Thermophysical characterization of a by-product from the non-metallic industry as inorganic PCM

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Abstract

Physical characterization and thermal properties of bischofite, a by-product from the non-metallic industry, were determined and compared with those to $MgCl_2 \cdot 6H_2O$ with the idea of using it as phase change material in thermal energy storage applications. The melting point and heat of fusion were measured in the temperature range from 30°C to 150°C, where T_{fus} and ΔH_{fus} were 100°C and 115 kJ/kg for bischofite, and 114.5°C and 135 kJ/kg for $MgCl_2 \cdot 6H_2O$. The solid heat capacity was determined from 25°C to 60°C, being 2.1 kJ/(kg·K) at 60°C for both samples. The measurements of the liquid heat capacity of bischofite were done from 105°C to 113°C and the Cp showed linear increase from 5.61 kJ/(kg·K) to 9.01 kJ/(kg·K). The thermal stability test (30 heating/cooling cycles) of bischofite and $MgCl_2 \cdot 6H_2O$ shows subcooling of about 37K and 29K, respectively. The solid and liquid densities were determined using the pycnometrically method; for bischofite, ρ_{solid} decrease from 1686 (at 30°C) to 1513 kg/m³ (at 50°C) and ρ_{liq} was 1481 kg/m³ (at 115°C). Based on the thermophysical properties evaluated, the energy storage density was evaluated for both materials, being 170 J/cm³ for bischofite and 192 J/cm³ for $MgCl_2 \cdot 6H_2O$. This study established that bischofite is a promissory PCM with similar thermophysical characteristics to magnesium chloride hydrate, but with a lower cost. Nevertheless, further work is needed to overcome the two main problems found, subcooling and segregation of the material.

Keywords: Bischofite, Phase change material, Thermal energy storage, Solar energy, Latent heat, by-product salt.

1. Introduction

A good part of the electrical energy produced in Chile, above all in the north of the country, is based on fossil fuels. However, the high level of demand at the world level, the high market

price and the negative impact of thermoelectrical plants on the environment makes this dependence unsustainable over time. Given the close relationship between energy and economic activity, it is clear that the current development of the country is in a critical situation, because of which some years ago government authorities took important steps toward developing a diversified energy matrix, as well as encouraging the rational energy use at the domestic and industrial levels.

Solar energy has an enormous potential for the heating and cooling of buildings, producing hot water for domestic and industrial purposes. However, solar energy is intermittent, unpredictable, and available only during the day. Hence, its application requires efficient thermal energy storage (TES) so that the surplus heat collected during sunshine hours may be stored for later use during the night.

In TES, useful energy is transferred from the solar collector to the storage media as internal energy. This heat transfer may be as sensible heat or latent heat, comparing both, the most attractive is the latent heat because it has a higher energy density of storage, so the volume of material required is less than in the case of storage sensible heat [1].

Latent heat of fusion is the energy released or absorbed, which is necessary for a material changes from the solid phase to the liquid phase or vice versa; generally the values for the energy involved are high [2]. Latent heat employs a phase change material as a storage medium. The principle of a phase change material (PCM) is very simple: as the temperature of the medium increases, the phase change occurs and the material passes from the solid state to liquid, absorbing heat and thus offsetting the rise in temperature. In the same way, when the temperature of the medium decreases, the PCM passes from the liquid to the solid phase releasing heat to the medium and thus offsetting the decrease in temperature.

Three main groups of PCM have been identified: organic, inorganic, and eutectic [3]. Salt hydrates (inorganic PCM), such as magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), are attractive materials to employ in thermal energy storage systems given that they have relatively high heat of fusion values (magnesium chloride hexahydrate: 168 kJ/kg), relatively high levels of thermal conductivity (approximately 0.570 W/(m·K)) and relatively moderate costs compared to alternative organic materials [2].

But new PCM are needed to get their deployment, materials either with much better performance, or materials with a much lower cost. One approach is the use of waste materials or by-products from the industry. For example, Miró et al. [4] studied the use of a potash salt, a

solid industrial by-product, as a material for sensible heat storage. The advantages of using the salt is its low price (from 5 to 100 times cheaper than other solid material candidates), its specific heat capacity (0.738 kJ/(kg·K)), and its thermal conductivity when wetted with water. Its disadvantage is mainly the high corrosion rate. This paper presents also results of the behavior of this salt in a thermal energy storage pilot plant.

Chile produces high amounts of salts for many applications. But in their processing, wastes and by-products also appear, products which are also salts but with no direct application in today's industry. Bischofite is a mineral that precipitates in the evaporation ponds during the potassium chloride production process in Salar de Atacama (north of Chile) and currently has a few practical applications: it is marketed in Europe for de-icing of roads, and in Chile, using its high hydroscopicity – to abate dust and to improve mining roads in the north. Bischofite is also obtained in similar processes in other parts of the world, such as Israel and The Netherlands. The main component of this by-product is $MgCl_2 \cdot 6H_2O$ with some impurities determined in this study. More than 100,000 tons of bischofite per year are marketed today in Chile. The price of low quality bischofite is around 40 US$/ton, while the price of purified bischofite is closed but lower to that of $MgCl_2 \cdot 6H_2O$, which is sold at around 155 US$/ton in the north of Chile.

An important parameter to evaluate the potential of a PCM is the energy storage density (*esd*), which is the ratio of specific latent heat to density [5]. In this research, we will quantify this parameter for bischofite and compare it with $MgCl_2 \cdot 6H_2O$, known as promising PCM [6-8] (Table 1 and Table 2). We will also include a study of the thermal stability and transition temperatures through DSC technique. All this information, as well as being important for the design of the storage system, will generate important knowledge about the behavior of the different PCMs analyzed.

2. Experimental

2.1 Materials and chemical analysis

To conduct the research, about 10 kg of bischofite corresponding to crops from brine evaporation ponds at different times of the year were used. The bischofite was homogenized and was divided into 10 samples of about 1 kg each. Chemical analysis was performed on the samples to determine the chemical composition of the samples and the concentration range of variation, corresponding to the main impurities. Based on the chemical analysis, a possible stoichiometric bischofite mineralization is suggested. The measurement results of the properties

obtained from bischofite were compared with those obtained for the synthetic $MgCl_2 \cdot 6H_2O$ Merck (>99%).

Previously, samples of both salts were subjected to a drying heat treatment at 40°C for 12 h, and the samples were kept in a desiccator.

Sodium, potassium, calcium, lithium and magnesium concentration were determined by atomic absorption spectrometry. Chloride, sulfate, and carbonates were determined by volumetric titration with $AgNO_3$, $BaCl_2$, HCl, respectively. Insoluble percentage was determined by leaching of 50 g of sample in 400 g of water, filtered, dried and weighted. Moisture was determined drying until constant weight at 40ºC.

2.2 Characterization

The mineral composition of bischofite was analyzed by a X-ray Powder Diffractometer. The powdered samples were positioned on a flat plate sample holder after sample powdering in an agate mortar. The technique was used to characterize the crystallographic structure by comparing the obtained diffraction data to a database maintained by the International Centre for Diffraction Data (www.icdd.com). Analysis of X-ray diffraction was performed on a X-Ray diffractometer SIEMENS model D5000 (40 kV, 30 mA); radiation of Cu Kα1 (λ = 1.5406 Å); Vertical Bragg-Brentano; Scan Range: 3 - 70° 2θ; Step Size: 0.020° 2θ; Step Time: 1.0 s. An scanning electron microscope (SEM) Jeol, Model JSM6360 LV was used for analyzing the morphology and composition of the bischofite sample, coupled to an energy dispersive X-ray spectrometer (EDX) Inca Oxford. Configuring a measurement was under vacuum, an electron beam used in 20 kV, work distance of 10 mm, spot size 60 mm, and backscattered electron signal.

2.3 Thermal properties

Thermal stability analysis was determinated with METTLER TOLEDO TGA-DSC 1 STARe, in a temperature range of 25°C to 150°C with heating rates 5°C/min and 10°C/min, under purified nitrogen atmosphere with a flow rate of 30 mL/min. Standar aluminium pan with lid (40 µL) were used.

To determine the melting point, heat of fusion, heat capacity and heating and cooling cycle, a DSC NETZSCH DSC 204 F was used, in a temperature rate from 25°C to 150°C to melting point and heat of fusion and from 40°C to 140°C to heating and cooling cycle with a heating and cooling rate of 5°C/min. The cycle was repeated for thirty times under purified nitrogen atmosphere with a flow rate of 20 mL/min. Standard aluminum pans with lid (40 µL) were used.

Heat capacity analysis were done in the temperature range of -5°C to 90°C for the solid phase of bischofite and $MgCl_2 \cdot 6H_2O$ and of 105°C to 115°C to the liquid phase of bischofite. In order to measure the specific heat, the sample holder temperature was programmed under purified nitrogen atmosphere with a flow rate of 30 mL/min, within three stages; an initial isothermal, a heating stage, with a heating ratio of 5 K/min and another isothermal at the end of the programme (the initial and final isothermal were determined according to temperature range of measurements).

2.4 Physical properties

2.4.1. Density

Densities of solid salts were determined pycnometrically [21] with dodecane as a displacement liquid. The dependence of n-dodecane with temperature was determinate with a densimeter Mettler Toledo DE50, wich change linearly, according to Eq. 1:

$$\rho_n \, [kg/m^3] = 969.36 + 0.7045 \, [T/K] \qquad (1)$$

Relatively liquid densities of bischofite were determined pycnometrically. The samples were melted for 90 minutes in a Wisetherm FH-27 muffle furnace, at 110°C and 120°C for the bischofite and $MgCl_2 \cdot 6H_2O$, respectively.

2.4.2. Viscosity

Viscosity measurements were made with molten bischofite and molten $MgCl_2 \cdot 6H_2O$ in a range temperature from 110°C to 150°C and from 120°C to 140°C, respectively, in a rotational rheometer BROOKFIELD DV-III Ultra with thermosel, SC4-18 spindle, 8 ml sample volume.

The measurements were performed with controlled shear from 40 RPM to 130 RPM. The viscosities reported are obtained when the torque percentage is 50%. The results were taken from a set of 5 tests for each temperature the two closest values, calculating their average and standard deviation.

3. Results and discussions

3.1 Chemical analysis and mineralization

Since the bischofite analyzed corresponds to real samples obtained from the production process of potassium chloride, it is necessary to establish the range of variation of the concentrations of impurities. Table 3 shows the chemical analysis of the main components of the bischofite, and the particular sample used in this study.

To determine the purity and quantity of $MgCl_2 \cdot 6H_2O$ present in the ore, the mineralization of the chemical analysis results was performed. The results are presented in Fig. 1.

As it can be seen in Fig. 1, the content of $MgCl_2 \cdot 6H_2O$, usually used as heat storage material, in the bischofite sample is nearly 95%. Furthermore, the mineralization indicates the existence of two major components, present as hydrated salts, carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and $Li_2SO_4 \cdot H_2O$.

3.2 XRD and SEM characterization

The characterization of the sample of bischofite with SEM-EDX is shown in Fig. 2. As it can be seen, the bischofite crystals present an undefined form. This is due to the high hydroscopicity of the mineral, which starts absorbing ambient humidity in the preparation of the sample for the analysis. The mapping analysis allows identifying the main impurities of the bischofite mineral (Fig. 2 right), KCl, NaCl and sulfate, probably with Li. XRD study indicates the presence of $MgCl_2 \cdot 6H_2O$ (Fig. 3). In this figure, the intensity of the peaks at high angles is not the same between the data base and measured patterns, probably due to the formation of grains with different shape during crystallization under natural uncontrolled evaporation in solar ponds.

3.3 Thermal Properties

3.3.1 Temperature and heat of fusion determination

Temperature and heat of fusion are important to establish if a material can be used as PCM. The measurement of one heating cycle for these properties is shown in Fig. 4.

It can be seen that bischofite has a broad peak with T_{onset}=98.9ºC, T_{peak}=136.6°C and a heat of fusion of 120.2 kJ/kg, whereas $MgCl_2 \cdot 6H_2O$ has a sharp peak with onset temperature of 114.6ºC and a heat of fusion of 126.6 kJ/kg. The bischofite melting point is lower than the one of

$MgCl_2 \cdot 6H_2O$, and this is explained by the presence of impurities in the ore. On the other hand, the bischofite heat of fusion is close to that of $MgCl_2 \cdot 6H_2O$, with a variation of 5% between the two values. Moreover, bischofite shows a shoulder in its melting curve, probably indicating the presence of impurities; $MgCl_2 \cdot 6H_2O$ does not show this behavior, because a pure substance was used.

3.3.2 Thermal Stability

The results of TGA performed with open and sealed crucibles are shown in Fig. 5. In general, very good stability is observed in both analyzed samples when closed crucibles are used. A deeper analysis shows that the more unstable sample was bischofite, with a mass loss of 0.4%; the sample of $MgCl_2 \cdot 6H_2O$ presented no mass loss, reaching 140ºC with 100% of the initial sample mass.

On the other hand, when open crucibles are used the thermal stability of $MgCl_2 \cdot 6H_2O$ is much better than that of bischofite. As expected, $MgCl_2 \cdot 6H_2O$ losses very little mass starting at around 90ºC. Bischofite shows about 2% mass loss at 50-60ºC and at 80ºC starts to loose mass gradually, showing an 8% mass loss at the end of the experimentation, at 130ºC.

3.3.3 Long term cyclic stability

Long term stability of samples was studied during 30 heating and cooling cycles by DSC. The DSC heating bischofite curves are shown in Fig. 6 (A) and compared with heating curves of $MgCl2 \cdot 6H2O$ (Fig. 6 (B)).

After this thermal stability test, melting enthalpy and temperature did not show significant changes after 30 cycles. In both case, for bischofite and $MgCl_2 \cdot 6H_2O$, uniform behavior was observed in the heating curves and the absence of phase segregation was observed.

The DSC cooling bischofite curves are shown in Fig. 7(A) and compared with cooling curves of $MgCl_2 \cdot 6H_2O$ (Fig. 7(B)).

For both samples freezing temperatures present fluctuating values during the tests. The freezing temperature varies with increasing cycles: for 10 cycles, freezing temperatures were 65.4°C and 88.8°C (both on-set DSC values), respectively for bischofite and $MgCl_2 \cdot 6H_2O$, for 20 cycles 70.1°C and 85.2 °C, and for 30 cycles were 58.7°C and 85.2 °C. Both samples exhibit the phenomenon of subcooling, near 37K and 29K for bischofite and $MgCl2 \cdot 6H2O$, respectively.

The results for $MgCl_2 \cdot 6H_2O$ are similar to those reported by other authors [17]. On the other hand, bischofite has two peaks during cooling, from the cycle 27 (not shown in Fig. 7) similar to cycle 30 (indicated in Fig. 7), probably due to the segregation of the impurities in the mineral. Therefore, longer stability test should be done to analyze this potential segregation of the material.

3.3.4   Heat capacity of solid and liquid samples

The heat capacity for solid samples (see Fig. 8) shows a constant behavior for a temperature range from 25°C to 60 °C, with heat capacity range from 1.6 to 2.1 J/(g·K) for bischofite and from 2.1 to 1.95 J/(g·K) for $MgCl_2 \cdot 6H_2O$. For both samples, the average heat capacity values are similar and close to values reported by Choi [22] for $MgCl_2 \cdot 6H_2O$.

Values of heat capacity for liquid phase are shown in Fig. 9, in a temperature range from 105ºC to 113ºC, with values from 5.6 to 9.0 J/(g·K). $MgCl_2 \cdot 6H_2O$ is solid at this temperature, so the heat capacity values are not shown in Fig. 9.

3.4 Physical Properties

Some parameters are important to determinate practical implementation of a PCM, as the energy storage density (esd), which is the ratio of the specific latent heat to the salts density. The results of the measurement of density and viscosity are below.

3.4.1   Density

The densities of solid bischofite were measured in temperature range from 30°C to 50°C. The densities of liquid samples were measured at 115°C for bischofite and at 128°C for $MgCl_2 \cdot 6H_2O$. The result of density measurements are shown in Table 4, these values are close to those reported by other authors for the $MgCl_2 \cdot 6H_2O$ in the solid state (see Table 2). For solid bischofite, density values decrease as the temperature increases and the density for liquid phase is 1481 kg/m^3 at 110°C.

3.4.2   Viscosity

The PCM studied in this paper showed Newtonian behavior and their viscosity values do not depend on the share rate. Viscosity measurements were made with molten bischofite and $MgCl_2 \cdot 6H_2O$ in the range from 115°C to 150°C and from 120°C to 140°C, respectively. The

maximum standard deviation for bischofite was 1.24 cP and for $MgCl_2 \cdot 6H_2O$ was 0.87 cP. The results are shown in the Fig. 10.

As expected, the viscosity decreased with increasing temperature. Values of molten bischofite viscosity increase from $22.9 \cdot 10^3$ to $13.8 \cdot 10^3$ kg/(m$^2 \cdot$s) in a temperature range from 110ºC to 150ºC. For $MgCl_2 \cdot 6H_2O$ values range from 16.7 to 12.4 kg/(m$^2 \cdot$s) in a temperature range from 120ºC to 140ºC.

3.5. *Summary of results*

Table 5 summarizes the melting and freezing temperatures and enthalpies of bischofite and $MgCl_2 \cdot 6H_2O$ determined in this work. Moreover, the subcooling value, ΔT, is also indicated for both materials.

For bischofite the thermophysical properties are similar to those obtained for $MgCl_2 \cdot 6H_2O$ in this research, and the results reported by other authors who have tested and proposed for applications such as phase change material (Table 1). The properties presented by bischofite are suitable for use as PCM over medium heat, around 100 ºC. It was proven that subcooling have the value of 37K for bischofite. Because of this, future studies are required to find nucleating agents, to mitigate this problem.

4. Conclusions

Thermophysical properties for bischofite was determined and they are similar to those obtained for $MgCl_2 \cdot 6H_2O$ in this research, and the results reported by other authors who have tested and proposed for applications such as phase change material. The melting point and heat of fusion were measured in the temperature range from 30°C to 150°C, where T_{fus} and ΔH_{fus} were 100°C and 115 kJ/kg for bischofite, and 114.5°C and 135 kJ/kg for $MgCl_2 \cdot 6H_2O$. The solid heat capacity was determined from 25°C to 60°C, being 2.1 kJ/(kg·K) at 60°C for both samples. The measurements of the liquid heat capacity of bischofite were done from 105°C to 113°C and the Cp showed linear increase from 5.61 kJ/(kg·K) to 9.01 kJ/(kg·K). The thermal stability test (30 heating/cooling cycles) of bischofite and $MgCl_2 \cdot 6H_2O$ shows subcooling of about 37K and 29K, respectively. The solid and liquid densities were determined using the pycnometrically method; for bischofite, ρ_{solid} decrease from 1686 (at 30°C) to 1513 kg/m^3 (at 50°C) and ρ_{liq} was 1481 kg/m^3 (at 115°C). Based on the thermophysical properties evaluated, the energy storage density was evaluated for both materials, being 170 J/cm^3 for bischofite and 192 J/cm^3 for $MgCl_2 \cdot 6H_2O$. The properties presented by bischofite are suitable for use as PCM over medium heat, around

100ºC. Nevertheless, further work is needed to overcome the two main problems found, subcooling and segregation of the material. Since this work has been already carried out for $MgCl_2 \cdot 6H_2O$, it is not audacious to think that this is possible.

Acknowledgements

5. References

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Tables

Table 1. Summary of melting and crystallization temperatures, and heat of fusion for $MgCl_2 \cdot 6H_2O$ found in the literature.

Reference	Cycle N°	T_F [°C]	$\Delta_F H$ [J/g]	T_C °C	$\Delta_C H$ [J/g]	ΔT [°C]
References without cycling the PCM	---	115 [6-10] 116 [6-8,11] 117 [3,6-8,12-16]	165 [6-8,11,13] 167 [3,7] 168.6 [6-8,12,15]	---	---	---
Pilar et al. 2012 [17]	0	117.15	170.1	87	115	30
	15	---	---	76	115	37
	50	117.45	168.9	76	115	37
El-Sebaii et al. 2009 [18]	0	122.95	155.11			5*
	63	106.76	152.85	---	---	---
	102	107.55	130.29			---
	500	134.22	85.00			2*
El-Sebaii et al. 2011 [19]	0	116.29	137.96			2*
	55	116.94	120.64	---	---	0.1*
	100	117.34	165.33			1.7*
	1002	119.86	130.28			0*

*Analysis not done with DSC, authors relate this low subcooling to the analytical method.

**Using the so-called "extra water principle"

Table 2. Summary of density for $MgCl_2 \cdot 6H_2O$ found in the literature.

Reference	Density solid [kg/m³]	Density liquid [kg/m³]
References without cycling the PCM	1569 (20ºC) [6-8,12,15] 1570 (20ºC) [6-8,11]	1442 (78 ºC) [6-8,11,20] 1450 (120 ºC) [6-8,12,15]

Table 3. Chemical analysis results of bischofite

Element	Average concentration range [%]	Concentration used in this study [%]
Sodium, Na	0.321 – 0.360	0.360
Potasium, K	0.259 – 0.301	0.301
Calcium, Ca	0.007 – 0.008	0.008
Magnesium, Mg	10.84 – 11.45	11.45
Lithium, Li	0.298 – 0.351	0.351
Chloride, Cl	33.66 – 34.92	34.92
Sulfate, SO$_4$	1.29 – 1.51	1.51
Moisture	1.42 – 1.50	1.48

Table 4. Solid and liquid density of bischofite [kg/m^3]

T[°C]	Bischofite	MgCl$_2$·6H$_2$O	phase
30	1686		
40	1598	---	Solid
50	1513		
115	1481	---	Liquid
128	---	1422	

Table 5. Summary of melting and crystallization temperatures, heat of fusion, and esd for bischofite and MgCl$_2$·6H$_2$O.

Sample	Cycle N°	T$_F$ [°C]	Δ$_F$H [J/g]	T$_C$ °C	Δ$_C$H [J/g]	ΔT [°C]	esd [J/cm^3]
Bischofite	10	100.9	116.2	65.4	115.2	35.5	
	20	101.1	116.0	70.1	115.5	31.0	170
	30	102.2	115.5	58.7	115.8	43.5	
MgCl$_2$·6H$_2$O	10	114.5	133.5	88.8	129.5	25.7	
	20	114.6	133.1	83.2	129.4	31.4	192
	30	114.4	136.9	85.2	132.3	29.2	

Figures
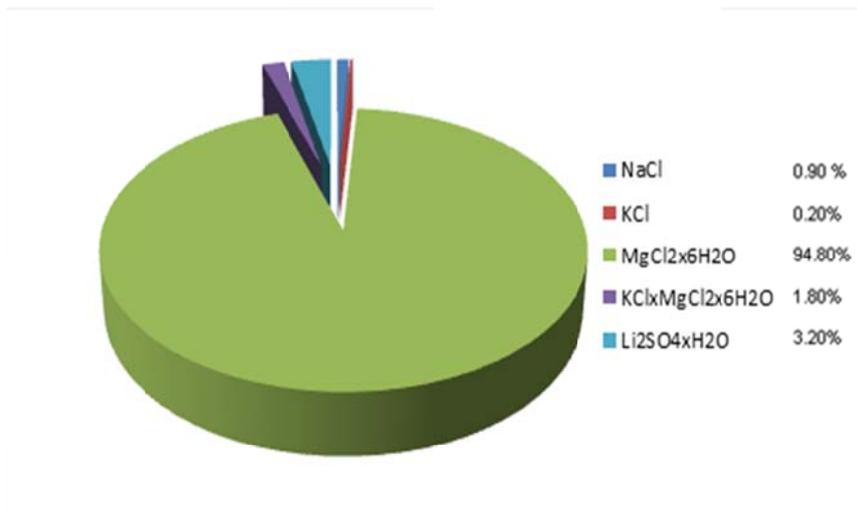
Fig. 1

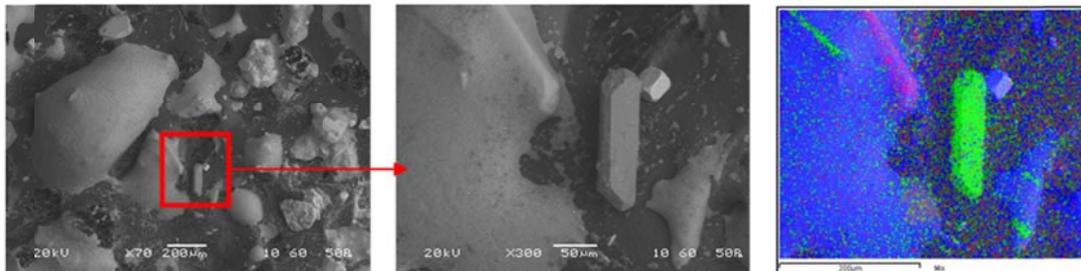Fig. 1. Mineralization resulting of a bischofite sample.

Fig. 2

Fig. 2. SEM image of bischofite at: from left to right x70, x300, and mapping: K (red), green (S), blue (Cl)
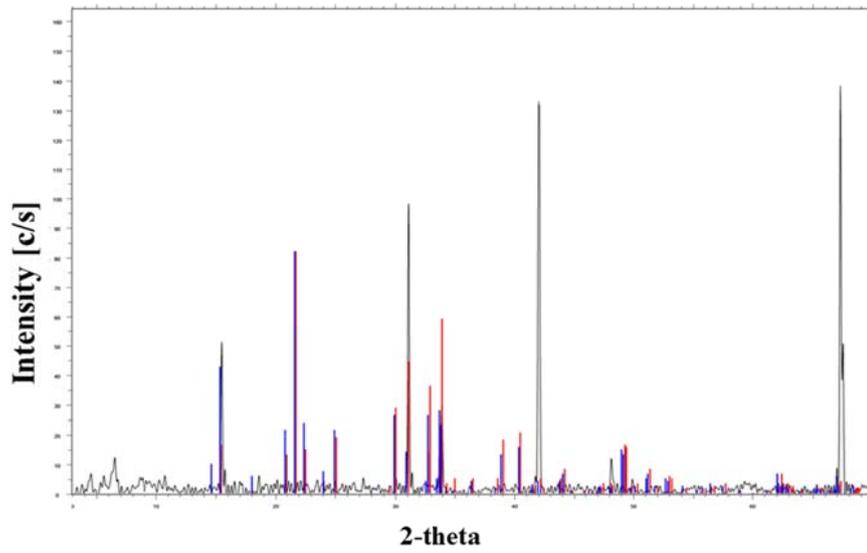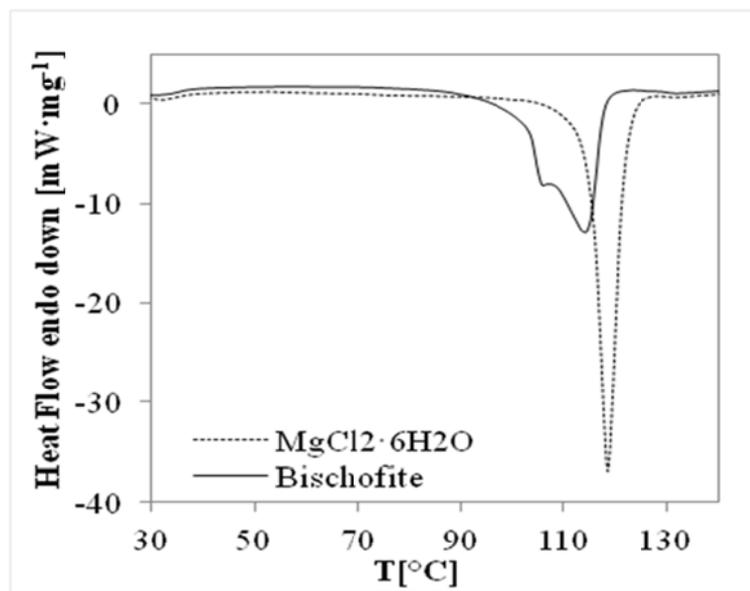
Fig. 3

Fig. 3. XRD pattern of bischofite.

Fig. 4

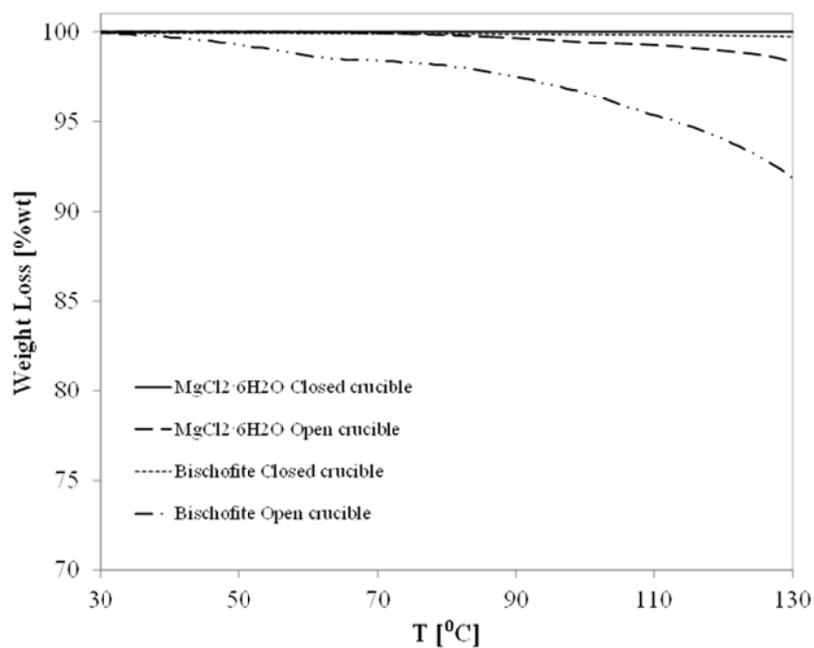Fig. 4. DSC measurement curves for one heating cycle of bischofite and MgCl2·6H2O.

Fig. 5
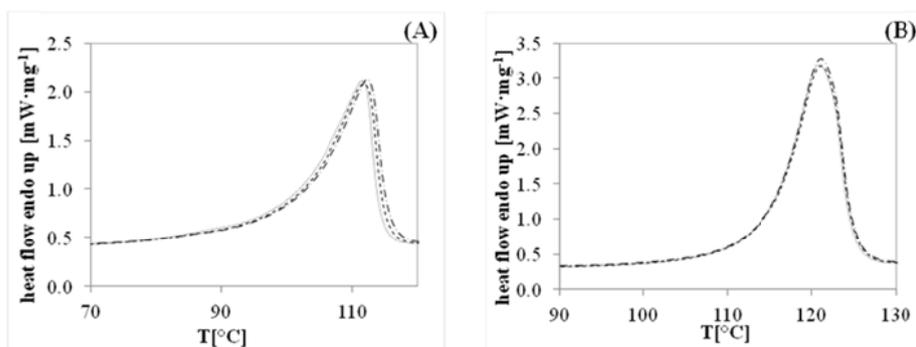
Fig. 5 Thermal stability of bischofite and MgCl2·6H2O.

Fig. 6

Fig. 6. DSC heating curves after various cycles, for (A) bischofite and (B) MgCl2·6H2O.
············· 10, ------ 20, and ▬ ·▬ · ▬ 30 cycles.
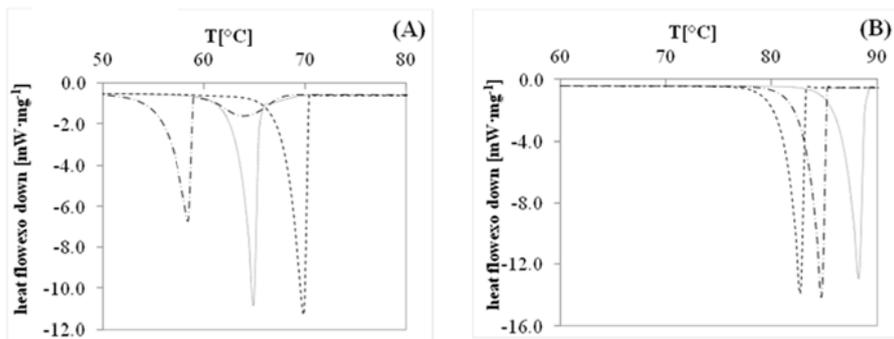
Fig. 7

Fig. 7. DSC cooling curves after various cycles, for (A) bischofite and (B) MgCl2·6H2O.
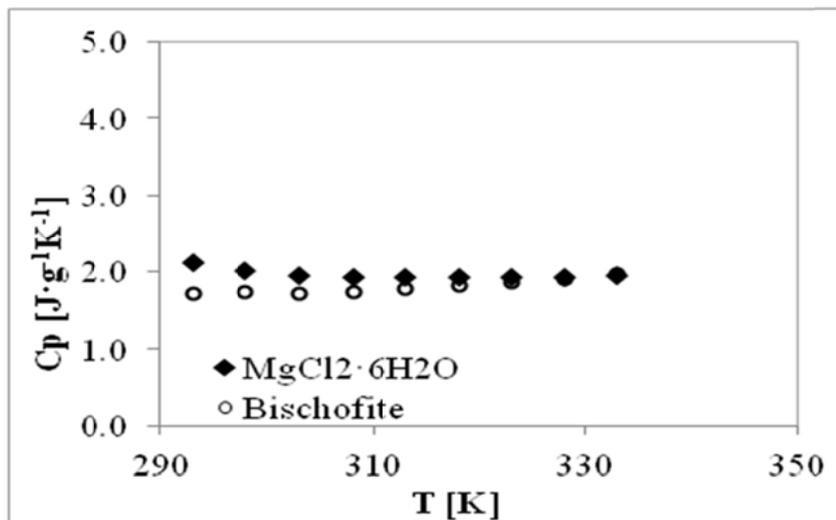⋯⋯⋯10, - - - - - 20, and ▬ · ▬ · ▬ 30 cycle.

Fig. 8

Fig. 8. Temperature dependence of heat capacity for solid samples.
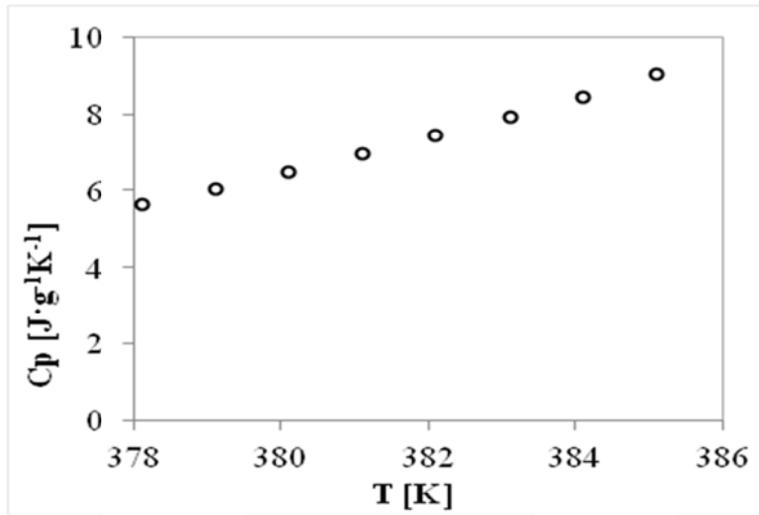
Fig. 9

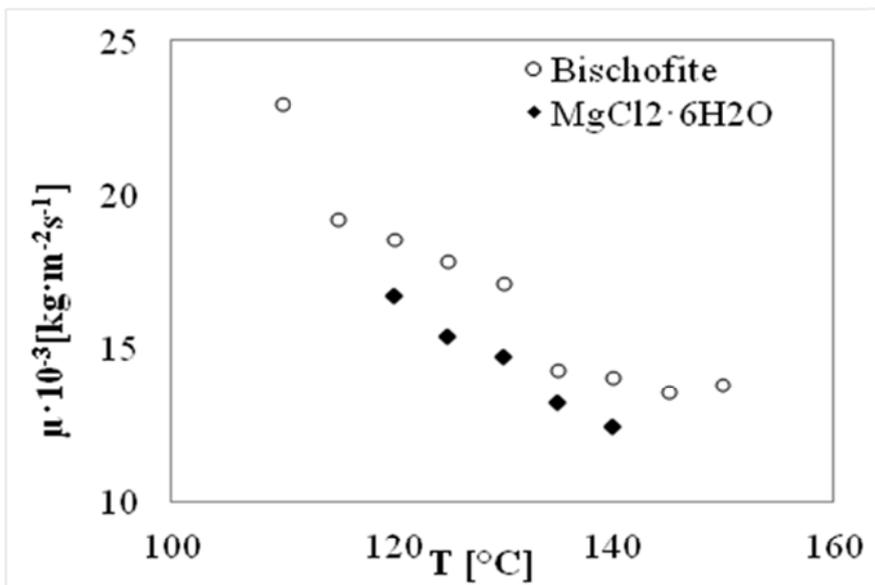Fig. 9. Temperature dependence of heat capacity for liquid bischofite.

Fig. 10

Fig. 10. Temperature dependence of dynamic viscosity for bischofite and MgCl2·6H2O.