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# Thermal performance evaluation of bischofite at pilot plant scale

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# HIGHLIGHTS

• A by-product from the non-metallic industry, bischofite, is tested as TES material.

• It is compared with other sensible and latent TES material candidates.

• Bischofite is thermally characterized at pilot plant scale.

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# ABSTRACT

The selection of the proper thermal energy storage (TES) material for an application is crucial. On the one hand, these materials should have suitable thermal properties for the operational temperatures range of the systems they are planned to work for, such as thermal stability, high latent heat and high heat capacity. On the other hand, they should be available on the market and at low price. Besides, researchers have to bear in mind the importance of testing TES materials not only at laboratory scale but also at higher scale, since it has been demonstrated that some thermal characteristics are volume-dependant. In the present study, bischofite, a by-product obtained from the non-metallic industry in the North of Chile with desired thermal properties for mid-temperature applications (around 100 °C), has been studied. A first analysis was performed in terms of comparing the thermal properties and cost of bischofite with other material previously studied as TES materials in order to evaluate its potential in both latent and sensible phases. Afterwards, a second analysis was experimentally performed in terms of testing bischofite at large-scale (204 kg) in a pilot plant facility. The experimental procedure consisted on several charging processes within two different temperatures ranges: from 50 °C to 80 °C and from 80 °C to 120 °C in order to study the behavior of the material in the sensible solid phase and latent phase respectively. The temperature profiles, the power given by the HTF, the energy balance in the storage system and the accumulation energy rate of the bischofite were analyzed. Results of both analysis showed that bischofite has potential as TES material for mid-temperature applications.

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# 1. Introduction

The population growth and the uncontrolled use of fossil fuels to supply the rising demand in the fields of industry and transport has a direct impact over the emissions of harmful gases, environment pollution and climate change. Therefore, the research for alternative sources of clean and renewable energies is crucial to overcome and address this conflict. Among all the alternative options, thermal energy storage (TES) is an effective technique which allows the storage of heat and cold when it is available

\* Corresponding author. E-mail address: lcabeza@diei.udl.cat (L.F. Cabeza). but no needed to be later used when it is needed but not available, allowing the use and implementation of renewable energies. However, the implementation of TES systems entails an initial high economic inversion because of the usually elevated prices of the commercialized TES materials. An important manner to reduce costs related to the TES materials is the usage of recycled materials, wastes and industrials by-products, which are known for their low cost. Moreover, these materials should have high availability and lack of conflict of use [1] due to the fact that a large range of material amount is needed for TES purposes, from few kilograms in domestic systems to thousands of tones in solar plants [2].

Gutierrez et al. [3] reviewed in a previous work the wastes and by-products used or proposed as TES materials for different





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А	heat exchange surface, m <sup>2</sup>		
ср	specific heat, $J \cdot (kg K)^{-1}$	Subscript	ts
СР	charging process, –	b	1
Ε	energy, J	cond	(
HTF	heat transfer fluid, –	ext	(
k	thermal conductivity, W∙(m K) <sup>-1</sup>	fg	1
т	mass, kg	g	,
'n	mass flow rate, kg s $^{-1}$	i	1
PCM	phase change material, –	in	i
Q	power, W	ins	i
t	time, s	int	i
Т	temperature, °C	loss	1
VHC	volumetric heat capacity, J $\cdot$ (K m <sup>3</sup> ) <sup>-1</sup>	п	(
		out	(
Greek symbols		rw	1
$\Delta H$	latent heat, kJ K <sup>-1</sup>	SS	5
$\Delta h$	enthalpy, kJ·(kg K) <sup>-1</sup>	1	(
$\Delta x$	thickness, m	2	(
$\rho$	density, kg·m <sup>−3</sup>		
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applications. This is the case of asbestos containing wastes (ACW) and fly ashes. ACW have been tested on the one hand as sensible TES material for adiabatic compressed air energy storages (ACAES), under operating condition within a temperature range from 50 to 650 °C and on the other hand for linear and central receiver concentrated solar plant (CSP), for a temperature range from 200 °C to 400 °C and from 400 °C to 800 °C, respectively [4]. Fly ashes, which are obtained from industrial combustions such as municipal solid wastes incinerators and coal fired power plants and are mainly composed of oxides such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO, have been tested and characterized to be used as sensible heat storage material. These materials have to be previously thermally treated in order to be inert, stable and suitable to be used as TES materials, and the final material obtained was considered inert and stable. The properties determined were density as a function of temperature (from 25 °C to 1000 °C) with values between 2962 and 2896 kg m<sup>-3</sup>, thermal capacity between 0.714 and  $1.122 \text{ kJ} \cdot (\text{kg K})^{-1}$ , thermal conductivity between 1.16 and  $1.59 \text{ W} (\text{m K})^{-1}$  and a coefficient of thermal expansion of  $8.7 \cdot 10^{-6} \text{ K}^{-1}$  [5]. Some other industrial by-products such as NaCl [6], bischofite [7], astrakanite and kainite [8] were previously tested both as sensible and latent heat TES materials in a temperature range from 100 to 200 °C. Possible applications for this range of temperature are the recovery industrial waste heat [9], solar food processing [10] and solar cooling [11]. Moreover, metal industry wastes as ferrous slags have been previously tested for high temperature applications, showing stable thermal behavior up to 1200 °C [12-14].

The objective of the present study is to evaluate the suitability of bischofite, a by-product obtained from the non-metallic industry in the North of Chile during the processes of obtaining mineral materials and other salts from the Atacama Desert, as TES material candidate. In order to perform this evaluation two different analysis were carried out. The first analysis consisted of comparing the main thermal properties and economic cost of bischofite with other TES material previously proposed in the literature in order to evaluate its potential as TES material in both latent and sensible phases. Afterwards, a second analysis was performed in terms of testing the material at large-scale (204 kg) in a pilot plant facility. Several charging processes were performed and parameters such as temperature profiles, power given by the HTF, energy balance

Subscript	TS .
b	bottom of the container
cond	conduction
ext	external wall of the container
fg	foamglass
g	ground
i	time interval
in	inlet
ins	insulation
int	internal wall of the container
loss	losses
п	control volume
out	outlet
rw	rock wool
SS	stainless steel
1	Charging Process 1
2	Charging Process 2

in the storage system and the accumulation energy rate were evaluated.

# 2. Material description

The material selected to be studied as candidate for TES applications in the present study is bischofite, which is a mineral that precipitates in evaporation ponds during the process of obtaining Li<sub>2</sub>CO<sub>3</sub> and KCl. It is collected and accumulated in discard piles, where about 8% is sold for its use for de-icing roads, for abating dust in the mining roads of the north of Chile and for specific industrial applications to avoid wind erosion, especially in mining tailings [15]. In a previous work bischofite was characterized at laboratory scale [7]. Results from this publication showed that bischofite is composed of nearly 95 wt% of MgCl<sub>2</sub>·6H<sub>2</sub>O and the remaining 5 wt% of KMgCl<sub>3</sub>·6H<sub>2</sub>O, Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O and ionic salts like NaCl and KCl. Moreover, other thermal properties such as a temperature of fusion of 98.9 °C, a latent heat of 120.2 kJ/kg and low volume change during melting and solidification (from 1481 kg/m<sup>3</sup> at solid state to 1686 kg/m<sup>3</sup> at liquid state) were determined. Finally, its temperature of fusion and its low price, which is function of MgCl<sub>2</sub>·6H<sub>2</sub>O price but always lower [7], makes bischofite attractive as TES material candidate for industrial waste heat (IWH) recovery as well as for combined heat and power (CHP) facilities

# 3. Experimental set-up and methodology

# 3.1. Experimental set-up

The pilot plant facility located at the University of Lleida (Spain) was used to perform the experimentation presented in the present study at pilot plant scale. As it can be seen in Fig. 1, it is composed of three main parts: the heating system, the cooling system and the storage system. The heating system consists of a 24 kW<sub>e</sub> electrical heater, which heats the heat transfer fluid (HTF) up simulating the energy source during the charging process in a real installation. In a facility based on solar energy this function is accomplished in the solar field by the solar collectors and in other facilities it is accomplished by fossil fuels or waste heat. The cooling system consists of



**Fig. 1.** Overview of the high temperature pilot plant used in this study and available at the University of Lleida.

a 20 kW<sub>th</sub> air-HTF heat exchanger, which simulates the energy consumption in a real installation during the discharging process. Finally, the storage system consists on a shell-and-tube heat exchanger, which stores the energy during the charging process to further release it during the discharging process. Silicone Syltherm-800 [16] is used as HTF, which flows by forced convection through the piping that connects the three different systems above-explained. Furthermore, temperature, pressure and flow measuring equipment is placed in different locations of the piping in order to control the operation of the facility and to acquire data related to the HTF temperature, pressure and flow rate, respectively.

The thermal behavior of bischofite at pilot plant scale is studied in the storage system. As previously said, it is based on a shell-and-tube heat exchanger entirely made of stainless steel 304 L consisting of a vessel which houses 49 tubes bended in U shape and distributed in square pitch. Bischofite is placed within the shell space between the vessel and the tubes. Moreover, 450 mm of foamglass are installed between the tank and the floor and 240 mm of rock wool are installed on the lateral walls and on the cover of the tank to reduce the heat losses to the surroundings. Table 1 shows the main characteristics of the storage system.

In order to study and evaluate the bischofite temperature distribution and the thermal behavior during the processes, 19 temperature sensors PT-100 with an accuracy of  $\pm 0.1$  °C are placed inside the TES material within the tubes bundle at different locations. As it can be seen in Fig. 2, the temperature sensors are placed along the storage system at three different heights (at 31, 126 and 190 mm from the bottom of the vessel) and with three different lengths (35, 114 and 194 mm). 16 additional temperature sensors PT-100 are placed inside the TES material at the corner part close

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Parameters	Units	Values
Material	(-)	Stainless steel 304 L
Tank width	(mm)	527.5
Tank height	(mm)	273
Tank depth	(mm)	1273
HTF pipes average length	(mm)	2485
Heat transfer surface	(m <sup>2</sup> )	6.55
Tank vessel volume ( $V_{tank}$ )	(m <sup>3</sup> )	0.183
Bischofite volume ( $V_{PCM}$ )	(m <sup>3</sup> )	0.143
Bischofite mass	(kg)	204



Fig. 2. Temperature sensors location within the main part of the storage system at three different levels highlighted in grey (lower), black (middle) and dotted (upper).

to the U bend and central part as well as outside the tank at the walls with the aim of studying the thermal losses. Finally, two temperature sensors PT-100 are installed in the inlet and outlet of the tubes bundle in order to measure the inlet and outlet HTF temperature. All the sensors in the facility are connected to a data acquisition system and recorded at a time interval of 30 s to further be processed.

However, in order to facilitate the understanding of the material behavior, only five temperature sensors located at the middle height (sensors 2, 8, 14, 11 and 5) and the inlet and outlet HTF temperature sensors will be shown.

Concerning the distribution of the TES material inside the storage system, Fig. 3 shows that the biggest amount (78%) is placed within the tubes bundle (denoted as main area) and therefore the sensors located in there can be considered as representative in terms of thermal behavior. The rest of the TES material is placed at the space existing between the tubes bundle in the middle of the storage system (denoted as central area and representing the 15% of the total amount of material) and at the corners (denoted as corner area and representing the 7% of the total amount of material), where the influence of the HTF is lower.

# 3.2. Methodology

#### 3.2.1. Material treatment before the experimentation

As previously said, bischofite is a mixture of several salts and its main component is MgCl<sub>2</sub>·6H<sub>2</sub>O, which turns to be a very hygroscopic salt. For this reason, bischofite absorbs a lot of moisture during its storage, its transport and its treatment and consequently the impurities existing in it are solubilized in the water and tend to decant the bottom of the pile, which causes the sample not to be



Fig. 3. Distribution of the amount of TES material within the storage system in three areas: main area, central area and corner area.



Fig. 4. Sample splitter used to quarter the bischofite.

homogenized. In order to avoid using a non-homogeneous material a treatment procedure known as quartering needs to be performed before the experimentation. This procedure consists of exponentially dividing the initial pile into several smaller piles using a sample splitter (Fig. 4) until the material is homogenized. Afterwards, the different piles were packed in bags in order to keep the bischofite moisture-free until the beginning of the experimentation.

## 3.2.2. Experimental procedure

The experimentation carried out at the pilot plant facility consisted of several charging and discharging processes in a temperature range of 50–120 °C and at an average flow rate of 1.5 m<sup>3</sup> h<sup>-1</sup> (Fig. 5). However, in the present study the authors focused only on the charging process, which was divided into two stages: the Charging Process 1 (CP1) within the temperature range of 50–80 °C in order to study the sensible phase in the solid region and the Charging Process 2 (CP2) within the temperature range of 80–120 °C in order to study the latent. Moreover, the unification of the flow rate was motivated due to the fact that previous studies had already shown the effect of varying the HTF flow rate on the behavior of different TES materials [11,17].

#### 3.2.3. Calculation procedure

To evaluate the behavior of the bischofite at pilot plant scale during the charging process, the power released by the HTF to the TES material, the energy balance in the system and the accumulation energy rates are studied.

The power given by the HTF during the charging process at a specific time interval  $(\dot{Q}_{HTF-i})$  is described as Eq. (1) shows:



Fig. 5. HTF and TES material (PCM) temperature profiles of the experimentation performed in the present study.

$$Q_{HTF-i} = \dot{m}_{HTF-i} \cdot Cp_{HTF-i} \cdot (T_{HTF-in-i} - T_{HTF-out-i})$$
(1)

where  $\dot{m}_{HTF-i}$  is the HTF mass flow rate evaluated at the specific time interval,  $Cp_{HTF}$  is the specific heat obtained with the data provided by the manufacturer and  $(T_{HTF-in-i} - T_{HTF-out-i})$  is the HTF temperature difference between the inlet and outlet of the tank.

Regarding to the energy evaluation of the system, the energy absorbed by the bischofite, the accumulated by the container material, and the insulation as well as the energy lost to the ambient were calculated. Moreover, an accumulation energy rate is defined in order to analyze the state of the charging process at different time intervals of the bischofite at the three different parts in which the tank is considered (main, corner and central).

In order to calculate the energy absorbed by the bischofite during the charging process ( $E_{PCM}$ ) some assumptions were taken into account. On the one hand, the mass evaluated was not considered as uniform but as 27 control volumes (CV) where a temperature sensor is associated and therefore the temperature in each CV is known. On the other hand, since the bischofite is a by-product, the  $Cp_{PCM}$  and  $\Delta H_{PCM}$  are not constant in the sensible and latent phase and therefore the authors changed such parameters using the equivalent heat capacity method. Hence, the energy absorbed was calculated as Eq. (2) shows:

$$E_{PCM} = \sum_{n=1}^{n=27} \sum_{i=1}^{i=t} m_{PCM,n} \cdot \Delta h_{PCM,i}(T)$$
(2)

where  $m_{PCM}$  is the mass of the bischofite,  $\Delta h_{PCM}(T)$  is the enthalpy of the bischofite, whose values were obtained with the DSC analysis and *T* is the temperature of the bischofite. Moreover, the subscripts *n* and *i* refer to the studied CV and the time interval evaluated, respectively.

The energy accumulated by the stainless steel of the container  $(E_{container})$  is calculated as Eq. (3) shows:

$$E_{container} = \sum_{i=1}^{i=t_{process}} (m_{ss} \cdot Cp_{ss}(T) \cdot T_{ss})_{i,i-1}$$
(3)

where *m* is the stainless steel mass of the container  $Cp_{ss}(T)$  is the stainless steel specific heat, whose values were obtained with the data obtained in previous laboratory analysis and *T* is the temperature of the stainless steel parts.

The energy accumulated by the insulation  $(E_{ins})$  is the summation of the stored energy in the rock wool and in the foam glass, which is calculated as Eq. (4) shows:

$$E_{ins} = \sum_{i=1}^{i=t_{process}} \left( m_{rw} \cdot Cp_{rw} \cdot T_{rw} + m_{fg} \cdot Cp_{fg} \cdot T_{fg} \right)_{i,i-1}$$
(4)

Here, the specific heat of both the rock wool and foam glass has constant values during all the experimentation.

The energy lost during the charging process to the ambient and ground ( $E_{loss}$ ) is calculated as a sum of the energy lost from the walls of the tank to the ambient and the energy lost from the bottom of the tank to the ground as Eq. (5) shows:

$$E_{loss} = E_{loss \cdot cond \cdot wall} + E_{loss \cdot cond \cdot bottom}$$
<sup>(5)</sup>

The energy loss by to the ambient ( $E_{loss.cond.wall}$ ) is calculated as Eq. (6) shows:

$$E_{\text{loss cond-wall}} = \sum_{i=1}^{i=t_{\text{process}}} \left( \frac{(T_{\text{container-int}} - T_{\text{container-ext}})}{\frac{\Delta x_{\text{container}}}{k_{\text{ss}} - A_{\text{container}}} + \frac{\Delta x_{\text{rw}}}{k_{\text{rw}} - A_{\text{rw}}}} \right)_{i,i-1}$$
(6)

The energy loss to the ground ( $E_{loss.cond.bottom}$ ) is calculated as Eq. (7) shows:

$$E_{loss-cond-bottom} = \sum_{i=1}^{i=t_{process}} \left( \frac{(T_b - T_g)}{\frac{\Delta X_{container}}{k_{ss} \cdot A_b}} + \frac{\Delta X_{fg}}{k_{fg} \cdot A_{fg}} \right)_{i,i-1}$$
(7)

Finally, the accumulated energy rate is defined as the percentage of energy accumulated by the TES material during the charging process in front of the total energy that the TES material has accumulated until the end of the process. The importance of evaluating this parameter lies in the fact that the evolution of the accumulated energy during charging processes does not behave linearly. Therefore results for another type of processes such as partial charging and discharging processes, which are more likely to happen in a real installation, can be extrapolated.

# 4. Results and discussion

## 4.1. Thermophysical properties and cost analysis

A comparison of bischofite with other TES materials in terms of thermophyisical properties and cost is performed in order to evaluate the suitability of this by-product as a candidate for TES purposes in both the sensible and latent phases.

Table 2 shows the comparison of bischofite with other materials that have previously been studied and tested in similar temperature ranges than bischofite as TES materials in previous experimental research for solid sensible TES purposes regarding the thermal conductivity (k), specific heat (cp), density ( $\rho$ ), volumetric heat capacity (VHC) and cost. The materials selected to compare with bischofite are reinforced concrete, silica firebricks, NaCl and MgCl<sub>6</sub>H<sub>2</sub>O. Even all the candidates have been tested in similar temperature ranges, could happen that their thermal properties have been studied at different temperatures since many sources do not specify. The reason why there is more than one reference of NaCl lies in the fact that this material has been tested by different authors and in different forms (in powder, compacted with water, etc.). Significant differences can be seen in the thermal conductivity, specific heat and density in NaCl values since these properties are difficult to be measured correctly with commercial equipment.

It can be seen that in terms of specific heat, bischofite has higher values than reinforced concrete, silica firebrick and NaCl and together with MgCl·6H<sub>2</sub>O, have the highest values. The same trend is observed for the VHC. Therefore, less volume of bischofite is needed to store the same amount of heat than the rest of materials proposed. VHC is an important parameter when designing the real TES facility. In terms of cost per unit of mass, bischofite is not the cheapest (less than  $0.14 \in kg^{-1}$ ) but it still is an attractive option.

In order to compare bischofite with other latent TES candidates, Fig. 6 shows the comparison of bischofite with other TES materials with similar melting points ( $T_m \pm 20$  °C) from the literature, such as acetamide ( $T_m = 82$  °C), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O ( $T_m = 89$  °C), xylitol ( $T_m = 93-94.5$  °C), d-Sorbitol ( $T_m = 97.7$  °C), MgCl<sub>2</sub>·6H<sub>2</sub>O ( $T_m = 117$  °C), erythritol ( $T_m = 118$  °C) and four different inorganic



Fig. 6. Comparative of some materials for latent TES purposes regarding their cost and energy density. Based on [7,15,18,22–24].

eutectic mixtures ( $T_{\rm m}$  = 95–117 °C). Notice that in this range of temperature there are not many TES candidates.

The parameters chosen to compare bischofite with other candidates are the energy density and the cost. These are important parameters when designing the TES system as they determine the cost and the volume of the system. A suitable TES material will be cheap and with high energy density (following the tendency outlined by the grey arrow). As it can be seen in Fig. 6, bischofite is the best candidate regarding the cost of the material but the one with lower energy density, which means that more material is needed to store the same amount of heat compared with the rest of materials.

#### 4.2. Pilot plant analysis

#### 4.2.1. Temperature evaluation

Fig. 7 shows the temperature profile of the temperature sensors located at the mid-height control volumes, which are considered as representative for their location (Fig. 2), when bischofite is used as TES material, as well as the inlet HTF temperature during the charging and discharging processes. The oscillation observed on the HTF temperature profile is due to the intrinsic configuration of the electrical heater. Regarding to the TES material temperature profiles, it can be seen that the Charging Process 1 (CP1) started 0.21 h after commencing the experimentation, since the previous period was used to ensure the homogenization of the material at the initial temperature of 50 °C, and finished after 1.78 h, once the specifications explained in the methodology were accomplished. Hence, bischofite took 1 h and 34 min to heat up from 50 °C to 80 °C in the solid sensible phase. Moreover, it can be noticed that the material located closer to the HTF inlet finished the process faster than the located at the end of the tubes bundle, since they received in the first stage the energy released by the

# Table 2

Main thermophysical properties and cost of different material tested for solid sensible TES purposes.

Material	$k (W \cdot (m K)^{-1})$	$cp (kJ \cdot (kg K)^{-1})$	$ ho~({ m kg~m^{-3}})$	VHC $(kJ \cdot (K m^3)^{-1})$	Cost ( $\in kg^{-1}$ )
Reinforced concrete [18]	1.5	0.85	2200	1870	0.05
Silica firebricks [18]	1.5	1.0	1820	1820	1
NaCl [18]	7	0.85	2160	1836	0.15
NaCl [19]	10.4-11.7	0.85-0.87	2120-2210	1802-1923	<0.01
Salt A (NaCl) [9]	0.33	0.738	1384	1021	n.a.
Salt B (NaCl) [9]	2.84	0.738	2050	1513	n.a.
MgCl <sub>2</sub> ·6H <sub>2</sub> O [20,21]	0.694	1.66-1.75	1569	2605	0.46
Bischofite [7]	n.a.	1.6-2.1	1686-1513	2698-3177	<0.14

N.a: not available.



Fig. 7. Bischofite and HTF temperature profiles during the charging and discharging process for an average flow rate of  $1.5 \text{ m}^3/\text{h}$ .

HTF. Charging Process 2 (CP2) started 3.14 h after commencing the experimentation and finished after 7.64 h and therefore 4 h 30 min were needed to increase the temperature from 80 °C to 120 °C in both sensible and latent phase. Within CP2, the melting process of the material located at the area evaluated by the mid-height temperature sensors started after 3.62 h and finished after 6.61 h. Finally, it can be observed that the discharging process started after 9.69 h and finished after 14.12 h.

## 4.2.2. Power evaluation

Fig. 8 shows the power given by the HTF to the system (Eq. (1)) as well as the HTF temperature profiles during the Charging Processes 1 and 2. Results show that the power given by the HTF followed the same pattern in both charging processes, achieving high values at the beginning of the processes since the HTF temperature differences between the inlet and the outlet presented maximum values. As the outlet temperature decreased because of the heat transfer from the HTF to the TES material, the power released by the HTF decreased.

# 4.2.3. Energy evaluation

Fig. 9 shows the energy balance between the energy accumulated by the TES material, the energy accumulated by the container material, the energy accumulated by the insulation, and the energy lost to the environment during the Charging Processes 1 (CP 1) and 2 (CP 2).



**Fig. 8.** Power given by the HTF and HTF temperature profiles during the Charging Processes 1 (CP 1, dotted lines) and 2 (CP 2, continuous lines).



**Fig. 9.** Energy balance during the Charging Processes 1 (CP 1, dotted lines) and 2 (CP 2, continuous lines) considering the bischofite, the container, the insulation and the losses to the ambient.

During the Charging Process 1, the energy required to heat up the TES material from the initial temperature of 50 °C to the final temperature of 80 °C in the sensible solid phase was 3.07 kW h. During this period, the container materials accumulated 0.64 kW h, and the insulation accumulated 0.25 kW h. Finally, notice that due to the good insulation of the system, the losses to the environment were 0.06 kW h, which corresponds only to 1.95% of the total energy accumulated by the TES material.

On the other hand, the energy accumulated by the TES material during the Charging Process 2 was 11.97 kW h, while the energy accumulated by container materials and the insulation was 0.85 kW h and 0.37 kW h, respectively. The losses to the environment were 0.31 kW h which corresponded to the 2.59% of the energy accumulated by the TES material, a percentage value very similar to Charging Process 1.

The significant difference between the TES material energy stored in the two charging processes are mainly due to two reasons. First, while in the Charging Process 1 the TES material increased 30 °C, in the Charging Process 2 increased 40 °C. Second, in the Charging Process 1 the TES material exclusively worked in the sensible phase whereas in the Charging Process 2, as Fig. 10 shows, the TES material worked 64% in the latent phase, which is fully known to store higher amounts of energy for the same amount of mass.

In order to analyze the thermal behavior of the different parts of the storage tank geometry, Fig. 11 shows the evolution of the accumulation energy rate of the bischofite in the main, corner and central parts of the tank (Fig. 3) as well as the total accumulation energy rate, which is calculated weighting the previous rates, during Charging Processes 1 and 2. It can be observed that in both charging processes the same tendency is followed, being the main part the one which accumulates faster the energy and the corner part the one which accumulated slower the energy. The reason lies in the proximity of this main part to the HTF bundle of tubes, which helps the heat transfer to be higher due to higher effective thermal conductivity values. The lower values of the corner and central parts are mainly due to two factors, the lower values of effective thermal conductivity and the higher on the other hand the higher values of thermal losses to the ambient. Moreover, notice that the TES material in the Charging Process 1 needed 67% of the time to store 90% of the total energy, whereas Charging Process 2 needed only 55.6% of the time.



**Fig. 10.** Distribution of the energy accumulated by the bischofite during the Charging Process 2.



**Fig. 11.** TES material accumulation energy rate during Charging Processes 1 (CP 1, dotted lines) and 2 (CP 2, continuous lines), at the total, main, corner, and central part of the storage system.

# 5. Conclusions

Bischofite is a by-product from the non-metallic industry composed of approximately 95% MgCl<sub>2</sub>·6H<sub>2</sub>O. The objective of this study is to assess the suitability of this by-product as TES material candidate at high scale. Bischofite was previously characterized at laboratory scale and its thermal properties and economic costs have been compared to other latent and sensible TES material candidates found in the literature. As latent TES material candidate, bischofite stands out because of its low cost (<0.14  $\epsilon$ /kg). As sensible TES material candidate, its volumetric heat capacity and specific heat is higher than the rest of the candidates.

The pilot plant designed and built at the University of Lleida (Spain) was used to study the thermal behavior of bischofite at large scale in two different charging processes. In the first charging process, the sensible state was studied by increasing the TES material temperature from 50 °C to 80 °C. In the second charging process, the influence of the latent state was studied by increasing the TES material temperature from 80 °C to 120 °C. Results showed a good behavior of the 204 kg of bischofite evaluated, which accumulated 3.07 kW h in the temperature range from 50 °C to 80 °C, being the losses to the environment of 1.95% of the total energy accumulated by the TES material and could also accumulated 11.97 kW h. In the temperature range from 80 °C to 120 °C, where the 64% corresponded to the latent phase of the TES material and the losses to the environment were of 2.59% of the energy

accumulated by the TES material. Finally, it could also be observed that for the current storage system configuration the TES material in the Charging Process 1 needed 67% of the time to store 90% of the total energy, whereas Charging Process 2 needed only 55.6% of the time.

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#### References

- Calvet N, Gomez JC, Faik A, Roddatis VV, Meffre A, Glatzmaier GC, et al. Compatibility of a post-industrial ceramic with nitrate molten salts for use as filler material in a thermocline storage system. Appl Energy 2013;109:387–93.
- [2] Py X, Calvet N, Olives R, Meffre A, Echegut P, Bessada C, et al. Recycled material for sensible heat based thermal energy storage to be used in concentrated solar thermal power plants. J Sol Energy-T ASME 2011. 33031008-1.
- [3] Gutierrez A, Miró L, Gil A, Rodríguez-Aseguinolaza J, Barreneche C, Calvet N, Py X, Fernández Al, Grágeda M, Ushak S, Cabeza LF. Review on industrial waste and by-product materials revalorization as thermal energy storage (TES) materials. Renew Sust Energy Rev (submitted for publication).
- [4] Meffre A, Py X, Olives R, Faure R, Tessier-Doyens N, Huger M. Thermomechanical characterization of recycled high temperature thermal energy storage material. In: Concentrating solar power and chemical energy systems SolarPACES, Marrakech; 2012.
- [5] Meffre A, Py X, Olives R, Guillot S, Faik A, Bessada C, Echegut P, Michon U. High temperature thermal energy storage material from vitrified fly-ashes. In: Concentrating solar power and chemical energy systems solarPACES, Granada, Spain; 2011.
- [6] Miró L, Navarro ME, Suresh P, Gil A, Fernández AI, Cabeza LF. Experimental characterization of a solid industrial by-product as material for high temperature sensible thermal energy storage (TES). Appl Energy 2014;113:1261–8.
- [7] Ushak S, Gutierrez A, Galleguillos H, Fernandez AG, Cabeza LF, Grágeda M. Thermophysical characterization of a by-product from the non-metallic industry as inorganic PCM. Sol Energy Mater Sol C 2015;132:285–91.
- [8] Ushak S, Gutierrez A, Flores E, Galleguillos H, Grageda M. Development of thermal energy storage materials from waste-process salts. In: ISES Solar World Congress, Cancun, Mexico; 2013.
- [9] Brückner S, Liu S, Miró L, Radspieler M, Cabeza LF, Lävemann E. Industrial waste heat recovery technologies: an economic analysis of heat transformation technologies. Appl Energy 2015;151:157–67.
- [10] Sharma A, Chen CR, Murty VVS, Shukla A. Solar cooker with latent heat storage systems: a review. Renew Sust Energy Rev 2009;13:1599–605.
- [11] Gil A, Oró E, Castell A, Cabeza LF. Experimental analysis of the effectiveness of a high temperature thermal storage tank for solar cooling applications. Appl Therm Eng 2013;54:521–7.
- [12] Motz H, Geisele J. Products of steel slags an opportunity to save natural resources. Waste Manage 2001;21:285–93.
- [13] Tayeb AM. Use of some industrial wastes as energy storage media. Energy Convers Manage 1996;37:127–33.
- [14] Gil A, Calvet N, Ortega I, Risueño E, Faik A, Blanco P, Rodríguez-Aseguinolaza J. Characterization of a by-product from steel industry applied to thermal energy storage in concentrated solar power. In: Proceedings of Eurotherm Seminar 99, Lleida, Spain; 2014.
- [15] SALMAG (Sales de Magnesio Ltda.) < http://www.salmag.com> [last accesed on 15.02.15].
- [16] SYLTHERM 800 technical data. DOW. http://www.dow.com/heattrans/ products/synthetic/syltherm.htm [last accessed on 11.07.14].

- [17] Jaume Gasia. Experimental analysis of RT-58 as phase change material for domestic hot water (DHW) applications. Master thesis at University of Lleida; 2014.
- [18] Kenisarin M, Mahkamov K. Solar energy storage using phase change materials. Renew Sust Energy Rev 2007;11:1913–65.
- [19] CES Selector 20012 software, Cambridge [UK]: Granta Design Limited; 20212. www. Grantadesign.com.
- [20] Lane GA. Low temperature heat storage with phase change materials. Int J Energy Res 1980;5:155–60.
- [21] Pilar R, Svoboda L, Honcova P, Oravova L. Study of magnesium chloride hexahydrate as heat storage material. Thermochim Acta 2012;546:81–6.
- [22] Cabeza LF, Castell A, Barreneche C, De Gracia A, Fernández AI. Materials used as PCM in thermal energy storage in buildings: a review. Renew Sust Energy Rev 2011;15:1675–95.
- [23] Sharma A, Tyagi VV, Chen CR, Buddhi D. Review on thermal energy storage with phase change materials and applications. Renew Sust Energy Rev 2009;13:318–45.
- [24] Cabeza LF, Gutierrez A, Barreneche C, Ushak S, Fernández AG, Fernádez AI, et al. Lithium in thermal energy storage: a state-of-the-art review. Renew Sust Energy Rev 2015;42:1106–12.