Novel inorganic binary mixture for low temperature heat storage applications

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Abstract

In this study an inorganic mixture based on bischofite (industrial by-product), was developed and characterized for its application as a phase change material for low temperature thermal energy storage (TES). The most appropriate composition was established as 40 wt.% bischofite and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$. Thermo-physical properties were defined and compared with those of the mixture with synthetic $MgCl_2 \cdot 6H_2O$. The heat of fusion and melting temperature were measured as 62.0 °C and 132.5 kJ·kg⁻¹ for the mixture with $MgCl_2 \cdot 6H_2O$, and 58.2 °C and 116.9 kJ·kg⁻¹ for the mixture with bischofite. The specific heat capacity values, cycling and thermal stability for both mixtures were also determined. For the mixture with $MgCl_2 \cdot 6H_2O$, the density of the solid and liquid states was of 1517 kg·m⁻³ (ambient temperature) and 1515 kg·m⁻³ (at 60-70 °C), respectively. For the mixture with bischofite, density of solid and liquid states was of 1525 kg·m⁻³ (ambient temperature) and 1535 kg·m⁻³ (at 60-70 °C), respectively. Both mixtures show supercooling of about 23.4 °C and 34.1 °C for the mixture with bischofite and $MgCl_2 \cdot 6H_2O$, respectively. In addition, it was shown that supercooling may be reduced by increasing the quantity of material tested. Thereby, it was established that an inorganic mixture based on bischofite is a promising PCM for low temperature TES applications.

Keywords: phase change material; thermal energy storage; waste or by-products; salt hydrates mixture.

Nomenclature

T_f	melting temperature, °C
T_c	crystallization temperature, °C
ΔH_f	latent heat of fusion, kJ·kg⁻¹
ΔH_c	latent heat of crystallization, kJ·kg⁻¹
C_p	specific heat capacity, J·g⁻¹·K⁻¹

1. Introduction

Efficient and economical heat storage is the key to balance energy supply and demand. Amongst the various heat storage techniques, latent heat storage stands out because of the capacity to provide high energy storage density and to store heat at a relatively constant temperature. This why a lot of attention has been paid recently to phase change materials (PCMs), due to their wide range of potential application in different fields of latent heat storage.

One of the methods to expand the possible uses of the particular PCM is its mixing with other materials and the formation of eutectic mixtures with the melting temperatures different from those of the pure substances. Moreover, eutectics have sharp melting point similar to pure substance and their volumetric storage density is above organic compounds [1]. The mixture with composition close to eutectic, selected and investigated in our study has the melting temperature about 60 °C. For this value, one of the most studied applications of PCMs to date is in thermal storage tanks for hot water, where the desired operation temperature is around 55-60 °C [2-5]. Moreover, in this temperature range phase change materials are already being used for thermal control of Li-ion batteries [6-8], air conditioning [9], transportation of food [10], temperature sensitive pharmaceuticals, chemicals, etc. [11].

For a PCM to be implemented on the industrial scale, a number of technical and economic requirements must be performed: firstly, a PCM must have a low cost USD/kWh$_t$ and secondly, it should be readily available. One of the trends in lowering the costs of PCM is to use waste, recycled materials, household and industrial wastes, or some low cost by-products [12]. In this sense, the mining industry of northern Chile produces tons of by-products and wastes accumulated with very low cost and no practical applications. In non-metallic mining, these by-products usually appear in brine processing. In one of the cases of brine processing to obtain Li_2CO_3 and KCl, in the last evaporation step bischofite precipitates [13]. The annual amount of the bischofite obtained is dependent on the production quantity of potassium and lithium compounds. In 2013 this amount was estimated about 100,000 t with the price of about 40 US\$/ton [14]. This inorganic material currently doesn't have a reasonable application and basically just being stockpiled in waste dumps. It was shown in several investigations that bischofite is a good candidate to be used as latent heat storage material. Its main benefit is extremely low cost [12-16]. Bischofite is a hydrated salt composed by $MgCl_2 \cdot 6H_2O$ (≥ 95wt. %) with some impurities. Its melting temperature is about 112 °C. That is why, to develop applications of this by-product as a PCM at lower temperatures, the mixture with magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ was selected.

The literature review indicates that it is possible to obtain a number of mixtures $MgCl_2 \cdot 6H_2O/Mg(NO_3)_2 \cdot 6H_2O$ with various fusion temperatures and heat of fusion, some of which are reported as eutectic, and have potential to be used as PCMs [17-23]. Available literature data related to the mixture of $MgCl_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ is summarized in the Table 1.

Table 1. Literature data for mixtures of $MgCl_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ studied as PCM.

wt.% of MgCl₂·6H₂O	T_f, °C	ΔH_f, kJ·kg⁻¹	Reference
7	78	152.4	[17]
10	64.4–93.2*	160.2 (after 80 cycles)	[18]
10	78	76**	[17]
15	around 70	no data	
20	62-72*	70**	
30	50-60*	87**	
40	50-60*	97**	
eutectic, 38.4 wt.%	58.3	no data	[19]
eutectic, 41.3 wt.% (47 mol.%)	59.1	no data	[20]
eutectic, 41.6 wt.%	59.0	132.2	[21]
eutectic, 47 wt.%	59.1	144	[22]
eutectic, 49.3 wt.%	58.2	no data	[23]

* useful temperature range for PCM
** avalaible specific enthalpy

Mixtures used in the present study were prepared with synthetic salts and then with bischofite to find out the possibility of using of bischofite instead of synthetic $MgCl_2 \cdot 6H_2O$ in the preparation of mixtures, which would significantly reduce the price of this PCM.

One of the main problems of PCMs based on salt hydrates is that of supercooling. Many authors indicate that adding of nucleating and thickening agents can decrease the supercooling value [24-26]. Recently, it has been shown that the increased volume of PCM used favors the nucleation process and also allows to reduce the supercooling [27]. In this study, the supercooling values obtained by DSC method were compared to those values, obtained by measurements using K-type thermocouples with larger quantity of substance.

Therefore, this paper presents the possibility of producing a low temperature PCM for applications where the operating temperature is 55-60 ºC. In addition, the main innovation of this study is the use of a by-product without any further processing, in a mixture to be used in thermal energy storage.

2. Experimental part

2.1. Materials

Both magnesium chloride $MgCl_2 \cdot 6H_2O$ and magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ were synthetic salts purchased from Merck (99.0 %). Industrial by-product bischofite used in this study, has the following composition summarized in the Table 2.

Table 2. Chemical analysis results of bischofite*.

Element	Concentration [%]
Lithium, Li	0.343
Sodium, Na	0.938
Potassium, K	0.740
Calcium, Ca	0.010
Magnesium, Mg	10.93
Chloride, Cl	33.78
Sulfate, SO_4	2.10
Boron, B	0.190
Humidity, H_2O	1.46

* Crystallization water is not included

2.2. Selection of mixture

Based on data from Table 1, preliminary measurements of thermal behavior for $MgCl_2 \cdot 6H_2O$/ $Mg(NO_3)_2 \cdot 6H_2O$ mixtures were performed. The results indicated that the mixture of 40 wt.% of $MgCl_2 \cdot 6H_2O$ and 60 wt.% of $Mg(NO_3)_2 \cdot 6H_2O$ is the most appropriate to be used, because it has the major wt.% of bischofite and its composition is close to eutectic as evidenced by the presence of a single peak on the melting curve and on the crystallization curve. Moreover, it has an adequate melting temperature (60.7 °C) and relatively high latent heat of fusion [17,19, 20,21,26,28].

Therefore, mixture of 40 wt.% of $MgCl_2 \cdot 6H_2O$ and 60 wt.% of $Mg(NO_3)_2 \cdot 6H_2O$ was initially analyzed with synthetic salts and then with bischofite, replacing the synthetic $MgCl_2 \cdot 6H_2O$. Thus, a novel PCM with the composition of 40 wt.% bischofite and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$ is proposed in this study.

2.3. Sample preparation

Initially, all salts samples were dried at 40 °C for 12 hours and then were placed in a desiccator, because of their strong hygroscopic properties. Then salts were grinded in a pounder and blended in the desired proportion (40-60 wt.%). The prepared mixtures were melted, well mixed and then crystallized again to ensure the composition homogeneity throughout the volume.

2.4. Thermal properties

Measurements of melting temperature, heat of fusion, specific heat capacity, thermogravimetric analysis and analysis of cycling stability were conducted.

A DSC Netzsch 204 Phoenix F1 with N_2 atmosphere (flow rate of 20 mL·min^{-1}) was used to measure the phase change temperature and the latent heat of fusion/crystallization, with the sample mass of about 10 mg. The measurements were performed in a range from 20 °C to 130 °C in sealed aluminum crucibles of 40 μL capacity. Moreover, the DSC method was used to determine the cycling stability of the samples between −15 °C and 130 °C, subjecting them to 50 freezing-melting cycles with a rate of 10 K/min.

Specific heat analysis was performed in the range from 20 °C to 130 °C with sapphire as a reference material. Sealed aluminum crucibles of 40 μL capacity were used. For each sample there have been carried out three measurements: with an empty crucible to obtain a baseline, with a reference material and with the hydrated salt mixtures.

In addition to the DSC method, measurements with PCE type-K temperature sensors (accuracy ±(0.4% + 1°C)) were performed to reveal the thermal performance of chosen mixtures with the larger amount of substance (about 7-8 g). The scheme of experiments is presented in Fig. 1.
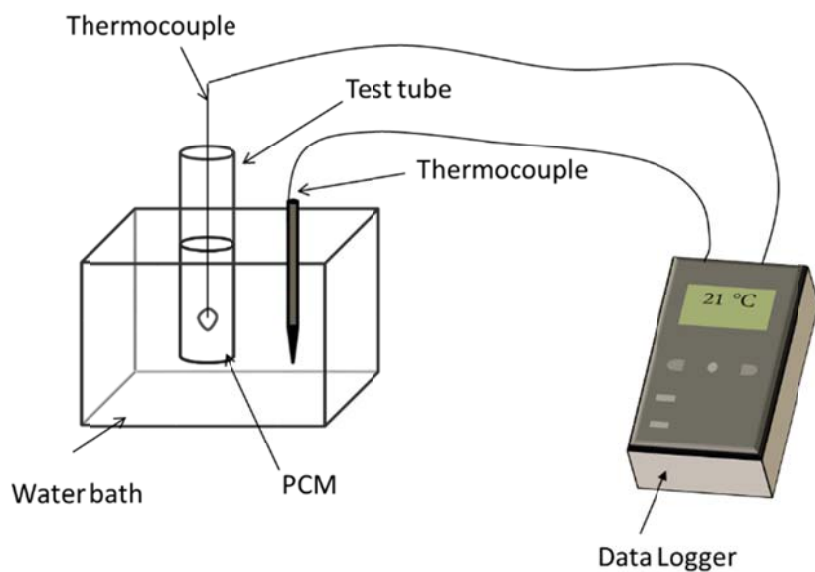
Fig 1. Scheme of experimental installation to reveal the thermal performance.

Thermal stability analysis was carried out using a Mettler Toledo Model TGA/DSC1 1100 LF in the temperature range from 20 °C to 130 °C with the standard aluminum crucibles (40 μL), under an atmosphere of ultra-purified nitrogen with flow rate of 30 mL/min.

2.5. Determination of density and viscosity

A pycnometer with n-dodecane was used to measure the densities of the solid salt mixtures. The liquid samples densities were performed with an oscillating densimeter (Mettler Toledo ED50).

The viscosity measurements were carried out with Brookfield Rheometer DV-III Ultra with different speeds of 10-80 rpm. Thermocel accessory was used to maintain temperature.

3. Results

3.1. Thermal properties

The results of the determination of melting/crystallization temperature and heat of fusion/crystallization, and also the variation of these parameters during the fifty cycles are summarized in Table 3.

Table 3. Measurement data of latent heat of fusion/crystallization, melting/crystallization temperatures and supercooling for both mixtures.

Sample	Cycle #	T_f [°C]	ΔH_f [kJ·kg^{-1}]	T_c [°C]	ΔH_c [kJ·kg^{-1}]	Supercooling [°C]
40 wt.% MgCl$_2$·6H$_2$O+ 60 wt.% Mg(NO$_3$)$_2$·6H$_2$O	10	62.0	132.3	25.1	119.1	36.9
	20	62.0	133.5	32.4	122.5	29.6
	30	62.0	132.2	27.4	120.8	34.6
	40	62.0	133.2	31.3	122.8	30.7
	50	62.0	132.7	38.5	127.3	23.5
	average of 50 cycles (± std deviation)	62.0±0.05	132.5±0.7	27.9±4.0	120.8±2.4	34.1±4.0
40 wt.% bischofite+ 60 wt.% Mg(NO$_3$)$_2$·6H$_2$O	10	58.1	116.7	32.3	106.4	25.8
	20	58.2	116.8	33.5	107.4	24.7
	30	58.2	115.3	35.3	107.4	22.9
	40	58.2	117.6	39.9	108.5	18.3
	50	58.2	115.1	38.1	107.2	20.1
	average of 50 cycles (± std deviation)	58.2±0.05	116.9±1.0	34.7±2.3	106.9±0.7	23.4±2.3

Fig. 2 shows examples of DSC curves for the 10th cycle for the ~~eutectic~~ mixture 40 wt.% MgCl$_2$·6H$_2$O + 60 wt.% Mg(NO$_3$)$_2$·6H$_2$O and the same mixture but with bischofite, replacing MgCl$_2$·6H$_2$O. DSC analysis (Table 3 and Fig. 2) indicates that the heat of fusion and the melting temperature of the mixture with bischofite are slightly lower than those of the mixture with MgCl$_2$·6H$_2$O. Moreover, peak of fusion/cristalization on the DSC curve of bischofite is wider

than that of $MgCl_2 \cdot 6H_2O$ indicating the presence of impurities. In case of mixture with bischofite the supercooling decreases by 10.7 °C, which may also be justified by the presence of various impurities in the mineral which act as additional nucleation centers (see Table 2). Both mixtures have shown good cycling stability during 50 melting-crystallization cycles.
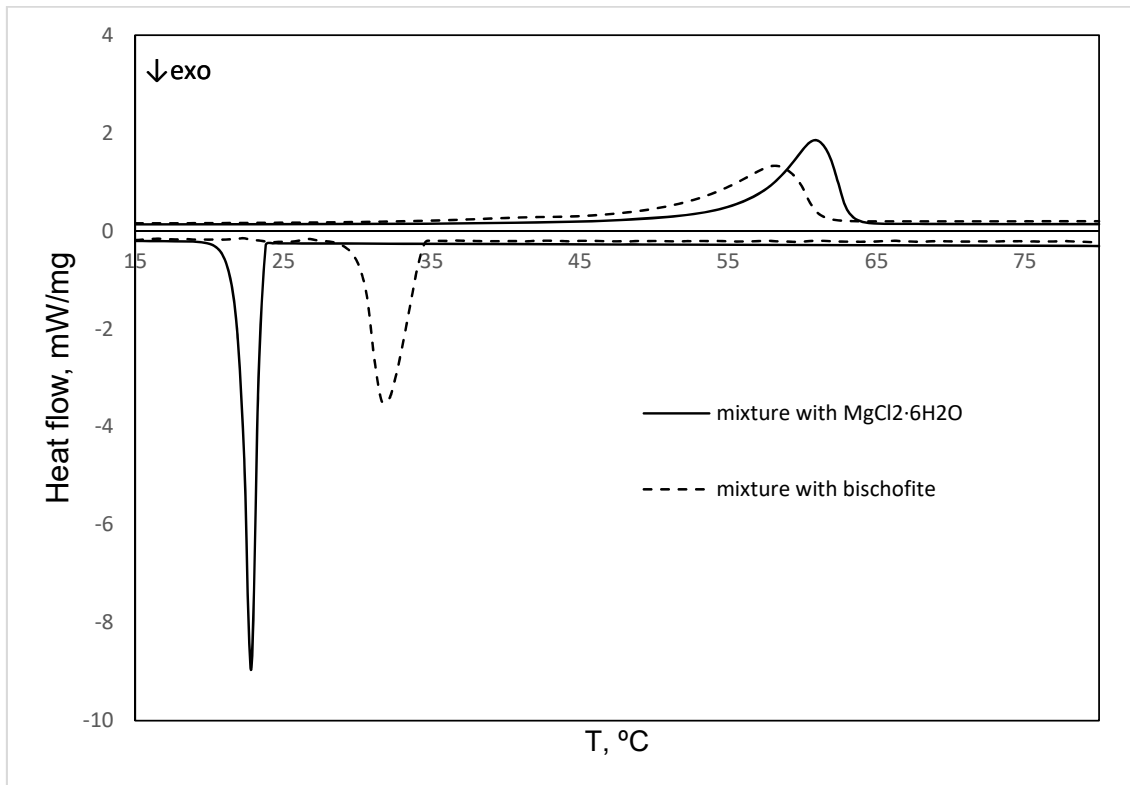
Fig. 2. DSC curves of the mixtures 40 wt.% $MgCl_2 \cdot 6H_2O$ + 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$ and 40 wt.% bischofite + 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$. Tenth heating and cooling cycle.

Fig. 3 shows dependence of the specific heat on temperature. For solid samples, the specific heat shows a slight increase in a temperature range 298.15–318.15 K (25–45 °C), with values from 1.0 to 2.3 $J \cdot g^{-1} \cdot K^{-1}$ for the mixture with $MgCl_2 \cdot 6H_2O$ and from 1.2 to 2.1 $J \cdot g^{-1} \cdot K^{-1}$ for the mixture with bischofite; therefore there are no big differences between both mixtures.
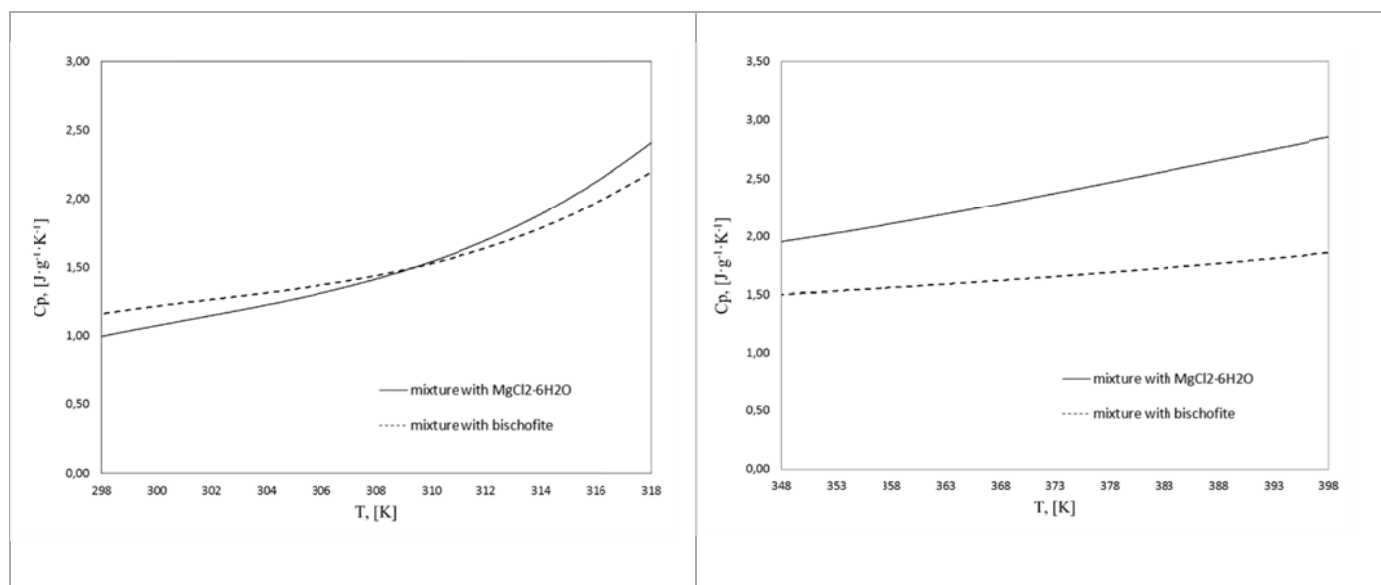
Fig. 3. Temperature dependence of specific heat for salt mixtures for the range 298.15 – 318.15 K (25–45 °C) (left) and 348.15 – 398.15 K (75– 125 °C) (right).

Specific heat values for the liquid phase in a temperature range 348.15–398.15 K (75– 125 °C) vary from 2.0 to 2.8 J·g^{-1}·K^{-1} and from 1.5 to 1.8 for mixtures with $MgCl_2\cdot6H_2O$ and bischofite, respectively. For both mixtures, the average values of heat capacity are similar, but slight lower than those reported by several authors for pure components of mixtures: synthetic magnesium chloride hexahydrate [14, 29], magnesium nitrate hexahydrate [30] and bischofite [14], and summarized in Table 5. The difference between pure substances and bischofite are due to the impurities present in bischofite [13], since most of them do melt at higher temperatures.

**Table 5.** Summary of Cp for hydrate salts and their mixtures used in this study.

Sample	Temperature range [K] (°C)	State	C_p [$J \cdot K^{-1} \cdot g^{-1}$]	Ref.
MgCl$_2$·6H$_2$O	298.15 - 333.15 (25 - 60)	solid	2.1 to 1.95	[14]
	298.15 - 371.15 (25 - 98) 371.15 - 387.15 (98 - 114)	solid solid	1.64 to 1.85 1.82 to 1.93	Calculated from [29]
Mg(NO$_3$)$_2$·6H$_2$O	not given	solid	1.92	[30]
	not given	liquid	2.37	[30]
bischofite	298.15 - 333.15 (25 - 60)	solid	1.6 to 2.1	[14]
	388.15 - 398.15 (115 - 125)	liquid	1.71 to 3.01	[14]
40 wt.%MgCl$_2$·6H$_2$O+ 60 wt.% Mg(NO$_3$)$_2$ ·6H$_2$O	298.15 – 318.15 (25 - 45)	solid	1.0 to 2.3	Present work
	348.15 – 398.15 (75 - 125)	liquid	2.0 to 2.8	Present work
40 wt.% bischofite+ 60 wt.% Mg(NO$_3$)$_2$ ·6H$_2$O	298.15 – 318.15 (25 - 45)	solid	1.2 to 2.1	Present work
	348.15 – 398.15 (75 - 125)	liquid	1.5 to 1.8	Present work

In addition to the DSC method, tests with K-type thermocouples were performed to reveal the thermal behavior of chosen mixtures. The results of these measurements are presented in Figure 4. By DSC it was established that mixtures 40 wt.% MgCl$_2$·6H$_2$O + 60 wt.% Mg(NO$_3$)$_2$·6H$_2$O, and 40 wt.% bischofite + 60 wt.% Mg(NO$_3$)$_2$·6H$_2$O present supercooling of 34.1 °C and 23.4 °C (average of 50 cycles), respectively. Tests with K-type thermocouples indicate that supercooling reduces to 6 °C and 15 °C, respectively. Therefore, supercooling is lower when the amount of material tested increases [27].
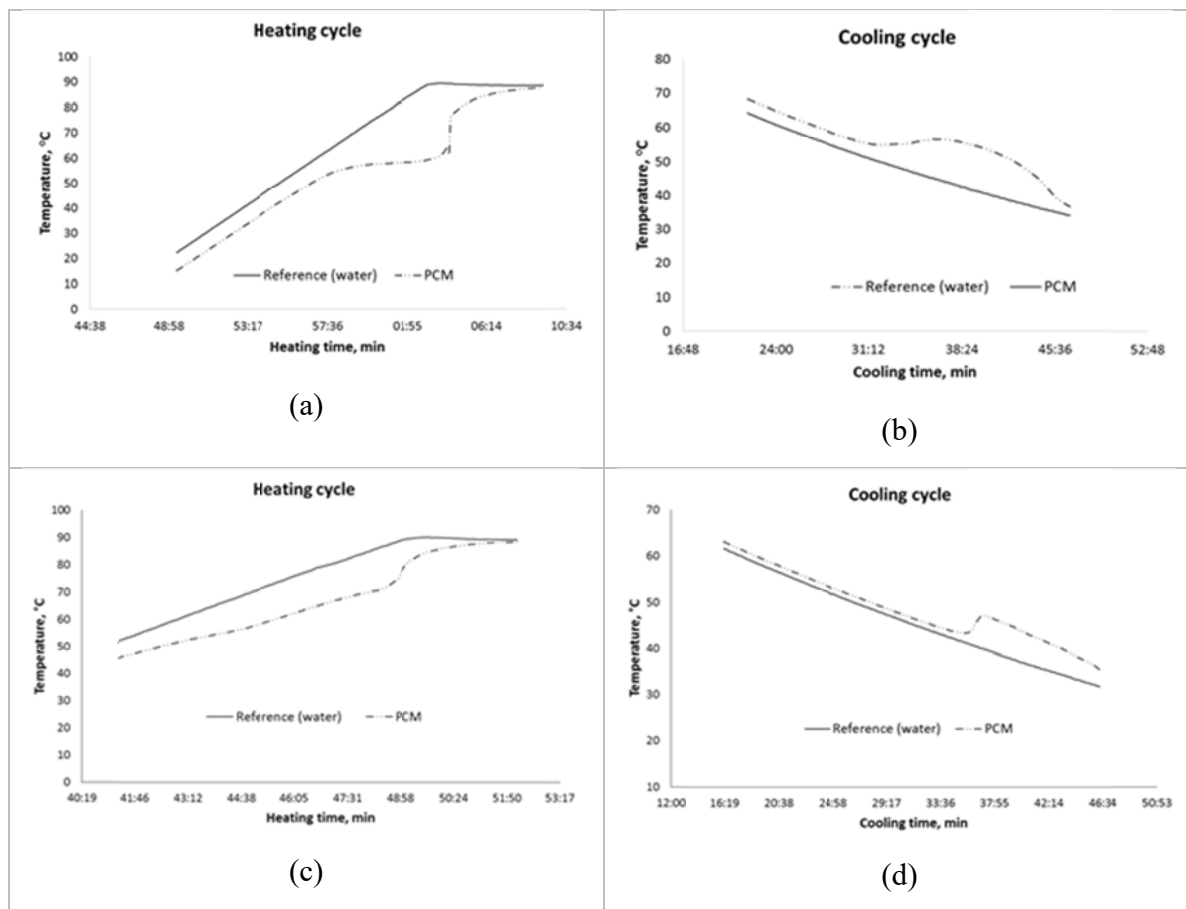
Fig.4. Analysis of eutectic mixtures studied using K-type thermocouples: (a) and (b) 40 wt.% $MgCl_2 \cdot 6H_2O$ + 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$; (c) and (d) 40 wt.% bischofite + 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$.

Thermal stability was determined in opened and sealed crucibles for both samples (Fig. 5). Eventually, both samples show good thermal stability in sealed crucibles reaching 130 °C with 100 % of the initial mass (curves for sealed crucibles coincide completely (Fig.5)). Analysis in opened crucibles reveals that the more instable sample is one with the bischofite in its composition, with a final mass loss of 5.2 % at 130 °C, while the sample with $MgCl_2 \cdot 6H_2O$ shows only 1.5 % mass loss at the same temperature. This why, for the practical applications of this mixture as PCM for TES it is recommended to use a closed system to avoid the mass loss.
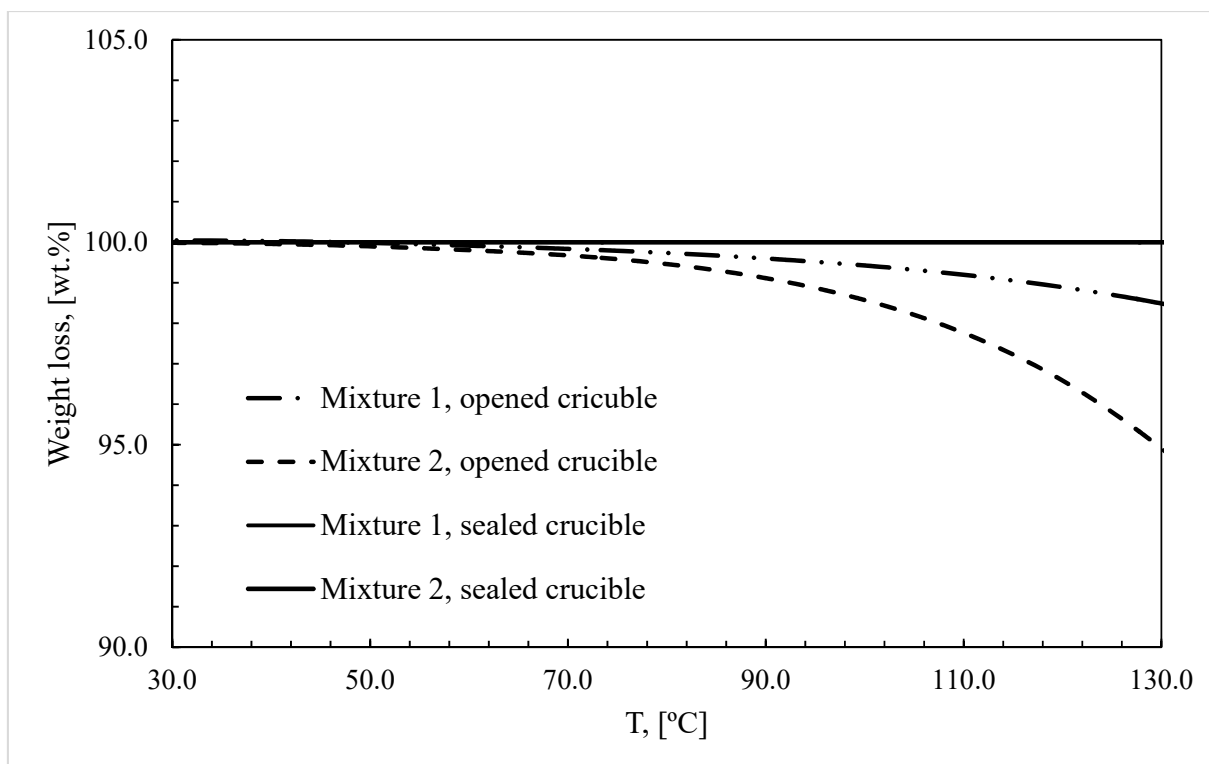
Fig. 5. Thermal stability of mixtures with $MgCl_2·6H_2O$ and bischofite, where: Mixture 1 – 40 wt.% $MgCl_2·6H_2O$ and 60 wt.% $Mg(NO_3)_2·6H_2O$; Mixture 2 – 40 wt.% bischofite and 60 wt.% $Mg(NO_3)_2·6H_2O$.

3.2. Physical properties: density and viscosity

The results of density and viscosity measurements are shown in the Table 6. Moreover, Table 7 contains data of pure salts densities in solid and liquid state reported in literature. Comparing the Table 6 and 7 it can be concluded that density values obtained for the mixtures during this study show similarity with the data available in literature for pure salts [14].

Table 6. Summary of the densities in solid and liquid state (± std deviation).

| T [°C]	Density [kg·m⁻³]		Phase
	40 wt.%$MgCl_2·6H_2O$+$Mg(NO_3)_2·6H_2O$	40wt.%bischofite+$Mg(NO_3)_2·6H_2O$	
ambient	1517 ± 0.037	1525 ± 0.087	Solid
60	$1518 \pm 1.63·10^{-5}$	$1535 \pm 6.39·10^{-5}$	Liq.
65	$1515 \pm 3.27·10^{-5}$	$1532 \pm 2.94·10^{-5}$	
70	$1512 \pm 1.41 ·10^{-5}$	$1529 \pm 3.30·10^{-6}$	

Table 7. Summary of the densities of pure salts in solid and liquid state reported in the literature [14].

T [ºC]	Density [kg·m^{-3}]		Phase
	bischofite	MgCl$_2$·6H$_2$O	
20	-	1569	Solid
30	1686	-	
40	1598	-	
50	1513	-	
78	-	1442	
115	1481	-	Liquid
120	-	1450	
128	-	1422	

Viscosity measurements were carried out with molten mixtures in the range from 60 °C to 110 ºC with different torque speeds from 10 to 80 rpm (Fig. 6, 7). It can be seen, that viscosity decreases with increasing temperature and moreover there is practically no dependence of viscosity values on torque speed, which indicates that the PCM shows behavior close to Newtonian.
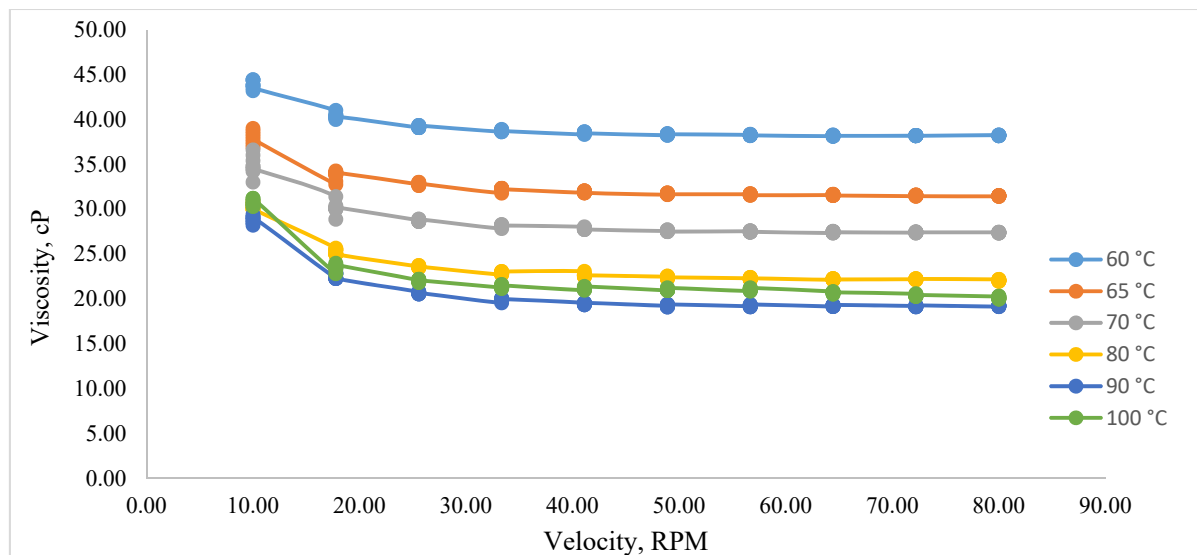
Fig. 6. Dependence of the dynamic viscosity on torque speed for the mixture of 40 wt.% MgCl$_2$·6H$_2$O and 60 wt.% Mg(NO$_3$)$_2$·6H$_2$O.
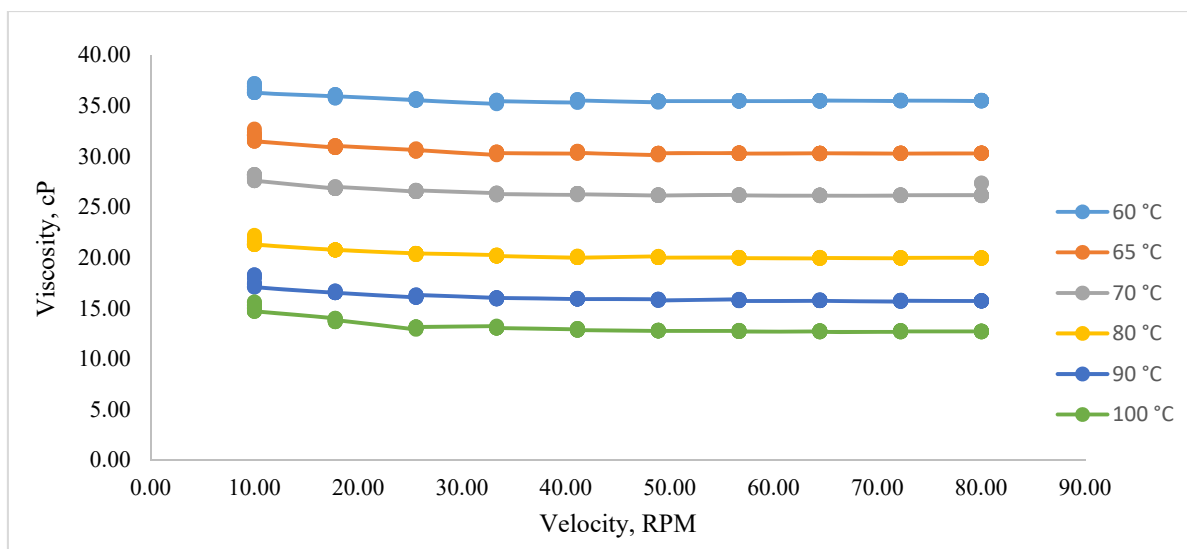
Fig. 7. Dependence of the dynamic viscosity on torque speed for the mixture of 40 wt.% bischofite and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$.

Therefore, 50 rpm velocity was chosen to represent viscocity dependence on temperature (tables 8 and 9).

Table 8. Viscosity values at different temperatures for the mixture of 40 wt.% $MgCl_2 \cdot 6H_2O$ and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$ (± std deviation).

Viscosity [cP]	Velocity [RPM]	Shear strength [D/cm^2]	Temperature [°C]
38.31 ± 0.05		24.72	60
31.70 ± 0.06		20.46	65
27.57 ± 0.06		17.79	70
22.38 ± 0.09	50.00	14.44	80
19.23 ± 0.10		12.41	90
21.02 ± 0.10		13.56	100
20.83 ± 0.16		13.44	110

Table 9. Viscosity values at different temperatures for the mixture of 40 wt.% $MgCl_2 \cdot 6H_2O$ and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$ (± std deviation).

Viscosity [cP]	Velocity [RPM]	Shear strength [D/cm^2]	Temperature [°C]
35.43 ± 0.04		22.87	60
30.25 ± 0.05		19.52	65
26.16 ± 0.03		16.88	70
20.03 ± 0.04	50.00	12.93	80
15.83 ± 0.04		10.21	90
12.78 ± 0.03		8.25	100
10.59 ± 0.09		6.83	110

Results of the measurements of density and viscosity are summarized in Fig. 8. Viscosity values of the molten salt mixture with $MgCl_2 \cdot 6H_2O$ decrease from 38.31 to 20.83 mPa·s in a temperature range from 60 °C to 110 °C. For mixture with bischofite the values range from 35.43 to 10.59 mPa·s in the same temperature range.
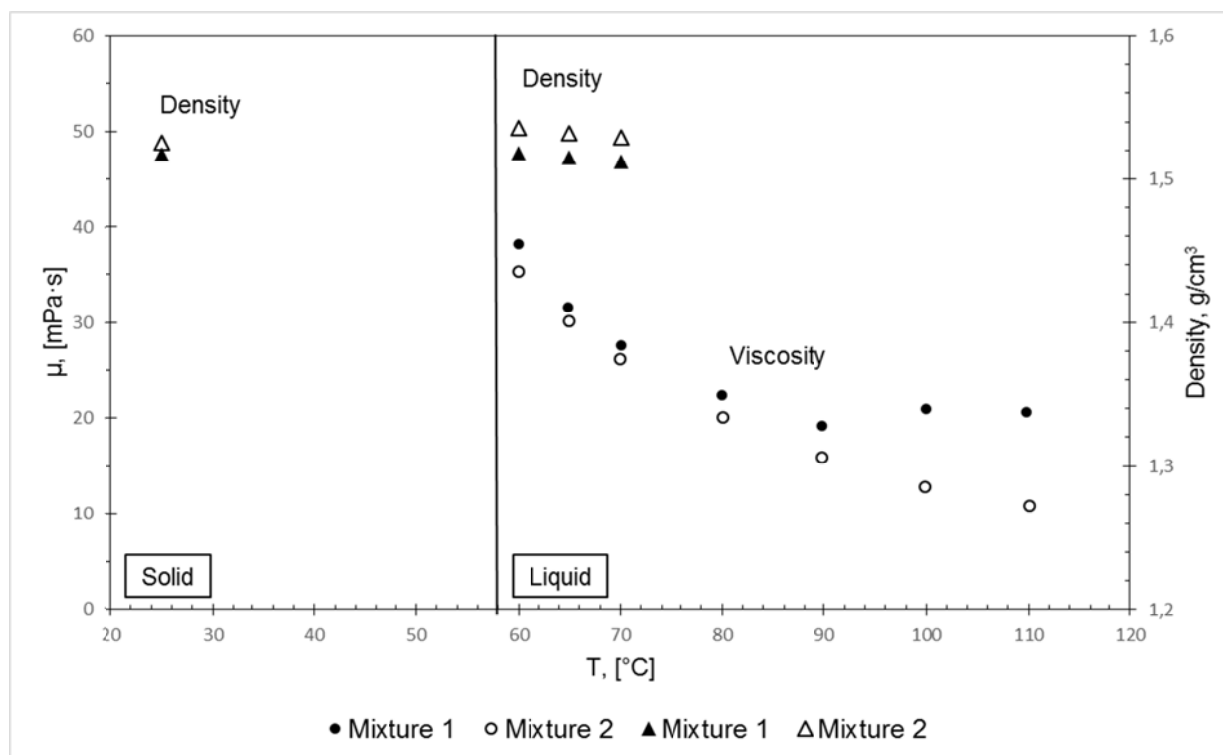
Fig. 8. Temperature dependence of the dynamic viscosity and density, where: Mixture 1 – 40 wt.% $MgCl_2 \cdot 6H_2O$ and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$; Mixture 2 – 40 wt.% bischofite and 60 wt.% $Mg(NO_3)_2 \cdot 6H_2O$.

4. Conclusions

An inorganic mixture for low temperature TES based on a by-product of Northern Chile's industry, with the composition of 40 wt.% of bischofite and 60 wt.% of $Mg(NO_3)_2 \cdot 6H_2O$ was investigated. Thermo-physical properties for this mixture were measured and compared with those of the mixture with the synthetic $MgCl_2 \cdot 6H_2O$. Melting temperature and heat of fusion were measured as 62.0 °C and 132.5 $kJ \cdot kg^{-1}$ for the mixture with synthetic $MgCl_2 \cdot 6H_2O$, and 58.2 °C and 116.9 $kJ \cdot kg^{-1}$ for the mixture with bischofite replacing the $MgCl_2 \cdot 6H_2O$. TGA analysis reveals that in sealed crucibles both samples reach 130 °C with 100 % of the initial mass. The thermal stability test (50 heating/cooling cycles) of the samples indicates supercooling of about 34.1 °C and 23.4 °C for the mixtures with $MgCl_2 \cdot 6H_2O$ and bischofite respectively.

The specific heat for solid samples shows a slight increase in a temperature range 298.15–318.15 K (25–45 °C), with values from 1.0 to 2.3 $J \cdot g^{-1} \cdot K^{-1}$ for the mixture with $MgCl_2 \cdot 6H_2O$ and from 1.2 to 2.1 $J \cdot g^{-1} \cdot K^{-1}$ for the mixture with bischofite. Specific heat values for the liquid phase in a temperature range 348.15–398.15 K (75–125 °C) vary from 2.0 to 2.8 $J \cdot g^{-1} \cdot K^{-1}$ and from 1.5 to 1.8 for mixtures with $MgCl_2 \cdot 6H_2O$ and bischofite, respectively.

The density values obtained for the mixtures show similarity with the available literature data for pure salts. For the mixture with $MgCl_2 \cdot 6H_2O$, the density of the solid and liquid state was of 1517 kg·m^{-3} (ambient temperature) and 1515 kg·m^{-3} (at 60-70 °C), respectively. For the mixture with bischofite the density of the solid and liquid state was of 1525 kg·m^{-3} (ambient temperature) and 1535 kg·m^{-3} (at 60-70 °C), respectively. Finally, as most inorganic salt hydrates, the studied mixture presents supercooling.

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