent heat storage material

The heat storage compositions on the basis DHPD were suggested by Telkes [156], Broadley and Townend [157] and Friedrichs and Friedrichs-Weinle [158]. The mixture compositions are presented in Table 9. Taking into account the unique feature of DHPD to remain in the supercooling state for a very long time, Hirano and Saitoh [159–164] investigated the performances of the solar energy system with a long-term heat storage using the thermo-physical properties which they previously had determined. It was shown that the DHPD heat storage was more efficient than the system with storages utilising the sensible heat. The efficiency of such the storage increases with a duration of the storage period. Hirano and Saitoh demonstrated that the application of DHPD in the solar space heating system with floor heating made it possible to decrease the heat consumption by 20%. Since the supercooling is the main barrier for DHPD's application, some mechanism is required to initiate the crystallisation when required. With this aim, the influence of ultrasonic vibration on supercooling degree was investigated. It was demonstrated that there was no influence of ultrasonic vibrations on supercooling but that the presence of a stainless steel bar in the capsule with DHPD stimulated its crystallisation due to bar's vibrations. A similar investigation of the effect of ultrasonic waves on nucleation phenomena in a  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was performed by Miyasaka et al. [165]. Despite a relatively large number of investigations being performed, currently there is no information on practical application of heat storage systems based on DHPD.

### 2.10. Calcium nitrate tetrahydrate (CNT – $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ )

The molecular weight of CNT is 236.149 g/mol. Weight proportions of salt and water are 69.48% and 30.52%, respectively. Calcium nitrate is extracted from water solutions as tetrahydrate which forms colourless hygroscopic monocline crystals. Calcium nitrate can be dissolved in water (121 g of anhydrous salt in 100 ml of water at 291.2 K) and above 373.2 K it transforms into anhydrous salt. The natural mineral is sodium–calcium. Calcium nitrate is prepared by dissolving calcium carbonate in dilute nitrogen acid. The phase diagram of the  $\text{Ca}(\text{NO}_3)_2\text{--H}_2\text{O}$  system which was created using results of investigations by Bassett and Taylor [166], Ewing et al. [167] and Sieverts and Petzold [168] is presented in Fig. 23. As it can be seen in this figure, CNT melts congruently.

#### 2.10.1. Melting temperature and heat of fusion

First studies on the determination of the melting temperature were performed as a part of investigations of the equilibrium diagram in the calcium nitrate–water system. Later measurements were carried out in calorimetric studies. Data on the melting point

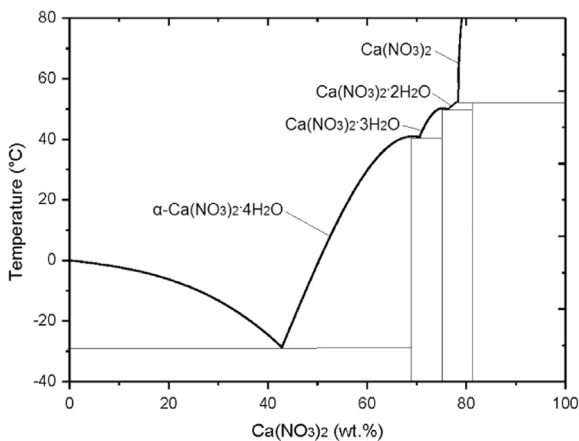


Fig. 23. Phase diagram calcium nitrate–water system.

and heat of fusion obtained in such studies are presented in Table 10, which shows that all reported values of the melting point coincide within measurements accuracy. The melting temperature and heat of fusion determined by Angell and Tucker [170], Guion et al. [15], and Xu and Hepler [171] were measured using the DSC technique. Only values provided by Angell and Tucker noticeably differ from data of other researchers and it is difficult to conclude what were factors that led to such the result.

#### 2.10.2. Density

The density was measured by various researchers using different methods and, as it can be seen in Fig. 24, the values are close to each other. Unfortunately, no data was found with regard to the density in the solid state. The sections of curves located in

Table 10  
Melting temperature and heat of fusion of CNT.

Melting temperature (°C)	Heat of fusion (J/g)	Ref.
42.3		Levingston et al. [169]
42.7		Bassett and Taylor [166]
42.7		Ewing et al. [167]
42.7		Sieverts and Petzold [168]
42.5	131	Angell and Tucker [170]
42.7	142	Guion et al. [15]
42.8	144	Xu and Hepler [171]

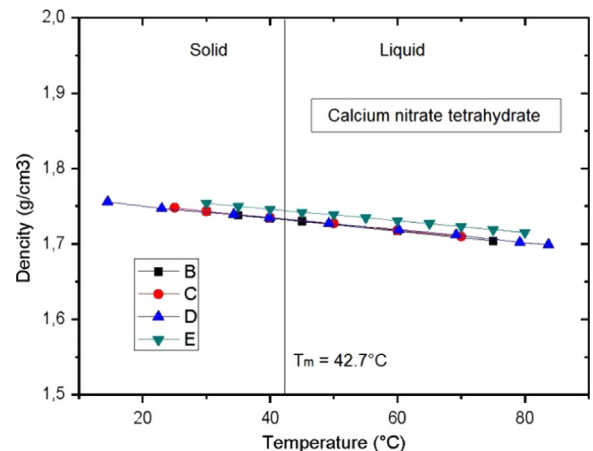


Fig. 24. Density of calcium nitrate tetrahydrate: B – Darbari [172]; C – Moynihan [173]; D – Jain [174]; E – Ramana [175].

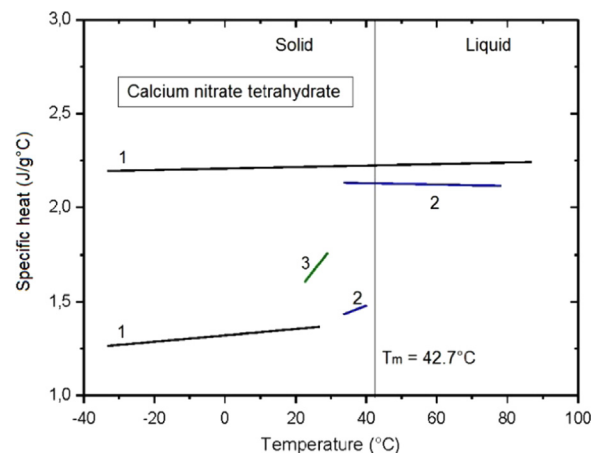


Fig. 25. Specific heat of calcium nitrate tetrahydrate: 1 – Angell and Tucker [170]; 2 – Xu and Hepler [171]; 3 – Zhdanov [176].

the temperature range, typical to the solid matter, are actually corresponding to the supercooled liquid. Experimental data obtained in several studies is in good agreement and therefore the density of CNT can be described by the following linear function:

$$\rho_1(\text{g/cm}^3) = 1.7683 - 7.558 \cdot 10^{-4} t \quad 10^\circ\text{C} \leq t \leq 90^\circ\text{C}.$$

### 2.10.3. Specific heat

The vacuum adiabatic calorimeter was used by Zhdanov et al. [176] for measuring the specific heat of CNT in the temperature range between 22.59 °C and 29.18 °C. The accuracy of measurements was estimated to be in the range of  $\pm 0.5\%$ . Other two measurements were performed by Angell and Tucker [170] and Xu and Hefler [171] using the DSC technique. Data obtained are shown in Fig. 25. Values obtained by Angel and Tucker, and Xu and Hefler are similar and these both differ from the value produced by Zhdanov et al. [176].

### 2.10.4. Thermal conductivity

There are only three research works in which the thermal conductivity of CNT was studied. Egorov et al. [177] and Nicolici with colleagues [154] used the steady-state method of coaxial cylinders for measuring the heat conductivity of CNT. The temperature dependence of this compound was determined by Sternberg and Mascas [178] using an apparatus specifically designed for the experiment. Thermal conductivity was determined by comparison of characteristics of the reference material and tested samples. The comparison was made based on application of the principle of a gas chromatography katharometer.

Experimental data obtained by Egorov et al. [177] were expressed as the following linear function:

in the solid phase

$$k_s(\text{W/m}^\circ\text{C}) = 0.43 + 0.001 t \quad -20^\circ\text{C} \leq t \leq 42^\circ\text{C};$$

in the liquid phase

$$k_l(\text{W/m}^\circ\text{C}) = 0.335 + 0.001 t \quad 42^\circ\text{C} \leq t \leq 95^\circ\text{C}.$$

The experimental results of Nicolici et al. [154] and Sternberg and Mascas [178] were approximated in this study using a linear function and presented in Fig. 26. It is obvious from this figure that further accurate measurements of the thermal conductivity are required.

### 2.10.5. CNT as the latent heat storage material

Despite the advantage of CNT having a congruent character of melting, its application in the thermal latent heat storage systems is not sufficiently studied [179].

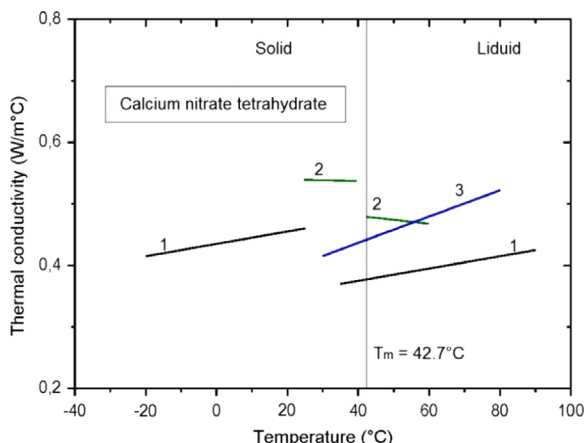


Fig. 26. Thermal conductivity of calcium nitrate tetrahydrate: 1 – Egorov et al. [177]; 2 – Nicolici et al. [154]; 3 – Sternberg and Mascas [178].

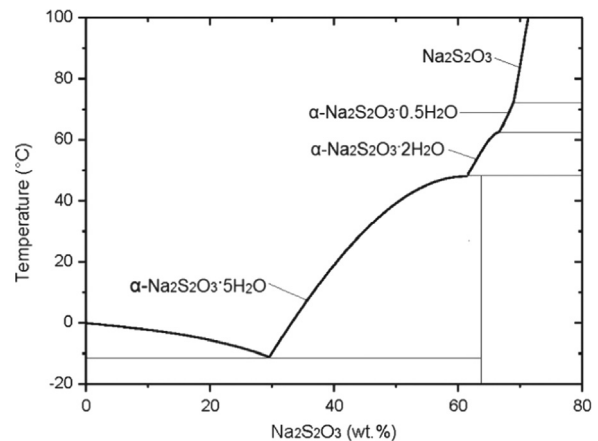


Fig. 27. Phase diagram of sodium thiosulphate–water system.

### 2.11. Sodium thiosulphate pentahydrate (STP – hyposulphite – $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )

Molecular weight of sodium thiosulphate pentahydrate is 248.186 g/mol. The weight proportions of salt and hydrate are 63.71% and 36.29%, respectively. STP is formed as transparent monocline crystals which are easily soluble in water. It melts at 48 °C in own crystallisation water and such the mixture undergoes a supercooling process and in such state it can be stored for several days. The hyposulphite is produced in large scale as the by-product in making sulphur colour agents. The phase diagram created by using mainly experimental data of Young and Burke [180] is shown in Fig. 27. As it can be seen, the melting of STP has a semi-congruent character.

#### 2.11.1. Melting temperature and heat of fusion

The melting temperature of STP was determined by Young and Burke [180] in their study of sodium thiosulphate–water system and the value obtained was 48.5 °C. The first determination of the melting point of sodium thiosulphate pentahydrate with the high accuracy was performed by Richards and Churchill [132] in their investigation of transition temperatures of several salt hydrates. The melting temperature of STP was found to be 48.0 °C. The calorimetric investigation of hyposulphite carried out by Grønvold and Meisingset [104] demonstrated that it melts at the temperature of 48.16 °C. The recommended value of the melting point of STP is 48.0 °C.

The first measurement of the heat of phase transition in STP was carried out by Sturley [181]. The heat of fusion was evaluated using a simplified drop calorimeter and the value was determined as 148 J/g. Abhat [182] reported the value of 201 J/g for the heat of fusion of sodium thiosulphate pentahydrate which had been determined using the DSC technique. Another measurement was performed by Grønvold and Meisingset [104] using an adiabatic calorimeter and the melting enthalpy was found to be 209 J/g. The results of last two measurements agree with each other with the accuracy within the range of experimentation errors. We recommend to use the value of 209 J/g for the heat of fusion of STP.

#### 2.11.2. Density

The density of molten STP has been investigated by Moynihan [183] and Bhattacharjee et al. [184]. The temperature dependence of the liquid hyposulphite density measured by Moynihan using a dilatometer can be presented as

$$\rho(\text{g/cm}^3) = 1.691 - 0.00071 t (\text{°C}). \quad 5^\circ\text{C} \leq t \leq 50^\circ\text{C}$$

The measurements performed by Bhattacharjee et al. [184] demonstrate that the temperature dependence of the molten STP density can be described as a linear function:

$$\rho(\text{g/cm}^3) = 1.696 - 0.00077 t (\text{°C}).$$

Measurement results in the two above studies are in good agreement with each other with the accuracy of 0.1%.

### 2.11.3. Specific heat

Regarding the specific heat of STP, two measurements were carried out, namely by Grønvold and Meisingset [104] and Abul-Enein and Ramadan [145]. Data obtained in these studies is presented in Fig. 28. These results are also in good agreement with each other.

### 2.11.4. Thermal conductivity

Nie and Zhang [185] determined the thermal conductivity of STP in the solid and liquid states. The obtained values are presented in Table 11. Measurement errors were estimated to be 3.4%. The value of 1.35 W/m °C found by Sturley [181] for the solid state is noticeably differs from the value by Nie and Zhang.

### 2.11.5. STP as phase change latent heat storage material

Due to the incongruent character of melting, the latent heat storage material based on hyposulphite requires corresponding additives to ensure the stability of the heat storage material during a large number of thermal cycling (1000 or greater). Garg and Nasim [190] did not discover such substances which would act as nucleating agents for sodium thiosulphate. The eutectic composition with the melting temperature of 22–23 °C based on STP and urea was proposed by Takeda et al. [193] to prevent the greenhouse overheating during the day time and its overcooling during the night time in a winter season. Canbazoglu et al. [194] experimentally investigated the unsteady thermal performance of an open loop passive solar water-heating system utilising the sodium thiosulfate pentahydrate-phase change material. The various aspects of the STP application as a phase change material were studied in [186–189,191,195].

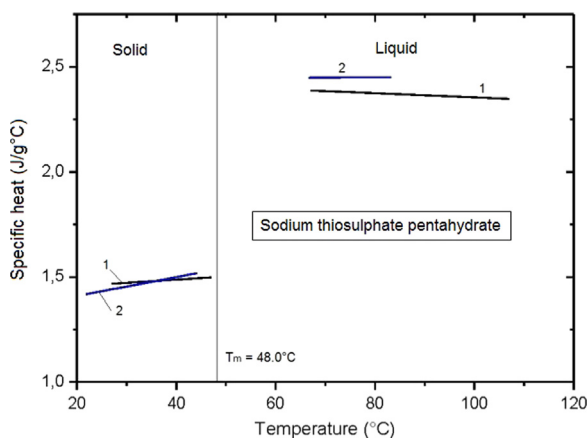


Fig. 28. Specific heat of sodium thiosulphate pentahydrate: 1 – Grønvold and Meisingset [104]; 2 – Abul-Enein and Ramadan [145].

Table 11

Thermal conductivity of sodium thiosulfate pentahydrate determined by Nie and Zhang [185].

T (°C)	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
$\lambda$ (W/m °C)	0.586	0.582	0.576	0.570	0.563	0.560	0.552	0.562	0.606	0.678	469	0.458	0.441	0.413	0.367

### 2.12. Sodium acetate trihydrate (SAT – $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ )

The molecular weight of SAT is 136.08 g/mol. The weight proportions of salt and water are 60.28% and 39.72%, respectively. SAT is formed as white colour crystals which are easily soluble in own crystallisation water. The phase diagram of  $\text{CH}_3\text{COONa}-3\text{H}_2\text{O}$  system created using experimental data of Green [196] and Sidgwick and Jentle [197] is presented in Fig. 29. As it can be seen in this figure, the peritectic composition is observed at the state corresponding to 58 wt% whilst the stable composition of SAT occurs at the state with 60.28 wt% of the sodium acetate. When heated to 58 °C, as a result of the peritectic reaction, the salt anhydrous and the solution containing 58 wt% of sodium acetate and 42 wt% of water are formed. This composition undergoes phase separation during thermal cycling. Another significant shortcoming of SAT is its supercooling (down to 80 °C) when it crystallises.

#### 2.12.1. Melting temperature

The fact that the value of the melting point equal to 58 °C had been cited in the most of publications, related to sodium acetate trihydrate, was highlighted by Green [196] from the University of Toronto in his paper on studying the solubility of sodium acetate in water. Jeannel [198] was the first who reported in 1866 that the melting process of SAT took place at 58 °C. Later on Prof. Lash Miller from the University of Toronto during investigations of sodium acetate trihydrate with a dilatometer confirmed that it melted at 58 °C. This value was confirmed by Green [196] and Sidgwick and Jentle [197] when they studied the solubility of sodium acetate in water and this value was cited by various scientists in further studies of sodium acetate trihydrate. Zhang et al. [199] used the *T-history* thermal analysis to confirm that SAT melted at 58 °C. The melting point of SAT obtained by Meisingset and Grønvold [200] from their measurements using an adiabatic calorimeter was 58.4 °C. The DTA and Q-TG measurements of

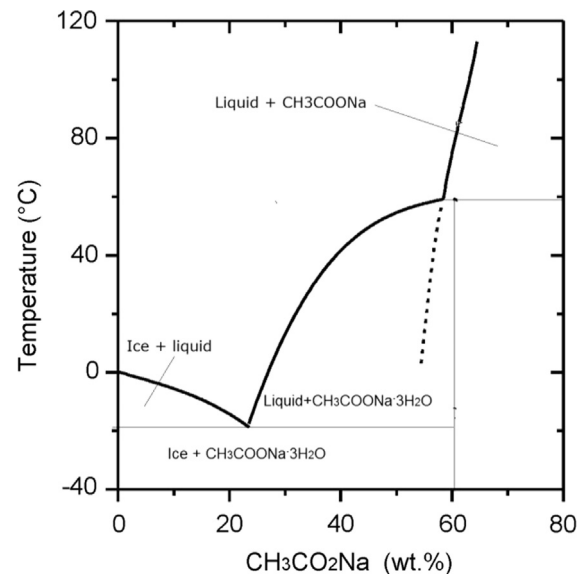
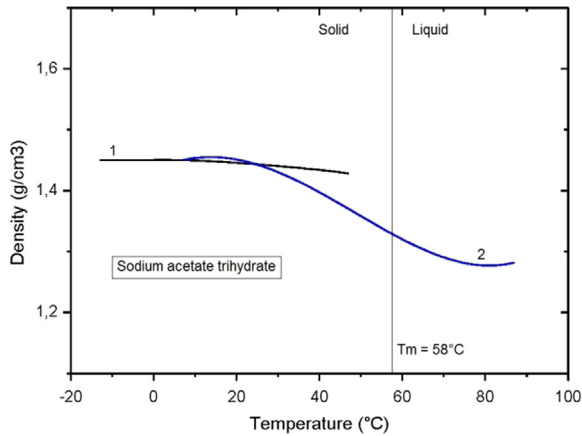


Fig. 29. Phase diagram of sodium acetate–water system.



**Fig. 30.** Density of sodium acetate trihydrate. Adapted from Inaba et al. [204]: 1 – solid phase; 2 – liquid and supercooled phase.

Nauman et al. [201] produced the melting temperatures equal to 56 °C and 57 °C, respectively. Cabeza et al. [202] reported the melting temperature of 55.6–56.5 °C for the composition made of 99 wt% SAT and 1 wt% additives. Wood et al. [203] using the DSC technique found that it melted at the temperature equal to 56.3–56.4 °C. From the information presented above it can be seen that there is a sufficiently large difference (2.9 °C) in the reported values of the SAT melting point.

### 2.12.2. Density

The only study on thermophysical properties of SAT in the solid and liquid states, including the density, was carried out by Inaba et al. [204] The results of the density measurements in that work are presented in Fig. 30. The accuracy of measurements was estimated to be  $\pm 1.5\%$ . The density of SAT in the solid and molten states can be approximated by following empirical equations:

in the solid state

$$\rho_s (\text{kg/m}^3) = 8.07 \cdot 10^2 + 4.77 T - 8.84 \cdot 10^{-3} T^2 \quad 260 \text{ K} \leq T \leq 329 \text{ K};$$

in the liquid and supercooled states

$$\rho_l (\text{kg/m}^3) = -1.99 \cdot 10^4 + 1.70 \cdot 10^2 T - 0.354 T^2 + 1.76 \cdot 10^{-5} T^3 - 1.80 \cdot 10^{-7} T^4 + 1.35 \cdot 10^{-9} T^5 \quad \text{For } 280 \text{ K} \leq T \leq 360 \text{ K}.$$

### 2.12.3. Specific heat and heat of fusion

Three original investigations were found in which the temperature dependence of the specific heat had been determined.

The specific heat of SAT measured by Inaba et al. [204] using a drop calorimeter can be presented as:

in the solid state

$$C_{ps} (\text{J/g K}) = 1.43 + 2.03 \cdot 10^{-3} T \quad 255 \text{ K} \leq T \leq 325 \text{ K};$$

in the liquid and supercooled states

$$C_{pl} (\text{J/g K}) = 2.96 + 1.51 \cdot 10^{-3} T \quad 265 \text{ K} \leq T \leq 365 \text{ K}.$$

The specific heat determined by Araki et al. [205] using a twin calorimeter of the heat transfer type also can be presented as linear functions:

in the solid phase

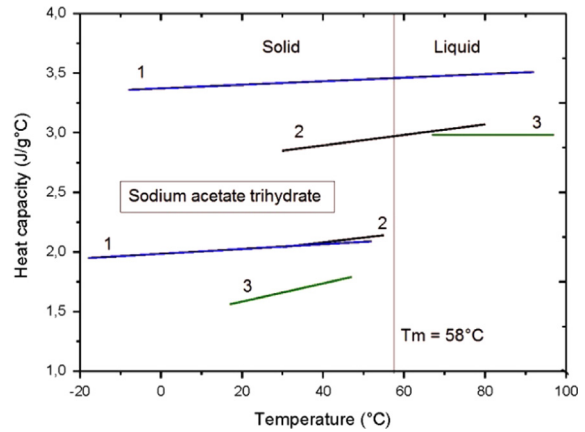
$$C_{ps} (\text{J/gK}) = 0.811 + 4.06 \cdot 10^{-3} T \quad 303 \text{ K} \leq T \leq 328 \text{ K};$$

in the liquid and supercooled phases

$$C_{pl} (\text{J/g K}) = 1.56 + 4.27 \cdot 10^{-3} T \quad 303 \leq T \leq 353 \text{ K}.$$

Finally, the specific heat of SAT reported by Meisingset and Grønvd [200] can be described by the following equations:

in the solid phase



**Fig. 31.** Specific heat of sodium acetate trihydrate: 1 – Inaba et al. [204]; 2 – Araki et al. [205]; 3 – Meisingset and Grønvd [200].

**Table 12**

Melting enthalpy of sodium acetate trihydrate.

Heat of fusion (J/g)	Measurement technique	Ref.
226	DSC	Schröder and Gawron [12]
289	DSC	Guion et al. [15]
278	Adiabatic calorimeter	Meisingset and Grønvd [200]
256 [(254+259)/2]	DSC	Wada et al. [206]
237 [(226+248)/2]	T-history thermal analysis	Zhang et al. [199]

$$C_{ps} (\text{J/g } ^\circ\text{C}) = 1.597 + 3.05 \cdot 10^{-3} t \quad -13 \text{ } ^\circ\text{C} \leq t \leq 47 \text{ } ^\circ\text{C};$$

in the liquid phase

$$C_{pl} (\text{J/g } ^\circ\text{C}) = 2.98 \quad 87 \text{ } ^\circ\text{C} \leq t \leq 127 \text{ } ^\circ\text{C}.$$

All the above functions presented as empirical equations to describe the temperature dependence of the specific heat of sodium acetate trihydrate are shown in Fig. 31. It can be seen in this figure that the values significantly differ from each other with discrepancies exceeding the measurement errors.

The original work, which was the source for the value reported by Telkes in Table 1, was not found. However, there is a number of other studies were performed to measure the heat of fusion. The results of these measurements are listed in Table 12. Preference should be given to the value of 278 J/g obtained by Meisingset and Grønvd.

### 2.12.4. Thermal conductivity

The thermal conductivity of SAT was measured by Inaba and his colleagues [204] and Araki et al. [205]. Nie et al. [185] performed similar measurements. Data obtained by Inaba and his colleagues can be described by the following equation (polynomial of the second order):

in the solid phase

$$k_s (\text{W/mK}) = 2.79 - 1.31 \cdot 10^{-2} T + 1.88 \cdot 10^{-5} T^2 \quad 240 \leq T \leq 325 \text{ K};$$

in the liquid phase

$$k_l (\text{W/mK}) = 0.925 - 3.64 \cdot 10^{-3} T + 6.62 \cdot 10^{-6} T^2 \quad 270 \leq T \leq 356 \text{ K}.$$

Experimental data by Araki et al. [205] in the solid state was described by authors of this study using the following equation:

$$k_s (\text{W/mK}) = 15.831 - 0.178 T + 1.796 \cdot 10^{-4} T^2 \quad 290 \leq T \leq 312 \text{ K}$$

Values for the liquid phase were fitted by Araki et al. into the following function:

$$k_l (\text{W/mK}) = -2.76 + 2.16 \cdot 10^{-2} T - 3.66 \cdot 10^{-5} T^2 \quad 293 \leq T \leq 343 \text{ K}$$



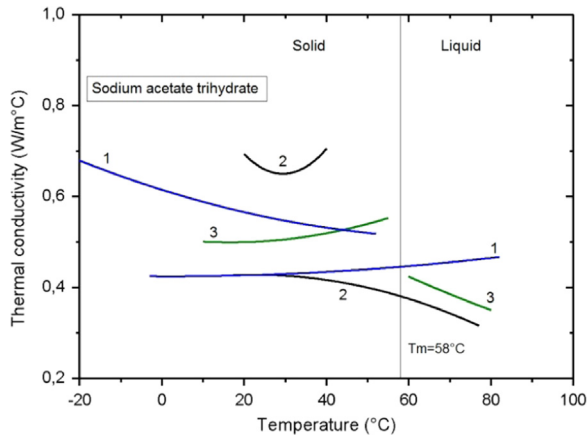


Fig. 32. Thermal conductivity of sodium acetate trihydrate: 1 – Inaba et al. [204]; 2 – Araki et al. [205]; 3 – Nie et al. [185].

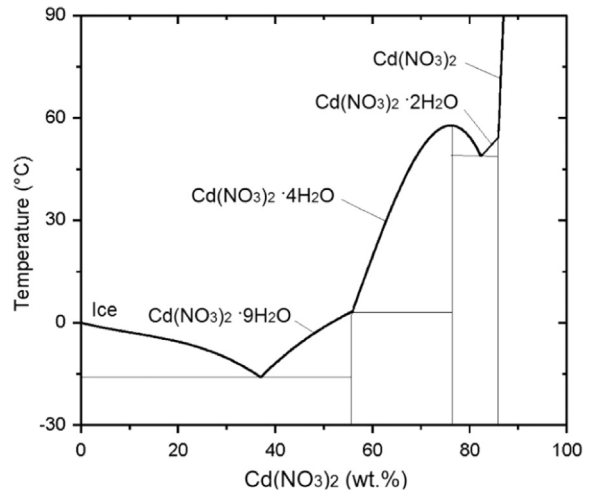


Fig. 34. Phase diagram of cadmium nitrate–water system.

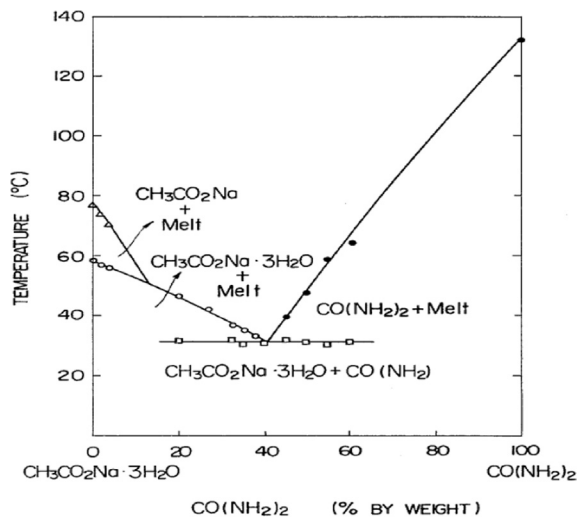


Fig. 33. Phase diagram of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ – $\text{CO}(\text{NH}_2)_2$  system [217].

Experimental information obtained by Nie et al. is presented by us as:  
in the solid phase

$$k_s (\text{W/m} \cdot ^\circ\text{C}) = 0.592 - 0.0192 t + 3.62 \cdot 10^{-5} t^2 \quad 10 \leq t \leq 55 \text{ } ^\circ\text{C};$$

and

$$k_l (\text{W/m} \cdot ^\circ\text{C}) = 0.727 - 6.08 \cdot 10^{-3} t + 1.71 \cdot 10^{-5} t^2 \quad 60 \leq t \leq 80 \text{ } ^\circ\text{C}$$

Experimentally obtained data on the thermal conductivity is summarised in Fig. 32.

#### 2.12.5. SAT as phase change latent heat storage material

Sodium acetate trihydrate due its low cost and abundance is the most extensively studied (along with calcium chloride hexahydrate) salt hydrate for application as the latent heat storage material [192,206–241]. The main attention of researchers and developers was focused on improving SAT's supercooling and stability. A number of additives were investigated as perspective nucleating agents and thickeners. The most suitable from that nucleating and thickening agents were patented which made it possible to decrease the level of supercooling to 5 °C and lower and withstand 1000 and greater thermal cycles without noticeable reduction in the heat of fusion [210–211,224–227].

In their studies of the pseudo-binary system  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  and  $\text{CO}(\text{NH}_2)_2$  Wada et al. [218] found that the 60 wt% SAT and

Table 13

Viscosity of molten cadmium nitrate tetrahydrate [243].

T (°C)	45.5	49.0	54.0	60.0	64.0	70.0	74.5
$\eta$ (P)	0.4874	0.4192	0.3430	0.2756	0.2413	0.1985	0.1741

40 wt%  $\text{CO}(\text{NH}_2)_2$  form the eutectic blend with the melting point of 31.5 °C (see Fig. 33). Investigations of this composition by Li et al. [212] using the DSC technique demonstrated that the mixture melted congruently at 30 °C and had the heat of fusion equal to 200 J/g.

Barret and Best [229,230] studied the heat storage capability of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  blends. The maximum heat storage capacity measured using a differential scanning calorimeter was 213 J/g for the mixture with 60:40 M ratio and its melting was observed at the temperature of 39 °C.

The research group of Furbo [238–241] investigated the possibility of utilising sodium acetate trihydrate for a seasonal storage of solar energy.

#### 2.13. Cadmium nitrate tetrahydrate (CNT – $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ )

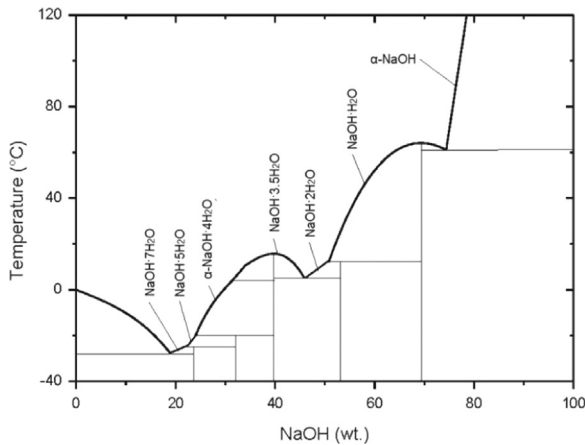
The molecular weight of CNT is 308.482 g/mol. The weight proportions of salt and water are 76.64% and 23.36%, respectively. CNT occurs as colourless rhombic crystals which melt in own crystallisation water. The phase diagram in Fig. 34 is created using experimental data of Funk [27], Sieverts and Petzold [139] and it shows that  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  melts congruently.

##### 2.13.1. Melting temperature and heat of fusion

The melting point with temperature of 59.5 °C was cited by Telkes using data from measurements by Funk [27] who was one of the first researchers to investigate the binary system of  $\text{Cd}(\text{NO}_3)_2$ – $\text{H}_2\text{O}$ . The graphical treatment of experimental data obtained by Sieverts and Petzold [139] produced for the CNT's stoichiometric composition the value of the melting temperature equal to 58.5 °C. Angell and Tucker [170] in their studies of the specific heat found that CNT melts at the temperature of 59.4 °C. Later, the calorimetric measurements by Marcus et al. [242] shown that the melting temperature of CNT was 58.8 °C. Thus, the results of all above mentioned studies are in a good agreement with each other with the accuracy in the range of experimenting errors. The recommended melting temperature for cadmium nitrate tetrahydrate is the average of all four measurements and equal to 59 °C.

**Table 14**  
Specific heat of cadmium nitrate tetrahydrate [170].

$T$ (K)	160	180	200	220	240	260	280	300	320	340	360	380
$C_p$ (J/g K)	0.76	0.80	0.83	0.87	0.91	0.93	0.94	0.94	1.00	1.65	1.67	1.69



**Fig. 35.** Phase diagram of sodium hydroxide–water system.

The heat of fusion measured by Angell and Tucker [170] using the DSC technique was equal to 137 J/g whilst the measurements performed by Marcus et al. [242] produced the value of 155 J/g. Comparison of these two results demonstrate that there is a considerable differences between the measured values.

### 2.13.2. Density and viscosity

The density of molten CNT has been measured twice by Jain [174,243] using a manometric densitometer. The values obtained in both measurements are very close to each other. This data obtained by Jain can be presented as the following equation:

$$\rho_1 (\text{g/cm}^3) = 2.324 - 0.001 t \quad 42^\circ\text{C} \leq t \leq 90^\circ\text{C}.$$

Jain [243] studied the viscosity of a set of nitrate hydrates including CNT. The obtained values are presented in Table 13.

### 2.13.3. Specific heat

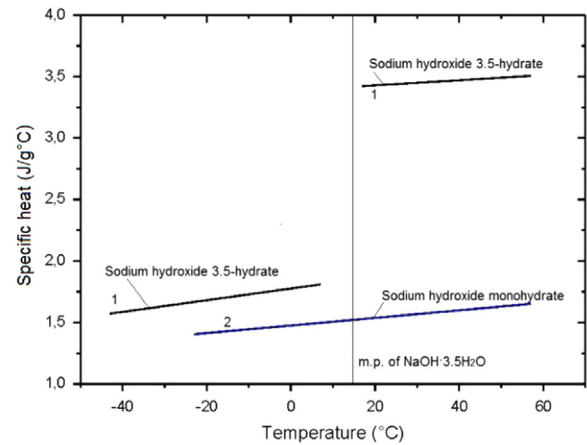
The specific heat of CNT was measured by Angell and Tucker [170] for the temperature range between 160 K and 380 K using the improved PerkinElmer differential scanning calorimeter (DSC-2 Model). Data obtained in this work are presented in Table 14.

### 2.13.4. CNT as phase change latent heat storage material

No information was found on using this crystal salt hydrate as the latent heat storage material. However, CNT has been used as the additive to other heat storage salt hydrates [147].

### 2.14. Sodium hydroxide 3.5-hydrate and monohydrate (SHH\_3.5 – NaOH · 3.5H<sub>2</sub>O; SHM – NaOH · H<sub>2</sub>O)

The phase diagram of sodium hydroxide–water system created using experimental data obtained by Pickering [244] is shown in Fig. 35 and two compounds and three eutectics can be seen in this diagram. The molecular weight of sodium hydroxide 3.5-hydrate is 103.05 g/mol and it occurs as colourless hygroscopic crystals which are highly soluble in water. The weight proportions of salt and water are 38.81% and 61.19%, respectively. The molecular weight of sodium hydroxide monohydrate is 58.012 g/mol and the weight proportions of salt and water in this compound are 68.95%



**Fig. 36.** Specific heat of sodium hydroxide hydrates: 1– Siemens and Giauque [245]; 2 – Murch and Giauque [246].

**Table 15**  
Density and viscosity of molten sodium hydroxide monohydrate.

$T$ (°C)	64	67	70	76.0	80	Ref.
$\rho$ (g/cm <sup>3</sup> )	1.5294	1.5268	1.5226	1.5191	1.5157	Sharma [144]
$\eta$ (cP)	10.542	9.657	8.541	7.215	6.057	Sharma [136]

and 31.05%, respectively. Both hydrate compounds occur as colourless hygroscopic crystals which are highly soluble in water. These hydrate compounds absorb CO<sub>2</sub> from air. From the literature search performed it can be concluded that their thermophysical properties are studied insufficiently.

### 2.14.1. Melting temperature and heat of fusion

The freezing temperatures for SHH\_3.5 and SHM reported by Pickering [244] are 15.5 °C and 64.3 °C, respectively. The melting point of NaOH · 3.5H<sub>2</sub>O found by Siemens and Giauque [245] using calorimetric measurements is 15.38 °C and NaOH · H<sub>2</sub>O, as it was observed by Murch and Giauque [246], melts at the temperature equal to 65.1 °C, so the melting temperatures obtained by groups of Pickering and Giauque are very close to each other within the range of measurements errors.

The heat of fusion for these hydrates was determined by the group of Giauque [245,246] using adiabatic calorimeter measurements which produced values of 272 J/g °C and 218 J/g °C for SHH\_3.5 and SHM, respectively.

### 2.14.2. Density

No information relating to the density of sodium hydroxide hydrates was found during the literature search in this study.

### 2.14.3. Specific heat

The specific heat of NaOH · 3.5H<sub>2</sub>O was measured by Siemens and Giauque [245] in the temperature range between 13 and 300 K using a gold adiabatic calorimeter. The specific heat of monohydrate was determined by Murch and Giauque [246] using the same type of calorimeter. Experimental data, which was

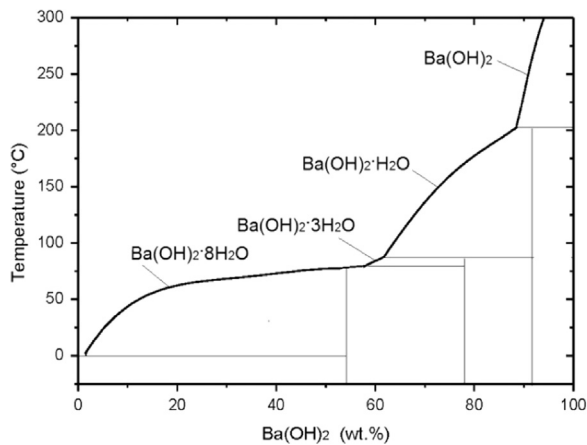


Fig. 37. Phase diagram of barium hydroxide–water system.

obtained for the temperature range relevant to the heat storage applications, has a linear trend as shown in Fig. 36.

#### 2.14.4. Other thermophysical properties

The density and viscosity of SHM in the molten state were measured by Sharma and his research group [136,144]. The density of molten sodium hydroxide monohydrate was determined using a modified Sprengel pycnometer, whilst the viscosity was measured using a modified Ubbelode's viscosimeter. Experimental data produced is presented in Table 15.

#### 2.14.5. SHH\_3.5 and SHM as phase change latent heat storage material

A number of characteristics of sodium hydroxide hydrates were investigated in [247–249]. Chabanon and Royer [250] proposed to use the phase change material on the basis of  $\text{NaOH} \cdot 3.5\text{H}_2\text{O}$  and additives of sodium chromate tetrahydrate as a nucleating agent for the thermal regulation inside solar greenhouses. The phase change composition containing SHH\_3.5 with additives of sodium chromate and disodium chromate with the melting point of 5–8 °C was presented as the cold storage material. The heat storage materials based on sodium hydroxide hydrates were discussed in [251–253].

#### 2.15. Barium hydroxide octahydrate (BHO – $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ )

The molecular weight of BHO is 315.47 g/mol and the weight proportions of hydroxide and water are 54.31% and 45.67%, respectively.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  occurs in the form of white tetragonal crystals, which melt in crystallisation water. The phase diagram of the barium hydroxide–water system created using experimental data by Michaud [254] is presented in Fig. 37. The diagram shows that BHO is stable in the room temperature – the melting point temperature range.  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is produced when barium oxide is mixed with hot water or in the boiling process of barium chloride and sodium hydroxide. Since BHO is chemical active, all experiments should be carried out using sealed containers.

##### 2.15.1. Melting temperature

The melting temperature which was cited by Telkes [10] and presented in Table 1 is 78 °C. It appears that the original source for this information was a study by Richards and Churchill [132] who studied salt hydrates and found that melting of BHO took place at the temperature equal to 78 °C. Studies performed by Guion et al. [15] and Kanwischer and Tamme [255] on the heat storage capacities of a range of materials using the DSC technique confirmed that barium hydroxide octahydrate melts at the temperature equal

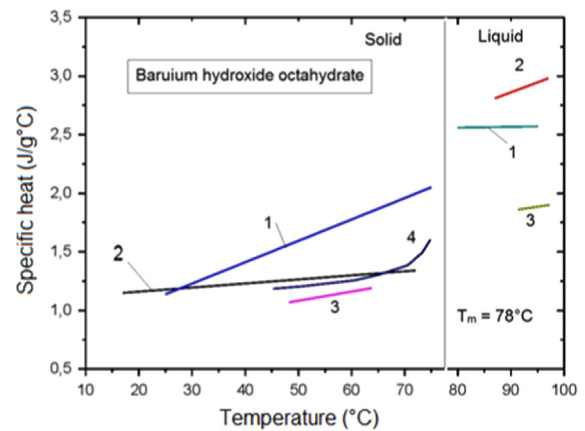


Fig. 38. Specific heat of barium hydroxide octahydrate: 1 – Ginzburg et al. [257]; 2 – Di et al. [258]; 3 – Aboul-Enein [145]; 4 – Lane [14].

to 78 °C. The DSC measurement carried out by Li with colleagues [256] showed that samples with high chemical purity also melted at 78 °C. A very close value, namely 78.5 °C, was obtained by Ginzburg et al. [257]. According to Di et al. [258] BHO samples of high purity (99.8%) melted at 81.8 °C. In their studies of the thermal conductivity, Nie et al. [259] found that barium hydroxide octahydrate melted at 76 °C. The melting point of BHO recommended for use is 78 °C.

##### 2.15.2. Density

No original studies were found on the measurement of the temperature dependence of the BHO density in the solid and molten states.

##### 2.15.3. Specific heat and heat of fusion

The values of the specific specific heat of BHO, which were determined by a number of researchers, are presented in Fig. 38. The measurements of Aboul-Enein et al. [145] and Schröder and Gawron [12] were performed using the DSC technique. Ginzburg et al. [257] used a drop calorimeter with isothermal capsule in their study. The samples to be investigated were placed into a sealed container. The temperature dependence of the specific specific heat obtained by Ginzburg et al. can be described by the following equations:

$$C_{ps} (\text{J/g} \cdot ^\circ\text{C}) = 0.6811 + 0.0182 t \quad \text{for } 25\text{--}78.5 \text{ } ^\circ\text{C}$$

and

$$C_{pl} (\text{J/g} \cdot ^\circ\text{C}) = 2.4995 + 0.000754 t \quad \text{for } 78.5\text{--}150 \text{ } ^\circ\text{C}.$$

The experimental results for the molar specific heat obtained by Di et al. [258] using an adiabatic calorimeter can be presented as the following function:

$$C_{ps} (\text{J/mol K}) = 292.998 + 129.774X + 32.294X^2 + 22.451X^3 + 13.129X^4 - 3.649X^5 \quad \text{for } 78\text{--}345 \text{ K},$$

$$\text{where } X = (T(\text{K}) - 211.5) / 133.5;$$

$$C_{pl} (\text{J/mol K}) = 904.215 + 40.507 X - 7.572 X^2 + 1.350 X^3 - 1.781 X^4 \quad \text{for } 356\text{--}369 \text{ K},$$

$$\text{where } X = (T(\text{K}) - 362.5) / 6.5.$$

It can be seen in Fig. 38 that the discrepancies in the obtained heat capacities for BHO noticeably exceed measurement errors reported by these researchers.

With regard to the heat of fusion, the value 301 J/g was cited by Telkes [10] but the original source of this information was not found. The values of the heat of fusion determined by Schröder and Gawron [12], Guion et al. [15] and Li et al. [256] using the DSC technique were 266 J/g, 295 J/g, and 289 J/g, respectively. Ginzburg

et al. [257] obtained the value for the melting enthalpy of BHO equal to 262 J/g. The enthalpy of the phase change was measured by Di et al. [258] using the adiabatic calorimeter and it was equal to 233 J/g. It is obvious that the reported values vary over a wide range and further accurate experiments are required to determine the heat of fusion for BHO.

#### 2.15.4. Thermal conductivity

Available experimental data on the thermal conductivity of BHO is very limited. The results of measurements found in the open literature are presented in Fig. 39. There are only three studies conducted in this topic. Thus, Specific heat [12] measured the thermal conductivity for three temperature values. The details of the experiment were not described. The temperature dependence of the thermal conductivity of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  was investigated by Egorov et al. [177] for the solid and liquid states using a stationary method of radial heat flow in coaxial cylindrical apparatus. The obtained experimental results can be described as following function:

$$k_s (\text{W/m} \cdot ^\circ\text{C}) = 1.15 - 5.75 \cdot 10^{-3} t (^\circ\text{C}) \quad \text{for } 50 - 78 \text{ } ^\circ\text{C}$$

and

$$k_l (\text{W/m} \cdot ^\circ\text{C}) = 0.41 - 2.76 \cdot 10^{-3} t (^\circ\text{C}) \quad \text{for } 78 - 95 \text{ } ^\circ\text{C}.$$

The maximum error was estimated to be  $\pm 8\%$ .

Nie et al. [259] also measured the thermal conductivity of BHO using a transient hot-wire system for the range of temperatures between 10 and 80 °C. They observed that about the melting point, the thermal conductivity had the tendency to rise.

#### 2.15.5. BHO as latent heat storage material

There are only few investigations, in which BHO was studied as the thermal energy storage material, and this can be explained by its toxicity and high chemical activity. Thus, the barium hydroxide

anhydrous when exposed to air interacts with carbon dioxide and forms barium carbonate.

Moraru and Zuca [260] were first who studied BHO as the potential thermal energy storage material. They observed that  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  is supercooled down to 51.5 °C. Addition of  $\text{Ba}(\text{IO}_3)_2$  as a nucleation agent made it possible to decrease the supercooling degree to 3–4 °C. In contrast to the observations of Moraru and Zuca, the supercooling of BHO was not observed in thermal analysis experiments of Di et al. [124].

Kanwischer and Tamme [255] studied the effect of an additional introduction of various concentrations of water into BHO and the use of this salt in heat storage systems, in which the storage material was in the direct contact with a heat carrier. The results obtained are presented in Table 16 and it can be seen that the addition of less than 6% of water did not affect the melting temperature whilst the heat of fusion was significantly decreased.

Tests of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  hermetically sealed in stainless containers coated with gold were performed by Li et al. [256] for the temperature range between 65 °C and 93 °C. The results demonstrated that the melting temperature and heat of fusion of BHO after 500 thermal cycles remained at the same original level. The investigation of barium and strontium octahydrate blend was carried out by Naumann and Schatz [263] for application as a heat storage material and its unsuitability for the purpose was demonstrated. The blends thermal cycling in the temperature range between 20 °C and 120 °C led to the decrease in the melting temperature from 85.4 °C to 70 °C after only first 10 cycles. The results obtained by Li et al. [256] showed that the thermal properties of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  are sufficiently stable and this hydrate can be used in hermetically sealed containers. The practical applications are currently limited [261,262] because of absence of reliable data on thermophysical properties. Further experiments over a significantly greater number of thermal cycles are required in order to propose engineering recommendations.

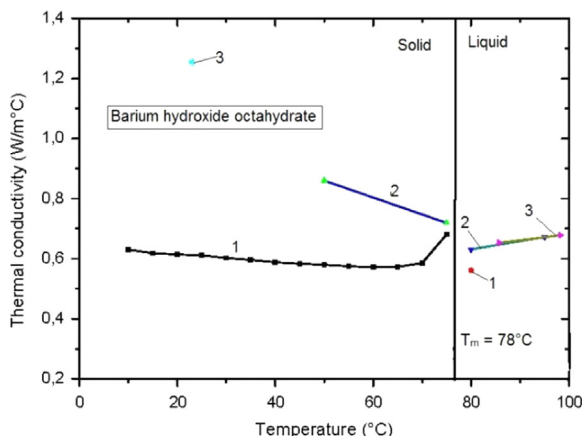


Fig. 39. Thermal conductivity of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ : 1 – Nie et al. [259]; 2 – Egorov et al. [177]; 3 – Lane [14].

Table 16  
Effect of addition of water on melting temperature and enthalpy of BHO [255].

Content (wt%)		Melting temperature (°C)	Melting enthalpy (J/g)
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	$\text{H}_2\text{O}$		
100		78	$301 \pm 12$
94	6	77.5	$280 \pm 12$
85	15	73	$230 \pm 10$
75	25	69	$207 \pm 9$
69	31	67.5	$171 \pm 9$
62	38	66	$147 \pm 9$

#### 2.16. Magnesium nitrate hexahydrate (MNH – $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )

The molecular weight of magnesium nitrate hexahydrate is 256.41 g/mol. The weight proportions of salt and water are 57.84% and 42.16%, respectively. Magnesium nitrate crystallizes from the water solution as colourless rhombic columns and needles of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and it is easily soluble in water (73.3 g of anhydrous in 100 ml of water at 20 °C). MNH turns into dehydrate if heated above 95 °C.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is produced in the reaction between magnesium oxide/carbonate and nitric acid. The equilibrium diagram of magnesium nitrate and water created using measurements of Ewing et al. [264] and Sieverts and Petzold [265] is

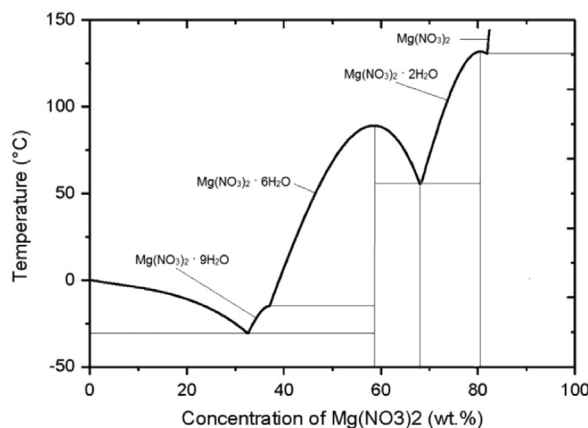
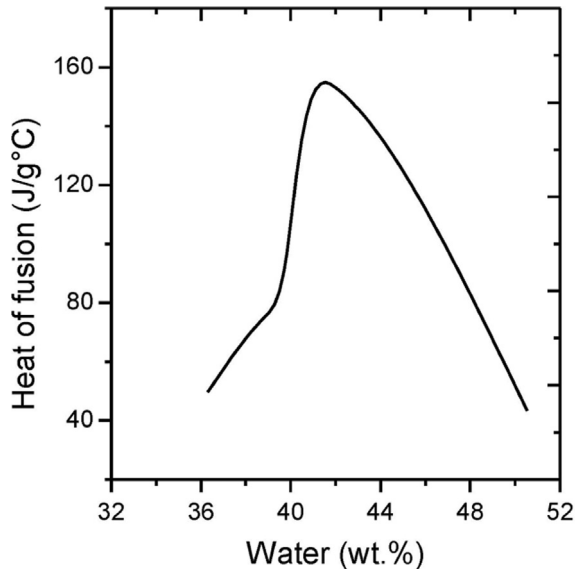


Fig. 40. Phase diagram of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  system.

**Table 17**  
Melting temperature and heat of fusion of magnesium nitrate hexahydrate.

Melting temperature (°C)	Supercooling (°C)	Heat of fusion (J/g°C)	Ref.
90.0		160	Riesenfeld and Milchsack [30]
89.9			Ewing et al. [264]
90.0		151	Cantor [266]
89.3	3	149	Schröder and Gawron [12]
90.0	22.5–30	150	Naumann and Emons [267]
90.0		152	Marcus et al. [269]



**Fig. 41.** Effect of stoichiometric water content on heat of fusion of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , adapted from Naumann and Emons [267].

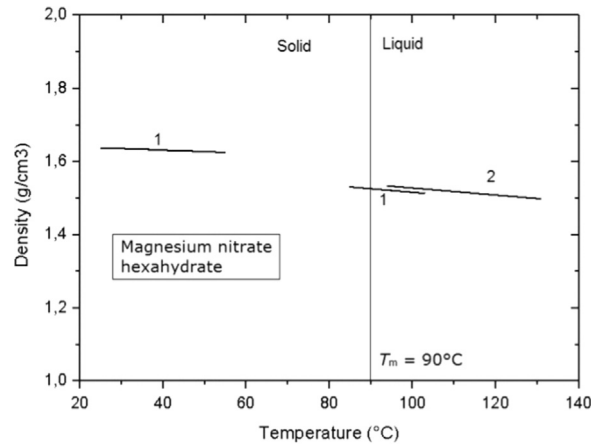
presented in Fig. 40 and it can be seen that MNH melts congruently.

### 2.16.1. Melting temperature and heat of fusion

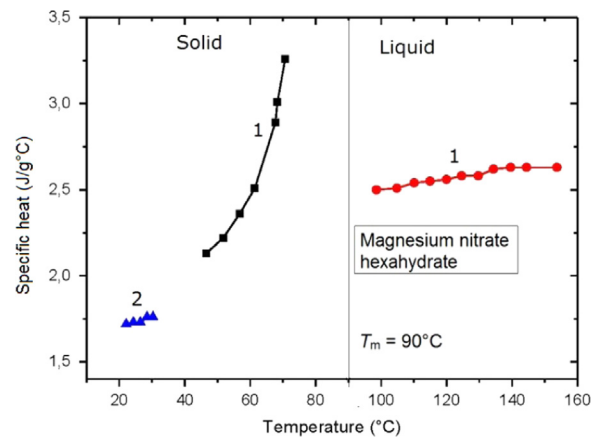
There is large number of original publications with results of measurements of the MNH melting temperature. Values cited by Telkes (90 °C) and Schröder and Gawron [12] (89.9 °C), see Table 1, were obtained in measurements of Riesenfeld and Milchsack [30] and Ewing et al. [264], respectively. The melting temperature and heat of fusion obtained by a number of scientists are listed in Table 17. It can be seen that the results obtained on the melting point value are very close to each other. With regard to the heat of fusion, the value obtained by Reisenfeld and Milchsack is marginally greater than measurements by other researchers. During their experiments on MNH, Cantor [266] and Naumann and Emons [267] observed the structural change at the temperatures between 69 and 73 °C with the thermal effect of about 12 J/g. These researchers pointed out that Riesenfeld and Milchsack did not register that effect. Taking this into account the value of the heat of fusion equal to 150 J/g appears to be more accurate. Naumann and Emons found that the only 2% deviation from the stoichiometric water content resulted in the 30–40% reduction of the storage capacity, see Fig. 41. Lane et al. [268] confirmed that MNH could be supercooled by 15 °C.

### 2.16.2. Density

The results on the MNH density measurements for the solid and liquid states were reported in two articles. The density of



**Fig. 42.** Density of magnesium nitrate hexahydrate: 1 – Minevich et al. [272]; 2 – Jain et al. [281].



**Fig. 43.** Specific heat of magnesium nitrate hexahydrate vs. temperature: 1 – Lane et al. [268]; 2 – Zhdanov et al. [176].

molten crystal hydrate was measured by Jain [271] in the temperature range between 97 and 131 °C using a modified dilatometer. The melting point was found to be 94.8 °C which is considerably higher than the values reported above. Data obtained by Jain can be described as

$$\rho_l(\text{g}/\text{cm}^3) = 1.6234 - 0.000958 t \quad (\text{g}/\text{cm}^3) \quad \text{for } 97 - 131 \text{ } ^\circ\text{C}.$$

Experimental data of Minevich et al. [272] was determined using a pycnometer and can be fitted into the following linear functions:

$$\rho_s(\text{g}/\text{cm}^3) = 1.756 - 0.0004(t + 273) \quad \text{for } 25 - 55 \text{ } ^\circ\text{C}$$

and

$$\rho_l(\text{g}/\text{cm}^3) = 1.874 - 0.00096 t \quad \text{for } 85 - 103 \text{ } ^\circ\text{C}.$$

Experimental data obtained on the density variations is shown in Fig. 42 and it can be seen that measurements of Minevich et al. also capture the supercooling liquid range. The density values for MNH found in both the above studies for the liquid phase are practically identical. The volume change  $\Delta V_m$  at the melting temperature calculated using extrapolation of values obtained by Minevich et al. to the melting point is 5.3%. This value is very close to 6.3% determined by Schröder and Gawron [12] (Fig. 42).

### 2.16.3. Specific heat

The specific heat was also measured in two studies. Zhdanov et al. [176] used an adiabatic calorimeter for determination the

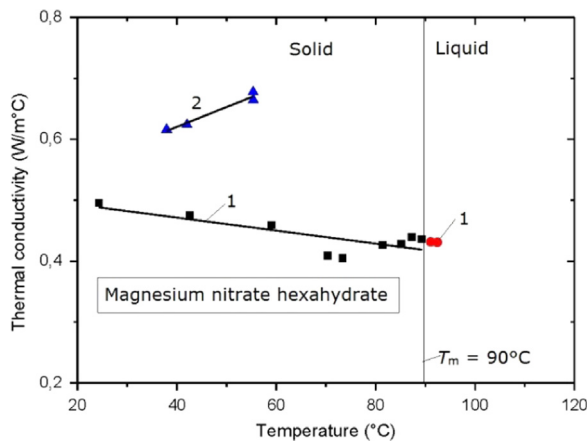


Fig. 44. Variation of the thermal conductivity of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with temperature: 1 – Nikolić et al. [154]; 2 – Lane et al. [268].

specific heat of solid MNH for the narrow temperature range between 22 and 31 °C. The DSC technique was used by Specific heat Lane et al. [268] to measure the specific heat in the solid and liquid states. The results obtained in above two studies are shown in Fig. 43.

#### 2.16.4. Thermal conductivity

Only two articles were found, namely by Lane et al. [268] and Nikolić et al. [154], which reported results of experimental investigations on the determination of the thermal conductivity of MNH. Data obtained is presented in Fig. 44. The steady-state method was used by Nikolić et al. and the accuracy of their measurements was estimated as being  $\pm 3\%$ . The experimental technique used by Specific heat is unknown. As it can be seen in Fig. 44, there is a noticeable discrepancy between two measurements for the solid state and, moreover, the trends in the change of the thermal conductivity are opposite. It appears that data obtained by Nikolić et al. [154] is more realistic.

#### 2.16.5. MNH as phase change latent heat storage medium

A number of studies were performed on the heat storage capacity of MNH and among them are ones performed by Lane and Rossow at Dow Chemical [268,273–280] and which are more detailed. Because of the tendency of MNH to the substantial supercooling, Lane and Rossow tested a large number of additives to find the most suitable ones to reduce the level of supercooling. Those additives, introduction of which provided the supercooling degree less than 2 °C, were patented. Since magnesium nitrate hexahydrate has the relatively high melting point, its application as a thermal storage material is very limited. From the practicality point of view, the mixtures on the basis of MNH have more advantages. For instance,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  form the eutectic blend with the melting point equal to 60 °C. Lane and Rossow found a number of additives, introduction of which made it possible to decrease the degree of supercooling of MNH to 5 °C. The same eutectic blend was also studied in [282–285]. Kniep et al. developed heat storage materials [286,287] on the basis of MNH and lithium nitrate.

#### 2.17. Ammonium alum dodecahydrate (AAD – $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ )

The molecular weight of AAD is 453.33 g/mol. The weight proportions of salt and water are 47.69% and 52.31%, respectively. AAD forms colourless cubic crystals with the boiling point at 120 °C. At this temperature, the crystal hydrate loses 10 molecules of water and if its temperature is risen to 200 °C then water is completely lost. The solubility of the alum is 2.6 g in 100 ml of

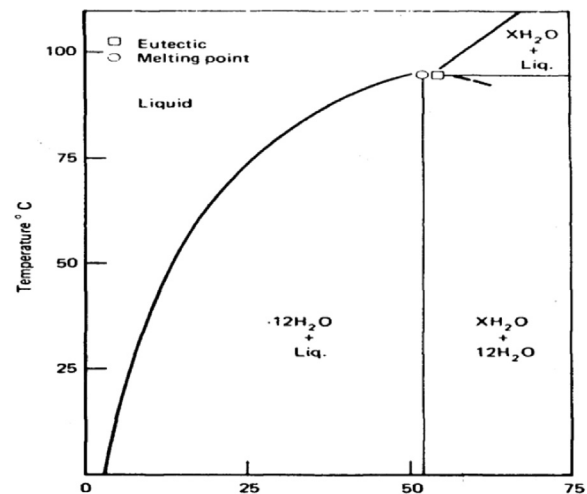


Fig. 45. Partial phase diagram of ammonium-aluminium sulphate-water system [13].

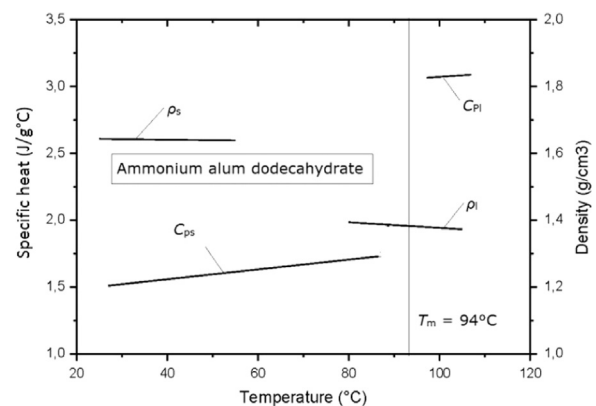


Fig. 46. Density and specific heat of ammonium alum dodecahydrate: Specific heat – Grønvold and Meisingset [104]; density – Marcus et al. [293].

Table 18

Specific heat of ammonium alum dodecahydrate. Adapted from Grønvold and Meisingset [104].

$T$ (K)	300	310	320	330	340	350	360	370	380
$C_p$ (J/g K)	1.51	1.55	1.59	1.62	1.66	1.70	1.73	3.07	3.09

water at 0 °C and 35.2 g at 80 °C.  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is produced by interaction of aluminium and ammonium sulphate solutions. It can be seen in Fig. 45 that AAD melts congruently.

##### 2.17.1. Melting temperature

The melting temperature of AAD was determined by Davletov et al. [290] using the derivative-graph method and Emons et al. [294] (DTA curves) and their values were identical and equal to 93.5 °C. Using the DSC technique, Guion et al. [15] observed that the melting of AAD took place at 93.8 °C. The value of the melting point found by Grønvold and Meisingset [104] using the calorimetric measurement was 93.95 °C. The above reported values are very close to each other. The value of  $90 \pm 1$  °C reported by Marcus et al. [270] is substantially lower in comparison with other reported melting temperatures.

##### 2.17.2. Density

Only one article was found, namely by Marcus et al. [293], with results of experimental measurements of the density of AAD in the solid and liquid states. The results of measurement of the density

and specific heat of AAD are shown in Fig. 46 and it can be seen that the density was determined also for the supercooled region.

### 2.17.3. Specific heat and heat of fusion

There is only one article, namely by Grønvold and Meisingset [104], in which the specific heat and heat of fusion of AAD was measured and reported. Data obtained using an adiabatic calorimeter is presented in Table 18 and the heat of fusion was found to be 269 J/g. Davletov et al. [290] and Guion et al. [15] reported the melting enthalpy values of 286 J/g and 228 J/g, respectively. There is a significant discrepancy in these results and we recommend using the value 269 J/g for the AAD heat of fusion as being more realistic.

### 2.17.4. AAD as latent heat storage material

ADD demonstrates congruent melting but despite this fact there are only two articles in the open literature in which feasibility studies were carried out on using AAD as a potential latent HSM. This apparent lack of interest can be explained by its relatively high melting point which is very close to the water boiling temperature. Vaccarino et al. [288,289] proposed a composition of AAD and  $\text{NH}_4\text{NO}_3$  in 1:1 weight proportion. The heat storage capacity of this composition in the temperature range between 25 °C and 60 °C was determined as 245 J/g. As a result of long-term tests of the composition it was established that the heat storage capacity decreased by 15% after undergoing 200 thermal cycles

Goswami et al. [291,292] investigated the eutectic blend of ammonium alum and ammonium nitrate, that was proposed by Vaccarino et al. [288,289]. The thermal analysis demonstrated that the blend changes its phase between 48 and 53 °C. The melting temperature and melting enthalpy were measured using the DSC technique at a heating rate of 5 °C/min and values obtained were 58.5 °C and 208 J/g, respectively. The difference in 5.5 °C is believed to be the result of the high rate in samples heating. The average specific heat in the solid state measured with a drop calorimeter in the temperature range between 24 °C and 50 °C was found to be 1.45 J/g°C and the eutectic enthalpy change in the temperature range between 24 °C and 65 °C was 287 J/g. Thermal cycling tests (1100 cycles) demonstrated that the eutectic composition was sufficiently stable. Over 1100 thermal cycles, the heat storage capacity decreased gradually from 285 J/g to 268 J/g. Some properties and performance of AAD were also investigated in [294,295].

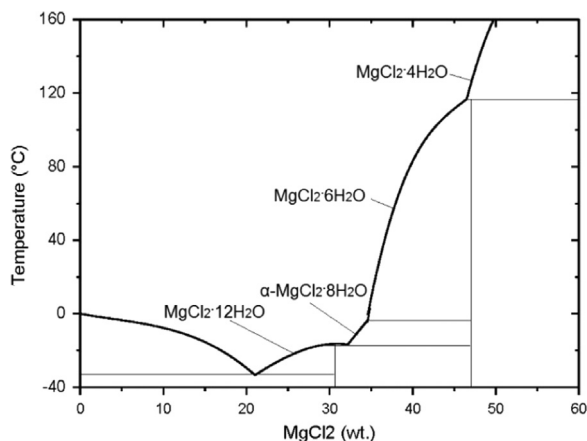


Fig. 47. Phase diagram of magnesium chloride–water system.

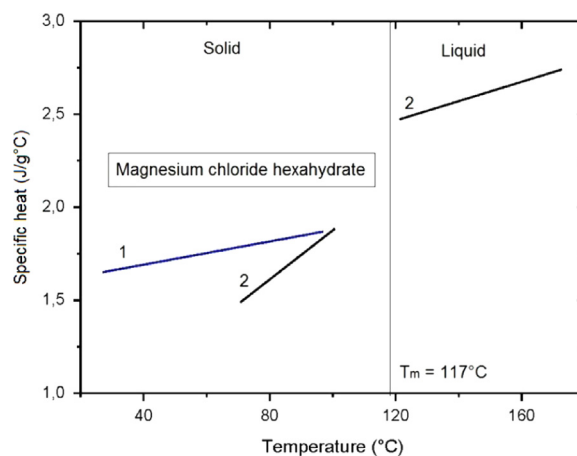


Fig. 48. Specific heat of magnesium chloride hexahydrate: 1 – Pilar et al. [298]; 2 – Lane [14].

### 2.18. Magnesium chloride hexahydrate (MCH – $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ – bishofite)

The molecular weight of MCH is 203.30 g/mol and the weight proportions of salt and water are 46.83% and 53.17%, respectively. It occurs as colourless hygroscopic monocline crystals and this salt is highly soluble in water (54.5 g in 100 g of water at 20 °C). Bishofite is stable in water solutions in the temperature range from 3.35 to 116.7 °C. The hydrated magnesium chloride is extracted from brine or seawater in a large scale. The phase diagram of  $\text{MgCl}_2$  and  $\text{H}_2\text{O}$  created using data of Zdanovsky et al. [20] is shown in Fig. 47 and it can be seen that the peritectic and stoichiometric compositions are very close to each other.

#### 2.18.1. Melting temperature and heat fusion

Riesenfeld and Milchsak [30] performed the first measurements of the melting temperature and heat of fusion of bishofite. They reported for 116.7 °C as the melting point and 172 J/g for the heat of fusion. In their study of the solubility of magnesium chloride in water Dietzel and Serowy [296] found that the peritectic reaction of MCH and  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$  takes place at the temperature equal to 117.2 °C. DSC measurements of Cantor [297] demonstrated that the melting of MCH took place at 116 °C and its heat of fusion was found to be 167 J/g. In additional experiments using a test-tube method, Cantor observed that the melting process took place over the temperature range from 117 °C to 120 °C. In cooling experiments of the melt, the solidification was found to take place at 117 °C. Measurements performed by Lane [14] produced the melting temperature of 117 °C and specific heat equal to 170 J/g. Pilar et al. [298] used DTA-TG and DSC techniques for studying the thermal properties of MCH. This study showed that MCH melted at 117.1 °C and its average value of heat fusion determined from 5 measurements was 170 J/g. Experimental data described above demonstrates that the values obtained are in good agreement with each other. Therefore, the melting point of magnesium chloride hexahydrate equal to 117 °C and heat of fusion equal 170 J/g appear to be accurate information.

#### 2.18.2. Specific heat and other thermophysical properties

The literature review conducted in this work shows that other thermophysical properties of magnesium chloride hexahydrate are not sufficiently investigated. The specific heat was studied by Lane [14] and Pilar et al. [298] and Kelley and Moore [299] for the low temperature range between 10 K and 300 K. Measurements in [14,298] were performed using the DSC technique. Data obtained is shown in Fig. 48 and it can be seen that the trends in the

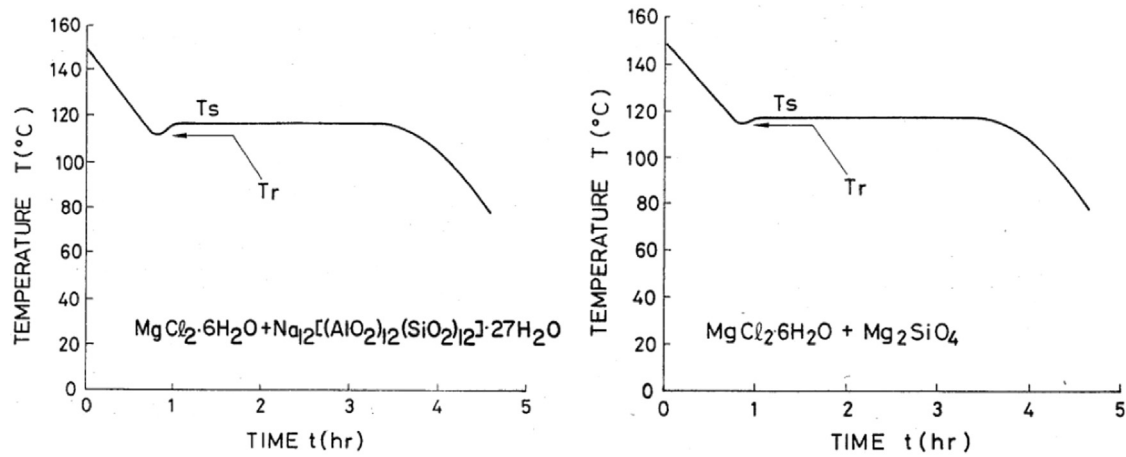


Fig. 49. Solidification curves of compositions developed by Yanadori and Miyamoto [300].

Table 19

Thermophysical properties of salt hydrate materials for latent heat storage manufactured by PCM Solutions [307].

PCM product	Melting point (°C)	Latent heat (J/g)	Density (g/cm <sup>3</sup> )	Specific heat (J/g °C)	Thermal conductivity (W/m °C)
<i>Sub-zero eutectic PCM Solutions</i>					
E-62	-62	180	1.300	4.01	0.58
E-60	-60	172	1.280	2.90	0.44
E-50	-49.8	218	1.325	3.28	0.56
E-46	-46	240	1.206	3.05	0.54
E-37	-36.5	213	1.500	3.15	0.54
E-34	-33.6	240	1.205	3.05	0.54
E-32	-32	243	1.290	2.95	0.56
E-29	-29	222	1.420	3.69	0.64
E-26	-26	260	1.250	3.67	0.58
E-22	-22	234	1.180	3.34	0.57
E-21	-20.6	263	1.240	3.13	0.51
E-19	-18.7	282	1.125	3.29	0.58
E-15	-15	303	1.060	3.87	0.53
E-14	-14.8	243	1.220	3.51	0.51
E-12	-12.3	250	1.110	3.47	0.56
E-11	-11.6	301	1.090	3.55	0.57
E-10	-10	286	1.140	3.33	0.56
E-6	-6	275	1.110	3.83	0.56
E-4	-3.9	282	1.080	3.78	0.58
E-3	-3.7	312	1.080	3.84	0.60
E-2	-2	306	1.070	3.80	0.58
E0	0	332	1.000	4.186	0.58
<i>Salt hydrate based positive temperature PCMs</i>					
S7	7	150	1.700	1.85	0.40
S8	8	150	1.475	1.9	0.44
S10	10	155	1.470	1.9	0.43
S13	13	160	1.515	1.9	0.43
S15	15	160	1.510	1.9	0.43
17	17	160	1.525	1.9	0.43
S19	19	160	1.520	1.9	0.43
S21	22	170	1.530	2.2	0.54
S27	29	183	1.530	2.2	0.54
S30	30	190	1.304	1.9	0.48
S32	32	200	1.460	1.91	0.51
S34	34	115	2.100	2.1	0.52
S44	44	100	1.584	1.61	0.43
S46	46	210	1.587	2.41	0.45
S50	50	141	1.600	2.31	0.62
S58	58	145	1.505	2.55	0.69
S72	72	127	1.666	2.13	0.58
S83	83	141	1.600	2.31	0.62
S89	89	151	1.555	2.48	0.67
S117	117	160	1.450	2.61	0.70



**Table 20**

Thermophysical properties of salt hydrate materials for latent heat storage manufactured by PCM Energy P. Ltd. [308].

PCM product	Melting point (°C)	Latent heat (J/g)	Density (g/cm <sup>3</sup> )	Specific heat (J/g °C)	Thermal conductivity (W/m °C)	Subcooling (°C)	Thermal stability
Latest <sup>TM</sup> 18T	17–19	175	1.48–1.50	2.0	1.0	2	> 10000 cycles
Latest <sup>TM</sup> 20T	19–20	175	1.48–1.50	2.0	1.0	2	> 10000 cycles
Latest <sup>TM</sup> 25T	24–26	175	1.48–1.50	2.0	1.0	2	> 10000 cycles
Latest <sup>TM</sup> 29T	28–30	175	1.48–1.50	2.0	1.0	2	> 10000 cycles
Latest <sup>TM</sup> 32S	31–32	230	1.45	2.0	0.6	Small	> 10000 cycles
Latest <sup>TM</sup> 34S	33–34	250	1.45	2.0	0.6	Small	> 10000 cycles
Latest <sup>TM</sup> 36S	36	260	1.45	2.0	0.6	Small	> 10000 cycles
Latest <sup>TM</sup> 48S	48	260	1.45	2.0	0.6	Small	> 10000 cycles

**Table 21**

Thermophysical properties of salt hydrate materials for latent heat storage manufactured by RGEES LLC [309].

PCM product	Melting point (°C)	Latent heat (J/g)	Density (g/cm <sup>3</sup> )	Specific heat (J/g °C)	Thermal conductivity (W/m °C)	Subcooling (°C)
savEnrg <sup>TM</sup> PCM-HS26N	– 25.6	205	1.20 <sup>25a</sup> (liq)	3.56		No
savEnrg <sup>TM</sup> PCM-HS23N	– 22	200	1.12 <sup>–33</sup> (sol)	3.47		No
savEnrg <sup>TM</sup> PCM-HS10N	– 11	220	1.10 <sup>25</sup> (liq)	3.56		No
savEnrg <sup>TM</sup> PCM-HS07N	– 6	230	1.07 <sup>17</sup> (liq)	3.77	0.55 (liq)	No
savEnrg <sup>TM</sup> PCM-HS01P	0	290	0.92 (liq)	4.14	2.20 (sol); 0.55 (liq)	No
savEnrg <sup>TM</sup> PCM-HS22P	23	185	1.84 <sup>12</sup> (sol); 1.54 <sup>32</sup> (liq)	3.05 <sup>32</sup> (liq)	1.09 (sol); 0.54 (liq)	Low
savEnrg <sup>TM</sup> PCM-HS24P	24	185	1.82 <sup>14</sup> (sol); 1.54 <sup>32</sup> (liq)	2.26 <sup>32</sup> (liq)	1.09 (sol); 0.54 (liq)	Low
savEnrg <sup>TM</sup> PCM-HS29P	29	190	1.84 <sup>19</sup> (sol); 1.55 <sup>39</sup> (liq)	2.26 <sup>32</sup> (liq)	1.09 (sol); 0.54 (liq)	No

<sup>a</sup> Superscripts indicate temperatures (in °C) for which the value was determined; the sign “–” (minus) indicates that the measurement was made at temperatures below 0 °C.

temperature dependence of the specific heat for the solid state considerably differ.

Lane [14] determined the density of 1.569 g/cm<sup>3</sup> at 20 °C and 1.45 g/cm<sup>3</sup> at 120 °C. He also measured the thermal conductivity as 1.255 W/m °C at 23 °C and 0.57 W/m °C at 120 °C.

### 2.18.3. MCH as phase change latent heat storage material

The average supercooling degree observed by Pilar et al. [297] during 50 thermal cycles of melting and crystallisation was found to be 37 °C. Introduction of SrCO<sub>3</sub> and Sr(OH)<sub>2</sub> as nucleating agents decreases the degree of supercooling to 2 °C. Similar results was obtained by Yanadori and Miyamoto [300] for MCH doped with synthetic zeolite, magnesium silicate etc. Fig. 47 illustrates the behaviour of the composition on the basis of bishofite. In order to extend the MCH application, Yoneda and Tanakashi [285] developed the eutectic composition (58.7 wt% Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O + 41.3 wt% MgCl<sub>2</sub>·6H<sub>2</sub>O). A set of additives to the eutectic composition was found by Lane and Rossow [276–278] which decreased the degree of supercooling to 5 °C. Kniep et al. [286,287] described the compositions based on MCH and lithium nitrate. Various aspects of application of phase change materials containing MgCl<sub>2</sub>·6H<sub>2</sub>O were considered in [301–306] (Fig. 49).

## 3. Commercial latent heat storage materials based on salt hydrates

In the previous section, a number of pure salt hydrates were considered which can be used as the basis for preparation of compositions suitable for latent heat storage in the temperature range from 8 °C to 120 °C. It was concluded that the thermophysical properties of some of salt hydrates were not sufficiently investigated. The developments during the last three decades made it possible to produce commercial phase change products for latent heat storage. The most of phase change materials available on the market for heat and cold storage are presented in Tables 19–22, which demonstrate that information provided on the performances of the listed compositions has the different level of details. Some properties were just

preliminarily assessed and quite often potential consumers of PCM products have to assume themselves the phase state and temperatures for which information was provided. Some of manufacturers provide information on the supercooling performance, thermal stability and the maximum operating temperature but very often such information is not included in the product description.

## 4. Prices of salts, salts hydrates and latent heat storage products based on salt hydrates

The cost of phase change materials for latent heat storage is the important factor for the scale of their applications. Table 23 presents the wholesale prices on salt and salt hydrates listed by relevant manufacturers at [www.alibaba.com](http://www.alibaba.com) (China). It can be seen that the most of presented salts have relatively low prices if purchased in large quantities (several tonnes). However, the transportation costs can increase the price of these products by factor of two or greater depending on the distance and geographic location. Small quantity trading (from several dozens to hundred kilograms) of these products has the same tendency. Prices of salt hydrates and their salt anhydrous are of the same order. Prices from manufactures of these salts in countries other than China might be significantly higher when compared to Chinese producers.

Table 24 provides comparison of prices for phase change heat storage products on the basis of salt hydrates and for organic PCMs produced in UK, Sweden, Germany, USA and India. Wholesale prices for these commercial PCM heat storage products substantially higher than the prices from Chinese manufacturers. It appears that such relatively high prices for PCM products are mainly dictated by a relatively small scale production.

## 5. Conclusion

The available information has been analysed for 18 salt hydrates which have feasible prospective for latent heat storage applications. Some of these, such as calcium chloride hexahydrate,

**Table 22**  
Thermophysical properties of salt hydrate materials for latent heat storage manufactured by Climator [310].

PCM product	Main ingredients	Melting/freezing point (°C)	Latent heat (J/g)	Density (g/cm <sup>3</sup> )	Specific heat (J/g °C)	Thermal conductivity (W/m °C)	Maximum temperature (°C)
ClimSel C-21	NaCl+water	-21	80	1.3	3.6	0.5–0.7	35
ClimSel C-18	NaNO <sub>3</sub> +water	-18	80	1.3	3.6	0.5–0.7	35
ClimSel C7	Na <sub>2</sub> SO <sub>4</sub> +water	7	35	1.4	3.6	0.5–0.7	35
ClimSel C10	Na <sub>2</sub> SO <sub>4</sub> +water	10.5/5.5	35	1.4	3.6	0.5–0.7	35
ClimSel C21	Na <sub>2</sub> SO <sub>4</sub> +water	21	31	1.38	3.6	0.5–0.7	35
ClimSel C24	Na <sub>2</sub> SO <sub>4</sub> +water	24	42	1.38	3.6	0.5–0.7	40
ClimSel C28	Na <sub>2</sub> SO <sub>4</sub> +water	28	45	1.42	3.6	0.5–0.7	45
ClimSel C32	Na <sub>2</sub> SO <sub>4</sub> +water	32	45	1.42	3.6	0.5–0.7	45
ClimSel C48	C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub> +water	48	50	1.36	3.6	0.5–0.7	65
ClimSel C58	C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub> +water	58	80	1.46	1.67–2.72	0.5–0.7	70
ClimSel C70	Na <sub>4</sub> O <sub>7</sub> P <sub>2</sub> +water	71	79	1.40	3.6	0.5–0.7	85

**Table 23**  
Wholesale prices of salt and salt hydrates (produced in China and India).

Salt	Purity (%)	Minimal order (Metric ton)	Company (country)	FOB price USD/ton
<b>Pure salts</b>				
Potassium fluoride	98	1	Shanghai Sungo Technology & Trade Co., Ltd. (China)	2800–3000
	99.3	25	Wuhan Xingzhengshun Import & Export Co., Ltd. (China)	1500–1600
	99	5	Tianjin Tiger International Trade Co., Ltd.	1500–1600
Calcium chloride	95	20	Weifang Dahe Snow-Melting Products Co., Ltd.	225–230
	94	5	Foodchem International Corporation	250–500
Lithium nitrate	99	1	Jiangxi Royal Import & Export Co., Ltd.	8350–9850
	99	0.001	Wuhan Rison Trading Co., Ltd.	7000–10000
	99	0.001	Haihang Industry (Jinan) Co., Ltd.	1000–3000
Sodium sulphate	99	25	Tianjin Credit International Co., Ltd.	98–110
	99	26	J&C Industry Corporation, Ltd.(nanjing)	87–90
	99.7	200	Sichuan Union Xinli Chemicals Co., Ltd.	70–200
Sodium carbonate	99.2	21	Zhengzhou Mahaco Trading Co., Ltd.	160–250
	99.2	20	Weifang Ruidesheng Chemical Co., Ltd.	203–208
	99.2	10	Wuhan Golden Fortune Technology & Trade Co., Ltd.	100–250
Disodium hydrogenphosphate	97–99	10	Sichuan Mianzhu Ronghong Chemical Co., Ltd.	390–600
Calcium nitrate	99	10	DEE PEE CHEM INDUSTRIES	350–380
Sodium thiosulphate	99	25	Henan Eastar Chemicals Co., Ltd.	220–300
	98	20	Tianjin Xibeier International Co., Ltd.	160–200
	99	22	Ningbo V&S International Trade Shipping Co., Ltd.	220–280
Sodium acetate	99	25	Weifang Ocean Trading Co., Ltd.	950–1300
	99	25	Zouping Changshan Town Zefeng Fertilizer Factory	700–1100
	99	1	ULTRA CHEMICAL WORKS (India)	1000
Sodium hydroxide	99	27	Tianjin Shengxinhai Chemical Co., Ltd.	300–400
	99	2	Tianjin Yuanlong Chemical Industry Co., Ltd.	350–437
	99	10	Wuhan Well Sailing Industry And Trade Co., Ltd.	400–600
Barium hydroxide	99	5	Richin International Trade (Dalian) Co., Ltd.	1000–2000
	99	10	Qingdao Yingfengyuan Industrial & Trading Co., Ltd.	755–936
	99	10	Tianjin Topglobal Technology Co., Ltd.	700–800
Magnesium nitrate	99	50	Sichuan Yimin Fertilizer Co., Ltd.	245–300
	98	20	Xiamen Vastland Chemical Co., Ltd.	200–300
	98	1	Shanxi Wencheng Chemicals Co., Ltd.	290–340
Ammonium alum	99.3	25	Gansu Jinshi Chemical Co., Ltd.	100–200
	99.7	25	Zibo Zichuan Chengpeng Chemical Factory	160–193
	99.3	20	Humate (Tianjin) International Limited	150–300
Calcium chloride	98	20	Shouguang Jinlei Chemical Co., Ltd.	350–390
	99	5	Dalian All World I/E Co., Ltd.	250–630
	99.8	20	Liaoning Metals & Minerals Enterprise Co., Ltd.	150–300
<b>Salt hydrates</b>				
Calcium chloride hexahydrate	94–97	15	Zhengzhou Macro Imp. & Exp. Co., Ltd.	220–340
Sodium sulphate decahydrate	99.5	25	Zhengzhou Clean Chemical Co., Ltd.	70–120
Sodium carbonate decahydrate	99	20	Wuhan Guotai Hongfa Commodity Co., Ltd.	200–230
Calcium nitrate tetrahydrate	99	25	Shanxi Jiaocheng Tianlong Chemical Industry Co., Ltd.	255
Sodium thiosulphate pentahydrate	99	25	Dahua Group Dalian Guanlin International Trade Co.,	160–180
	99	5	Changsha Weichuang Chemical Co., Ltd.	285
Sodium acetate trihydrate	99.8	5	Foodchem International Corporation	500–600
	99	1	Tianjin Flourish Chemical Co., Ltd.	400–892
Barium hydroxide octahydrate	99	10	Richin International Trade (Dalian) Co., Ltd.	700–800
Magnesium nitrate hexahydrate	98	25	Tianjin Crown Champion Industrial Co., Ltd.	230–250
	98–99	1	Shanxi Wencheng Chemicals Co., Ltd.	240–280
Ammonium alum dodecahydrate	99.5	25	Henan Allrich Chemical Co., Ltd.	300–500
	99.5	12	Chance Sun Import & Export (Dalian) Co., Ltd.	177–300
Calcium chloride hexahydrate	98	20	Weifang Bell Chemical Co., Ltd.	90–120
	99	10	Weifang Menjie Chemicals Co., Ltd.	110–300

**Table 24**

Wholesale prices of some latent heat phase change materials.

PCM manufacturer	Kind of PCM	Minimal order (ton)	FOB price (US\$/ton) <sup>a</sup>
PCM Solutions (UK)	Inorganic salt solutions	1	2250–3750
	Organic compounds	1	3750–7500
Climator AB (Sweden)	Inorganic salt solutions	1	6900–78200
	Organic compounds	1	5750–17250
Entropy Solutions Inc. (USA)	Organic compounds	0.5	4400–8800
RGEES LLC (USA)	Inorganic salt solutions	1	4000
PCM Energy P. Ltd. (India)	Inorganic salt solutions	1	3450

<sup>a</sup> The used exchange rates: 1GBP=1.5USD=1.3EURO.

sodium sulphate, disodium hydrogen phosphate dodecahydrate and sodium acetate trihydrate, have been investigated by a number of researchers and others attracted less attention. Most of phase diagrams for salt–water systems were produced about 60–70 years ago. Not all melting temperatures were determined accurately for salt hydrates in the process of studying their phase diagrams. Such thermophysical properties as heat fusion, density, specific heat, thermal conductivity, thermal diffusivity, viscosity of salt hydrates are not sufficiently studied. As it was mentioned above, Schamberger and Reid [26,86] had performed the measurements of the set of thermophysical properties of potassium fluoride tetrahydrate and lithium nitrate trihydrate. The thermophysical properties of commercially produced phase change salt hydrate materials are studied to less extent and none of properties and the stability of most of commercial products are currently certified by relevant authorities. There are no national or international standards which were set to define the minimally acceptable set of thermophysical properties and the temperature range for which these thermophysical properties should be determined. Also, there are no internationally accepted regulations on the procedures and instrumentation to be used in measurements, on minimal number of thermal cycles to be performed during tests, on the supercooling degree etc.

It is necessary to mention that recently the first steps have been made towards comparative tests of capability of methods and instruments used for determination of PCM thermophysical properties. For example, comparative tests were performed on PCMs characterisation with the use of differential scanning calorimeters in [311,312]. Similar tests on the determination of thermal conductivity of n-octadecane were performed in [313] in the framework of IEA/ECES programme considering this as a potential standardised benchmark phase change material. The analysis of non-classical techniques, which have been recently developed for characterisation of some thermal properties of PCMs, is carried out in [314]. All investigations described in [311–314] were performed by scientists based in European research organisations.

The large scale applications of the latent heat storage technology in various fields require thermal storage systems to be carefully designed taking into account their life time economic and technical performance. To achieve the above goal it is of a paramount importance to create database with accurate information on physical and chemical properties of working agents in the solid and liquid states, their supercooling and thermal cycling stability performances along with data on the energy transfer between heat storage and heat demand systems. The narrow operating temperature range of latent heat storage systems reinforces the criticality of the accuracy and reliability of above data.

Completion of the following measures would be required to progress from the R & D to commercial stage:

1. Pure salt hydrates are the main component in the working agent in phase change latent heat storage systems for the

temperature range between  $-50\text{ }^{\circ}\text{C}$  and  $120\text{ }^{\circ}\text{C}$  and therefore the thermophysical properties of pure salt hydrates as well as commercial PCM products should be further investigated using modern experimental test hardware and software.

2. To have a single approach to certification of commercially produced heat storage phase change materials, it is necessary to initiate work on development of international standards for methods and apparatus to be used in measurements of thermophysical properties (the melting point, heat of fusion, density, specific heat, thermal conductivity, thermal diffusivity, viscosity in the solid and liquid states), the temperature range for which the properties should be defined, the maximum temperature of exploitation, the minimum number of thermal cycles in tests, the degree of supercooling etc.
3. As part of the above activities, international collaborative investigations of the selected set of thermophysical properties for a number of high purity organic materials (for instance 2–3 n-alkanes) should be performed and the set of this data published in the form that it can be used as a template or reference material for other future studies in this area.
4. To select several well equipped research laboratories with the high international recognition and reputation to act as certification authorities for commercially produced or new PCMs under development.

The above tasks cannot be completed without close cooperation of interested parties including research laboratories, commercial manufacturers of PCMs and such organisations as the International Energy Agency and national and international Renewable Energy or Professional Associations. International coordination of the above activities would ensure a high quality of produced phase change latent heat storage materials and efficiency in their application.

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