



# Characterization of calcium chloride tetrahydrate as a phase change material and thermodynamic analysis of the results



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## ABSTRACT

To study the feasibility of calcium chloride tetrahydrate as a phase-change material, we determined its melting point and heat of fusion using differential scanning calorimetry (DSC) in the temperature range of 0 °C–60 °C. We also determined the density and viscosity of molten calcium chloride tetrahydrate in the temperature range of 40 °C–65 °C and studied the effect of adding small quantities of LiCl, NaCl and KCl (1 mass %) on the resulting thermal and physical properties. Based on the determination of the thermophysical properties, the energy storage density was evaluated for the different systems. The  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} + 1$  mass % of LiCl exhibited higher values ( $174 \text{ J/cm}^3$ ) than pure  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  ( $156 \text{ J/cm}^3$ ), and the  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O} + 1$  mass % of NaCl ( $151 \text{ J/cm}^3$ ).

Some of the results were interpreted using thermodynamic models and functions, indicating that the addition of alkaline chlorides contributes to releasing water molecules from the hydration layer of  $\text{Ca}^{+2}$  ions, which appears to have a determining effect on the behavior of molten  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ .

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## 1. Introduction

Storing thermal energy as latent heat is a good storage method when the availability of energy is discontinuous and variable over time, as is the case with solar energy. The materials used in this type of storage are termed phase-change materials (PCMs), which have high heat of fusion levels, which allow them to store or release large amounts of energy in melting or freezing processes [1]. Organic or inorganic compounds can be used as PCMs in thermal energy storage systems. However, these materials have their advantages and disadvantages. Some advantages of organic PCMs are good thermal and chemical stability, little or no subcooling and they are not corrosive. The advantageous features of the inorganic PCMs are high fusion heat, low cost and ready availability. In terms of disadvantages, organic PCMs have relatively low fusion enthalpy

and relatively low thermal conductivity values, they are more expensive, and they are flammable. Inorganic compounds exhibit subcooling and phase separation and therefore are more thermally and chemically unstable, as well as being corrosive [2,3].

Recently several studies dealing with organic PCMs have been reported; Graphite impregnated paraffin wax were used by Atkin and Farid [4] for the thermal regulation of photovoltaic panels. A similar work was done by Hasan et al. [5] but using paraffin waxes and mixtures of fatty acids as PCMs. Harikrishnan et al. [6] investigated composite PCMs prepared from a mixture of lauric and stearic acids plus small addition of metallic oxides nanoparticles for building heating applications. A mixture of organic acids impregnated in expanded graphite was prepared by Yang et al. [7] for the use in thermal energy storage in solar heating or other potential applications. Similar works using a variety of composite PCMs as alternatives for solar domestic hot water systems and energy absorbing building material were done by Haillot et al. [8] and Karaipekli and Sari [9]. Additional polymer microcapsules containing various organic compounds have been characterized as promising energy storage materials [10–13].

Also several hydrated inorganic salts have been studied as

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Nomenclature			
$a$	activity of water	$y_i$	ionic strength fraction of electrolyte $i$
$a_1, a_2$	constants in Eq. B.12	$z_+$	cation charge
$a^*, b^*$	constants in Eq. 2	$z_-$	anion charge
$A, B, T_0$	free volume model parameters (Eq. (3))	<i>Greek letters</i>	
$b_1, b_2, b_3$	constants in Eq. B.12	$\Delta\mu_{H_2O}$	chemical potential difference (Eq. (1))
$A^*, B^*, C^*, D^*$	CL model constants (Eq. (B.1))	$\epsilon$	BET model parameter
$c, r$	BET model parameters (Eq. (A.1))	$\eta$	viscosity (mPa s)
$\Delta H_M$	heat of crystallization (J/g)	$\mu$	chemical potential of water
$\Delta H_C$	heat of fusion (J/g)	$\rho$	density (g/cm <sup>3</sup> )
$I$	ionic strength (mol Kg <sup>-1</sup> )	$\sigma$	standard deviation
$K$	CL model parameter (Eq. (B.1))	$\varphi$	fluidity (mPa <sup>-1</sup> s <sup>-1</sup> )
$M_S$	molecular weight of water	$\nu_+$	cation stoichiometric factor
Onset $T_M$	melting point (°C)	$\nu_-$	anion stoichiometric factor
Onset $T_C$	crystallization point (°C)	<i>Subscripts</i>	
Peak $T$	peak on DSC heating curve (°C)	C	crystal
$R$	gas constant	$i$	electrolyte
$T$	temperature (K)	$M$	subcooled melt
$T_g$	glass transition temperature (K)	MIX	mixture property
$x_W$	mole fraction of water	S	saturated aqueous solution
$X$	CL model parameter (Eq. (B.2))	W	water

potential PCMs to apply to solar energy storage at low temperatures [14], given that their melting points are between 7 and 117 °C and they have higher capacities to store latent heat of fusion per unit volume than do organic compounds [15,16]. Some of the problems presented by these salts are the phase separations and subcooling. Thickening agents and nucleating materials are added to minimize these effects and have achieved good cycling stability in different heating-cooling processes [17,18].

Calcium chloride forms four types of hydrated salts: CaCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>·4H<sub>2</sub>O, CaCl<sub>2</sub>·2H<sub>2</sub>O, and CaCl<sub>2</sub>·H<sub>2</sub>O, with melting points of 30.1 °C, 45.1 °C, 175.5 °C, and 260 °C, respectively [19]. Meisingset and Gronvold report that transition temperatures of hexahydrate and tetrahydrate are 29.5° C and 45.6° C, and the fusion enthalpies are 198.1 J/g and 167.2 J/g, respectively [20]. An interesting recently published review reports thermophysical properties and costs of different hydrated salts used as PCMs [21]. The authors of this review recommend to use 29.5 °C and 198 J/g as melting point and heat of fusion for calcium chloride hexahydrate, respectively. However, Voigt [22] reports an enthalpy of crystallization of 37.7 J/mol (172.3 J/g) obtained from the experimental study of Chmarzynski and Piekarski [23]. On the other hand, Sharma and Sagara [24] and Voigt and Zeng [25] report a fusion enthalpy of 158 J/g for the tetrahydrate. Voigt also reports that between 302.85 K and 318.55 K (29.8–45.4 °C) there are three crystalline forms of the tetrahydrate denoted as  $\alpha$ ,  $\beta$ , and  $\gamma$  [22].

Calcium chloride hexahydrate is the most intensively studied of the four hydrates. There is no information on the other hydrates, although two works mentioned calcium chloride tetrahydrate as a potential PCM [20,24]. However, the majority of references to CaCl<sub>2</sub>·4H<sub>2</sub>O report that it has a negative effect when CaCl<sub>2</sub>·6H<sub>2</sub>O is used as a PCM. The melting point of calcium chloride hexahydrate is within the human comfort temperature range [26], and thus it has been studied for application to residential solar-energy systems. Thirty years ago, Lane et al. [27] performed the first broad and systematic study of this PCM, including the construction of a small-scale thermal energy storage unit with CaCl<sub>2</sub>·6H<sub>2</sub>O encapsulated in high-density polyethylene bottles (HDPE) to investigate its behavior in heating systems using air as the heat-transfer fluid. The

results of these experiments were used to predict the behavior of a full-scale storage unit using CaCl<sub>2</sub>·6H<sub>2</sub>O encapsulated in HDPE tubes. A preliminary design and economic assessment were then made for domestic solar heating using forced-air systems. Volker et al. [16] used a modified CaCl<sub>2</sub>·6H<sub>2</sub>O (0.5% of NaCl, 2% of KCl, and 1% of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O) to study its impact on reducing the room temperatures of a lightweight construction with single-glazed windows. A reduction of up to 4 K in peak temperatures was observed using this PCM. Several researchers have studied other applications of calcium chloride hexahydrate; for example, Bourdeau [28] tested and modeled a Trombe wall, Kaygusuz [29] determined the performance of calcium chloride hexahydrate in a solar water-heating system, Takakura and Nishina [30] and Boulard et al. [31] applied this PCM in greenhouses, and Bajnoczy et al. [32] studied a heat storage system in two temperature ranges (60 °C – 30 °C and 30 °C – 20 °C) based on CaCl<sub>2</sub>·6H<sub>2</sub>O and CaCl<sub>2</sub>·4H<sub>2</sub>O and its possible application for heating water for domestic use. Aristov et al. [33,34] also studied various properties of calcium chloride confined in mesopores of silica gel in order to observe their behavior for selective water sorption. The results were very good and for this reason the authors postulate that this composite can be used in different applications, such as drying gas, thermal insulation, air conditioning, accumulation of low temperature heat, and cooling electronic devices.

Calcium chloride hexahydrate presents problems of subcooling and phase separation [35], which have led several authors to recommend the use of different additives, such as NaCl, KCl, Ba(OH)<sub>2</sub>·8H<sub>2</sub>O, NaF, BaCO<sub>3</sub>, SrCO<sub>3</sub>, BaF<sub>2</sub>, BaF<sub>2</sub>-HF and/or SrF<sub>2</sub> to avoid subcooling [16,35]. Kimura and Kai [36] noted that the problem of phase separation is caused by the formation of CaCl<sub>2</sub>·4H<sub>2</sub>O during repeated freeze-thaw cycling and suggested three ways to avoid this issue: modifying the melting behavior of CaCl<sub>2</sub>·6H<sub>2</sub>O, accelerating the nucleation of CaCl<sub>2</sub>·6H<sub>2</sub>O crystals, and delaying the nucleation of CaCl<sub>2</sub>·4H<sub>2</sub>O crystals. Reznitskii [37] reports that subcooling is avoided by adding 0.3 wt.% of SrCl<sub>2</sub>. Additionally, the nucleation properties remained without variation for about one year when 1 cm<sup>3</sup> crystals were added. Different researchers have performed significant work on this problem

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