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Physical and thermal properties of $MgCl_2$–NaCl mixtures with varying concentrations for solar thermal energy storage applications

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Abstract

Thermal Energy Storage (TES) is a system capable of absorbing and releasing heat when a material undergoes a phase change. Materials commonly used in such systems are known as Phase Change Materials (PCMs). Salts are among the most frequently utilized PCMs due to their low cost and favorable physicochemical properties. This study aims to investigate the effect of mixing NaCl with $MgCl_2$ on the properties and performance of PCMs. The preparation process involved manually grinding a mixture of NaCl and $MgCl_2$ until a homogeneous blend was achieved. The samples were then placed in a muffle furnace and heated to 600°C. Physical properties such as density, specific heat capacity, and thermal conductivity were evaluated, and the charging–discharging performance was tested using a thermal box. The results indicated that increasing the $MgCl_2$ content enhanced both the specific heat capacity and thermal conductivity. However, a higher $MgCl_2$ proportion corresponded with a decrease in density. These changes significantly improved the rate of thermal energy absorption and storage capacity. The eutectic salt mixture developed in this study demonstrates strong potential as a material for solar TES applications.

Keywords:
PCM, $MgCl_2$, NaCl, thermal energy storage capacity, thermal energy

1 Introduction

Technological advancement is one of the main driving forces behind a country's development. In line with this, energy consumption continues to increase across various sectors, including industry, transportation, and domestic needs [1]. Energy is a critical resource as it is used in many aspects of life, such as lighting, space heating, communication, and both small- and large-scale industrial operations [2]. However, dependence on non-renewable fossil energy sources has prompted extensive research and development of renewable energy alternatives, one of which is solar energy.

Solar energy, derived from solar radiation, can be converted into electricity or heat. One of the rapidly developing methods of utilizing solar energy is through Thermal Energy Storage (TES) systems [3]. TES systems allow heat to be stored in a material and used later as needed. Among various TES methods, latent heat storage using Phase Change Materials (PCMs) is considered one of the most effective. PCMs function by absorbing and releasing energy in the form of latent heat during phase transitions from solid to liquid or vice versa at a specific temperature [4].

Numerous PCMs have been developed for TES applications, including both organic and inorganic materials. Inorganic salts such as nitrate salts, carbonate salts, and chloride salts are promising candidates due to their high TES capacities, good thermal stability, wide availability, and relatively low cost [5], [6]. Among these, NaCl–$MgCl_2$ mixtures have shown great potential for TES in Concentrated Solar Power (CSP) systems [7], [8]. This is attributed to several favorable properties, including high thermal stability, a broad operating temperature range, and thermophysical characteristics that support efficient heat storage and transfer [1], [9], [10].

However, several challenges remain in the application of NaCl–$MgCl_2$ as PCMs. One of the primary issues is the limited experimental data on the physical and thermal properties of salt mixtures with varying concentrations. This limitation hinders the optimal utilization of eutectic salt mixtures for solar TES applications. Some previous studies have explored the characteristics of molten salts for heat storage. For example, Liu *et al.* [11] investigated chloride salt mixtures for CSP applications and found that increasing $MgCl_2$ content improved latent heat storage capacity. Additionally, research by Wang *et al.* [12] indicated that chloride salt mixtures have better thermal conductivity than nitrate salts. Nonetheless, a research gap still exists regarding the effects of NaCl and $MgCl_2$ blending on heat storage capacity, specific heat, density, and thermal conductivity. Therefore, this study aims to investigate the physical and thermal properties of NaCl–$MgCl_2$ mixtures with different concentration ratios. Specifically, the study focuses on the influence of NaCl and $MgCl_2$ composition variations on density, thermal conductivity, and heat release rates during discharge processes using a solar collector.

It is important to note that although the operating temperatures in this study are below the melting points of the PCMs, this research still provides valuable insight into the physical properties and sensible heat capacity of NaCl–$MgCl_2$ mixtures. This helps to identify candidate materials with favourable thermal characteristics before proceeding to high-temperature phase transition studies. Therefore, this research contributes to a preliminary evaluation of thermal performance within the medium temperature range as a pre-characterization approach for solar TES applications. The novelty of this research lies in the evaluation of thermal behaviour at sub-melting temperatures, which is often overlooked in the literature. This could serve as a foundation for subsequent studies focusing on latent heat storage and full melting-solidification cycles.

2 Literature review

A wide variety of PCMs, both organic and inorganic, are available within the required temperature ranges. Numerous organic and inorganic chemical compounds have been identified as PCM, as shown in Fig. 1, based on their melting points and latent heat of fusion characteristics [13].

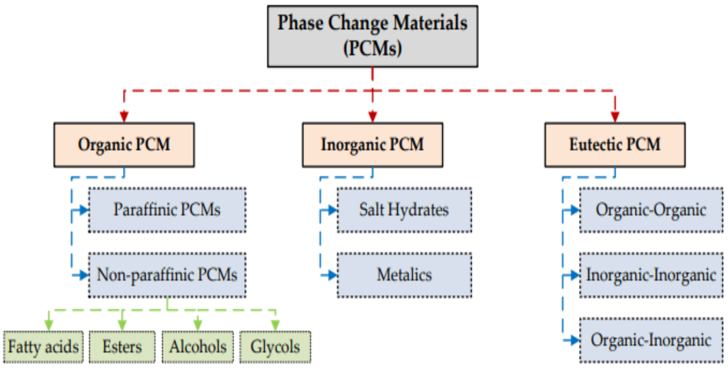


Fig. 1. PCM category [15]

In general, inorganic compounds possess nearly twice the latent heat storage capacity (250–400 kJ/kg) compared to organic compounds (128–200 kJ/kg). Due to their significantly different thermal and chemical behaviors, the properties of each subclass of materials must be carefully considered, as they greatly influence the design of TES systems [14].

Eutectics are compositions with the minimum melting point formed by two or more components, in which each component melts and solidifies congruently. During the crystallization phase, the components act as a single entity, forming a mixture wherein the constituents solidify into an intimate crystalline structure and melt together without phase separation. Eutectic mixtures of inorganic salts have melting points ranging from 250°C to 1680°C and latent heats of fusion between 68 and 1041 J/g [16].

When a substance freezes, the temperature often drops below its melting point without immediate crystallization, due to insufficient nucleation sites. This delay in solidification, caused by the absence of initial crystals, is known as the phenomenon of supercooling [17]. A notable challenge associated with inorganic salts is the volume change during phase transitions. This issue arises primarily from the limited available data on the temperature dependence of density [18]. Table 1 summarizes previous studies on the physical and thermal properties of chloride salt mixtures or their eutectics.

Table 1. Characterization of chemical-physical properties of some inorganic PCMs

PCM	wt%	Tm (°C)	ΔH (kJ/kg)	Cp (kJ/KgK)	ρ (kg/cm^3)	k (W/mK)	Ref.
$MgCl_2$/KCl/NaCl	60/20.4/19.6	380	400	0.96	1800	-	[19]
$MgCl_2$/NaCl	43.1/56.9	459	333	-	-	-	[6]
$MgCl_2$/NaCl	52/48	450	430	0.92	2230	0.95	[20]

3 Materials and methods

3.1 Materials

The materials used in this study were local NaCl salt from Tanoh Anoe Village, Jangka Bireun, Aceh. The $MgCl_2$ salt was a technical grade compound (purity >98%) purchased from Multi Kimia, a chemical supplier in Indonesia, via the Tokopedia™ e-commerce platform.

3.2 Preparation of eutectic salt

$MgCl_2$ was mixed with NaCl at various weight ratios, 70:30, 50:50, and 65:35 wt%, and manually ground until a homogeneous mixture was obtained. The samples were then dried in a Memmert™ UN110 oven at 100°C for one hour to remove moisture content. After drying, the mixtures were heated in a Muffle Furnace (Thermolyne™ Thermo Scientific FB1310M-33) to 600°C for six hours and then gradually cooled to room temperature. Sample codes were assigned based on their compositions: Na70Mg30 (70% NaCl and 30% $MgCl_2$), Na50Mg50 (50% NaCl and 50% $MgCl_2$), and Na35Mg65 (35% NaCl and 65% $MgCl_2$). For PCM performance testing using a thermal box, the samples were molded into cylindrical shapes with a diameter of 5 cm and a thickness of 1 cm.

3.3 Physical properties testing of eutectic salt

3.3.1 Specific heat capacity

The specific heat capacity is calculated based on the amount of energy obtained by multiplying the power by the temperature difference. Once the energy value (E, in J) is obtained, it is divided by the mass of the salt (m, in g) multiplied by the temperature difference (ΔT, in °C), as expressed by Eq. (1).

$$C_p = \frac{E}{m \times \Delta T} \tag{1}$$

3.3.2 Density

Density is a parameter that indicates the compactness of a material. Mathematically, density is defined as the ratio of mass to volume, typically expressed in kg/m³ (Eq. (2)) [6], where *m* is the mass (kg) and *V* is the volume (cm³):

$$\rho = \frac{m}{V} \tag{2}$$

3.3.3 Thermal conductivity

Thermal conductivity is the ability of a material to conduct heat. The value of thermal conductivity indicates how quickly heat energy transfers from one point to another within the material. This quantity is expressed in units of W/m°C (Eq. (3)) [21], where Qd is the rate of heat transfer (W), A is the cross-sectional area of the material (m²), t is the duration of the test (s), and ΔT is the temperature difference (°C).

$$k = \frac{Qd}{a \times t \times \Delta T} \tag{3}$$

3.3.4 Performance test of eutectic salt

The performance testing of the eutectic salt consists of two phases: charging and discharging, using a thermal box setup as shown in Fig. 2. The test is conducted for two hours using the thermal box [22], [23]. During the charging phase, the rate of heat absorption and thermal storage capacity are measured until saturation is reached, i.e., when the salt sample can no longer absorb energy from the heat source.

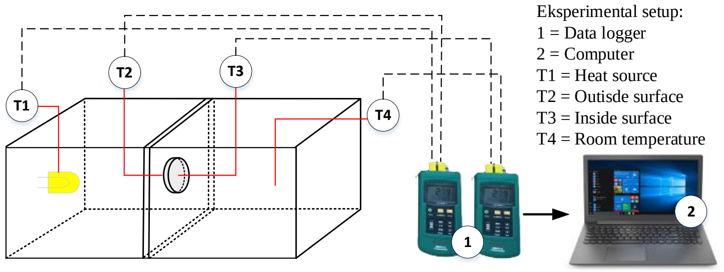


Fig. 2. Experimental setup for PCM charging and discharging

Meanwhile, during the discharging phase, the rate of heat release is monitored until the sample reaches thermal equilibrium with the surrounding environment. The process stops once the salt sample's temperature equals the ambient temperature [8]. The TES capacity is calculated using Eq. (4).

$$Q = m \times C_p \times \Delta T \tag{4}$$

Q is the absorbed/stored thermal energy (Joules), m is the mass of the salt (kg), Cp is the specific heat capacity (kJ/kg·°C), T_1 is the initial temperature (°C), and T_2 is the final temperature (°C).

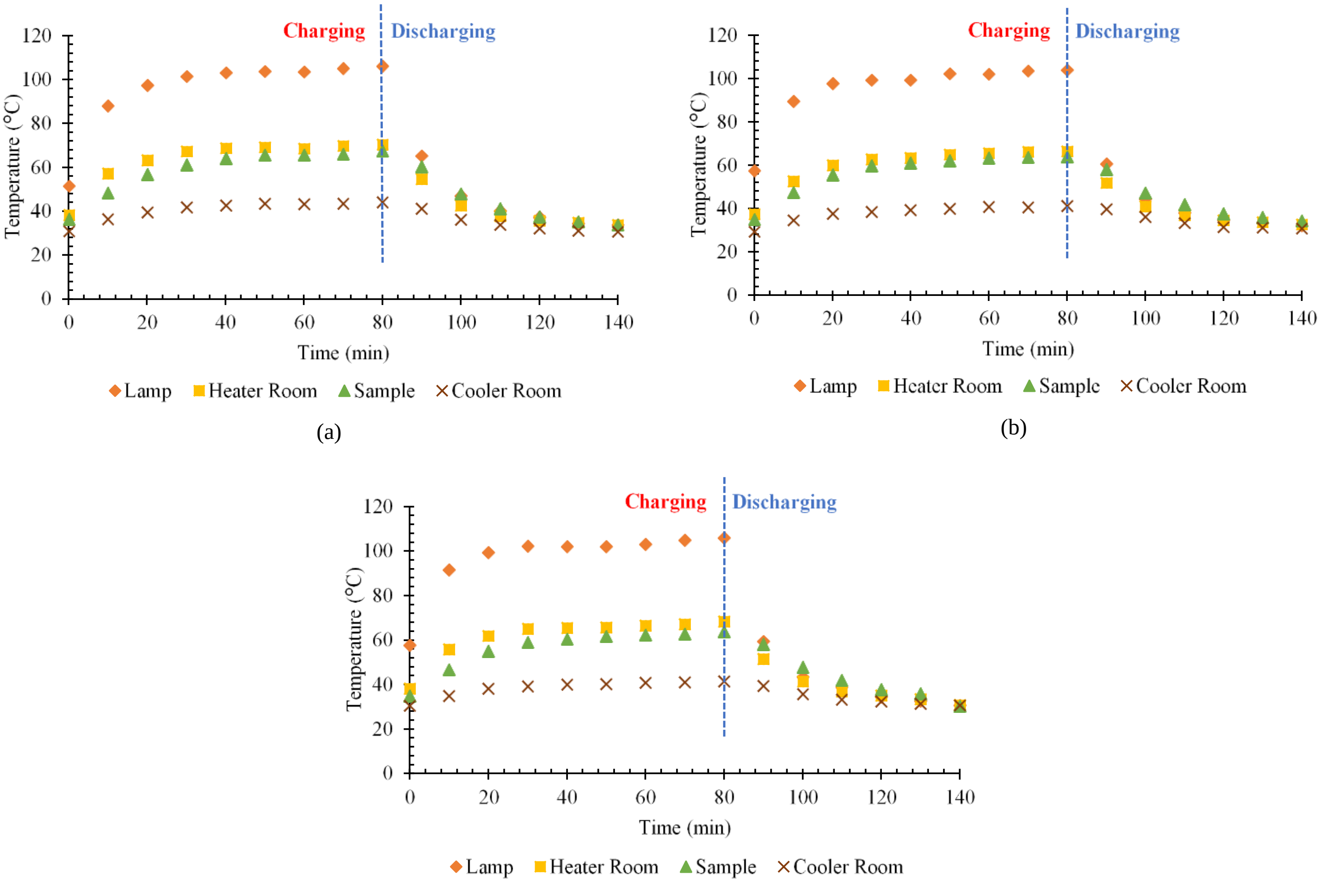
4 Result and discussions

The performance testing results of the PCM provide insights into the ability of each sample to store and release thermal energy. Fig. 3 illustrates the charging and discharging temperature profiles recorded during the performance tests for each sample. The results indicate that the higher the $MgCl_2$ content in the mixture, the greater the TES capacity and the faster the heat release rate. Conversely, the sample with the highest NaCl content exhibited the lowest thermal energy absorption rate, indicating a lower energy storage capacity.

In the Na70Mg30 sample, thermal energy was absorbed during the charging process, reaching 31.5°C for 1 hour and 26 minutes. The highest temperature reached during the thermal energy absorption was 67.5°C, starting from an initial temperature of 36°C. During the charging process, the thermal energy release lasted for 59 hours, with the temperature dropping from 67.5°C to 33.5°C, a decrease of 34°C.

The testing was conducted at temperatures of up to 67.5°C, which are indeed below the eutectic melting point of the salt mixtures. Nonetheless, this approach was taken to provide an initial understanding of each composition's sensible heat capacity and thermal energy release rate. This study serves as a preliminary step for material characterization, which will later be extended to high-temperature phase transition analysis for evaluating latent heat storage capabilities.

In the Na50Mg50 sample, the charging process increased the temperature to 29.25°C over 1 hour and 25 minutes. During discharging, the thermal energy released decreased by 30.25°C over 57 minutes. For the Na35Mg65 sample, during charging, the temperature increased from an initial 35°C to a final 64°C over 1 hour and 23 minutes.



(a)

(b)

(c)

Fig. 3. (a) Na70Mg30 charging and discharging process; (b) Na50Mg50 charging and discharging process; and (c) Na35Mg65 charging and discharging process

While discharging, the thermal energy released dropped by 33.75°C over 56 minutes. The thermal storage capacity, energy absorption rate, and energy release rate can be determined from the charging and discharging processes. See Table 2 for further details.

Table 2. The thermal storage capacity and energy absorption rate

Sample	q^1 (J/min)	q^2 (J/min)	Q (Joule)
Na70Mg30	9.795	45	1121.6
Na50Mg50	11.129	61.34	1826.2
Na35Mg65	11.352	91.23	2598.5

From Table 2, it is observed that the thermal energy absorption rate for Na35Mg65 is 13.78% higher than for the other samples. Meanwhile, in terms of thermal energy release rate, Na35Mg65 outperforms Na70Mg30 by 50.67%. This results in Na35Mg65 having a 56.84% higher TES capacity. Therefore, it can be concluded that Na35Mg65 has a higher energy storage capacity with better energy absorption and release rates compared to the other two samples.

Agyenim et al. [24] showed that inorganic salt mixtures as PCM have higher energy storage efficiency than organic-based PCMs. Additionally, a study by Lu et al. [25] found that $NaCl-MgCl_2$-based PCM has higher thermal conductivity than single salts, enhancing heat transfer effectiveness in energy storage systems. Another study by Pinto et al. [26] also revealed that the eutectic composition of inorganic salts can improve latent heat storage efficiency with better thermal stability.

The physical properties tests showed that the higher the $MgCl_2$ content in the sample, the higher the specific heat capacity and thermal conductivity. This is inversely related to the density value, which decreases as the $MgCl_2$ content increases. More details can be seen in Table 3.

Table 3. Physical characteristics of eutectic salts

Parameter	Unit	Sample		
		Na70Mg30	Na50Mg50	Na35Mg65
Specific Heat Capacity	J/g°C	1.874	3.286	4.716
Bulk Density	g/cm^3	0.7065	0.6171	0.5732
Thermal Conductivity	W/m°C	1.474	1.764	1.922

From Table 3, it is evident that the specific heat capacity and thermal conductivity values of all three salt samples increased significantly as the $MgCl_2$ content increased. This aligns with the values found for eutectic salts, which range from 1.94 J/g·°C to 2.13 J/g·°C [27]. The highest specific heat capacity value, 4.72 J/g·°C, is 81.7% higher than the average thermal conductivity value, which ranges from 0.27 W/m·K to 0.61 W/m·K [28].

In contrast, the bulk density analysis shows that as the concentration of $MgCl_2$ increases, the density tends to decrease. This is because the ionic interactions between Na^+ and Cl^- are weaker compared to those between Mg^{2+} and Cl^-, so in mixtures with higher NaCl content, the density is lower [29]. However, it is known that the density values typically range from 1.976 g/cm^3 to 0.302 g/cm^3 [30], and the density values obtained in this study fall within that range.

5 Conclusions

This study has evaluated the effect of mixing NaCl with $MgCl_2$ through experimental investigations using a thermal box testing device. The analysis results indicate that increasing the $MgCl_2$ content in the mixture contributes to enhanced TES capacity, highlighting the significant role of $MgCl_2$ in improving heat storage efficiency. This confirms that $MgCl_2$ plays a key role in improving PCM performance, particularly in energy absorption and release. However, the increase in the $MgCl_2$ fraction also leads to a decrease in PCM density, which may affect the mechanical properties and material stability during heating and cooling cycles. Therefore, optimization of the composition is necessary to balance the thermal storage capacity and the physical properties of the material for solar TES applications.

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