UNIVERSITY OF ANTOFAGASTA

DEPARTMENT OF CHEMICAL AND MINERAL PROCESS ENGINEERING

PHD PROGRAM IN MINERAL PROCESS ENGENEERING

DESIGN AND CHARACTERIZATION OF MATERIALS BASED ON INORGANIC SALTS AND MIXTURES TO BE APPLIED AS SOLAR THERMAL ENERGY STORAGE (TES) MATERIALS.

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Nomenclature

IAE	International Energy Ageng*y*
TPES	Total Primary Energy Supply
Mtoe	Million tonnes of oil equivalents
SING	Interconnected System of “Norte Grande” (Know in Spanish as Sistema Interconectado del Norte Grande)
SIC	Interconnected Central System (Know in Spanish as Sistema Interconectado Central)
TES	Thermal Energy Storage
SHS	Sensible Heat Storage
LHS	Latent Heat Storage
THS	Thermochemical Heat Storage
HTF	Heat Thermal Fluid
DHW	Domestic Hot Water
ACW	Asbestos Containing Wastes
LCA	Life Cycle Assessment
esd	Energy Storage Density
PEG	Polyethylene glycol
IWH	Industrial Waste Heat
DoE	Design of Emperiment
DRX	X-Ray Difraction
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis

ABSTRACT

The gap between the demand and supply of energy we face in different areas of our daily life creates the necessity of a more efficient management and dispatchability of energy. In order to make this possible, different systems of thermal energy storage (TES) have been studied, through either storing energy from renewable resources such as solar energy or industrial heat recovery. These systems implement methods based on the materials they use: sensible, latent of thermochemical heat storage. A wide variety of materials have been studied and some of them are being applied for TES systems, mainly sensible heat storage method using molten salts for electric power production. However, there are other applications, which need to be covered at different scales and ranges of temperatures. To make these systems be feasible it is important to find materials with thermophysical properties suitable for the applications, chemically stable and low cost. Accordingly, this PhD thesis presents some industrial by-products and waste materials from non-metallic industry, potential to be applied as TES at low and high temperature.

The inorganic materials presented in this document are bischofite, an hydrated salt mainly composed by $MgCl_2 \cdot 6H_2O$, which has potential to be applied as a phase change material (PCM) at low temperature, with a melting point of 98 °C and heat of fusion of 114 J g^{-1}. Astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) and Kainite have potential to be applied as sensible heat storage at low temperature (<100 °C) and a heat-treated material from astrakanite salt has potential to be applied as a PCM at high temperature from 550 °C to 750 °C. Also, a heat-treated material of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) has potential to be applied as a sensible heat storage material at high temperature, from 200 °C to 400 °C.

Chapter I.

INTRODUCTION

I.1 World energy situation

The fast worldwide increase of energy use also generates concern because of the difficulties of supply, energy sources exhaustion and environment impact (ozone layer depletion, global warming, climate change, etc.). The International Agency of Energy (IAE) has collected data of supply energy and also alarming data about energy consumption. Fig. 1 shows the distribution of sources of energy supply in 1973 and 2012. During the last decades (1973-2012) the total primary energy supply (TPES) increased 119% corresponding mainly to fossil fuels. Also, some other sources of energy have increased their presence as renewable sources (these sources are identify in Fig. 1 as "other"), but in a small amount for the last 40 years. In Table 1 are shown the Total Mtoe of Primary Energy Supply in 1973 and 2012 [1].

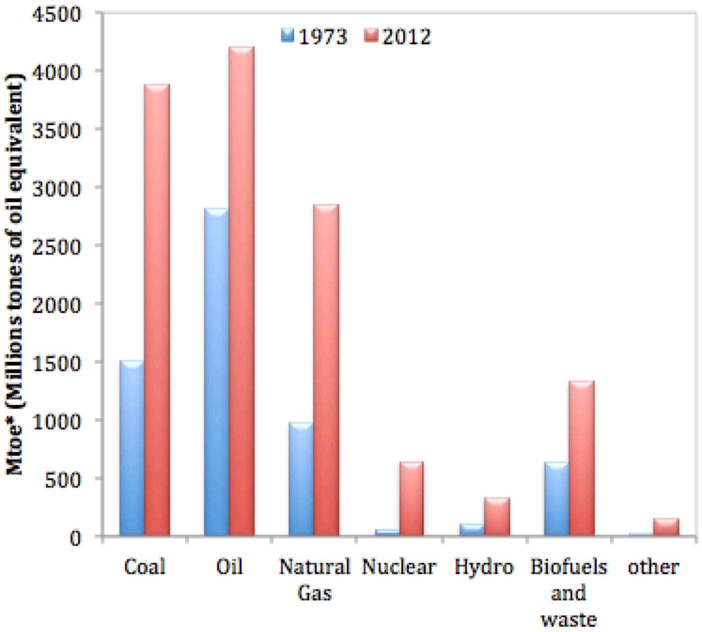


Fig. 1World primary energy supply from 1973 to 2012 by fuel (Mtoe). (Adapted from [1])

Table 1 World total primary energy supply in 1973 and 2012.

Year	TPES [Mtoe]
1973	6 106
2012	13 371

The consumption also has increased. Fig. 2 shows this behavior, in 1973 the energy consumption was 4 672 Mtoe and in 2012 the consumption increased to 8 979 Mtoe (see Table 2 It can be seen that electricity has had the biggest increased with almost 200% followed by natural gas with an increase of around 120%. These values response to the population growth, increase of agriculture and industrial activities, furthermore the tendency it remains increasing. As a consequence the CO_2 emissions are also increasing from 1973 and will continue. Fig. 3 shows the tendency from 1973 to 2012, with alarming values of increasing of CO_2 emissions by coal and natural gas during the last four decades. As it is expected, renewable energy sources don't have CO_2 emissions, make them the best option to choose to reduce the use of conventional source of energy, thus reduce CO_2 emissions. The total Mt of CO_2 emissions in 1973 and 2012 are shown in Table 3[1].

Table 2 World total final consumption in 1973 and 2012.

Year	TFC [Mtoe]
1973	4 672
2012	8 979

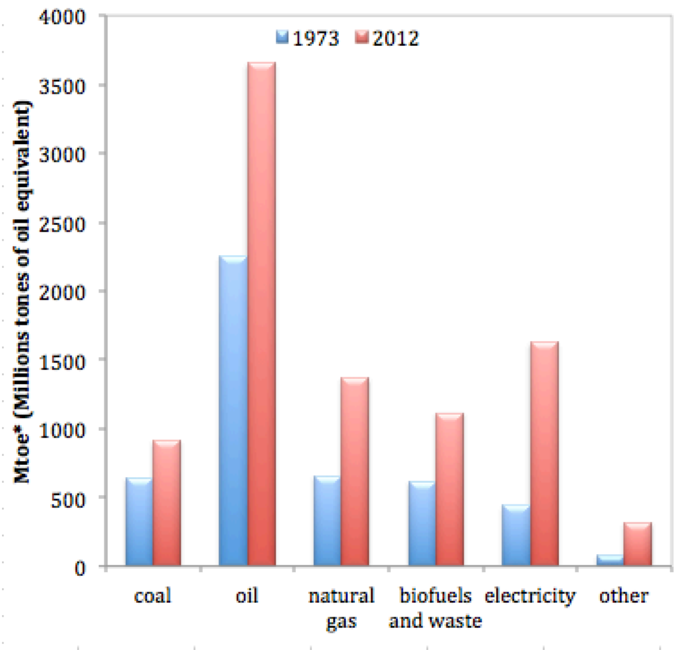


Fig. 2 World final consumption from 1971 to 2012 by fuel (Mtoe) (adapted from [1]).

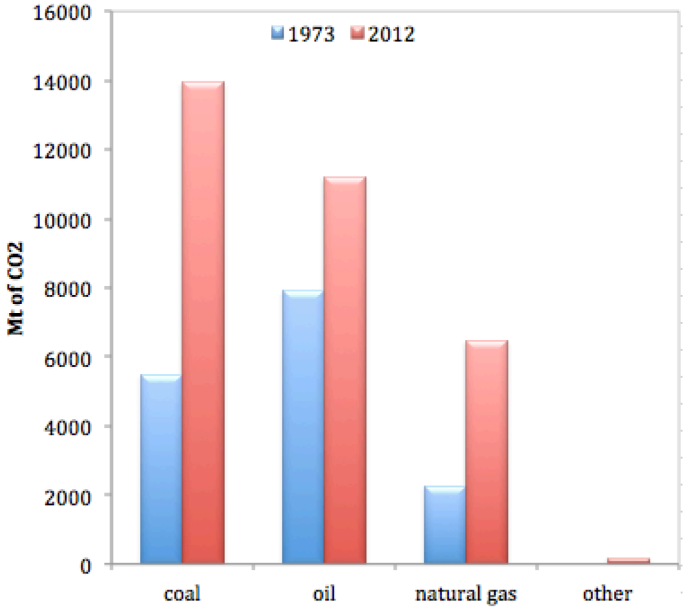


Fig. 3 World CO_2 emissions from 1973 to 2012 by fuel (Mt of CO_2) (adapted from [2]).

Table 3 Million tones of CO_2 emissions in 1973 and 2012.

Year	**Mt of CO_2**
1973	15 633
2012	31 734

This is also the case for American countries; data for some countries of this continent have been collected by IEA. Table 4 shows the increase of the emissions for South American countries from 1971 to 2012. In Fig. 4 it can be seen that the country that has increased the most its CO_2 emission during the last 40 years is Brasil, with 846% of increasing from 1971. This is because the large number of population and also because the industrial activities of this country have increased very fast. The same figure shows that the country that has increased its CO_2 emissions the less is Uruguay with 62% of increasing the last 40 years. The total million tones of CO_2 emissions in 1973 and 2012 for each country are reported in Table 4. In general, all countries have increased their population and industrial activities, being these values the rate of growing for each of them [2].

Table 4 CO_2 emissions by South American countries [2].

Country	**Million tones of CO_2 Emissions**	
	Year 1971	**Year 2012**
Argentina	82.8	188.5
Brazil	90.2	440.2
Bolivia	2.2	16.3
Colombia	26.7	67.4
Chile	20.8	77.8
Ecuador	3.5	33.1
Uruguay	5.2	8.4
Paraguay	0.6	5.1
Venezuela	52.1	178.3
Peru	15.6	45.8

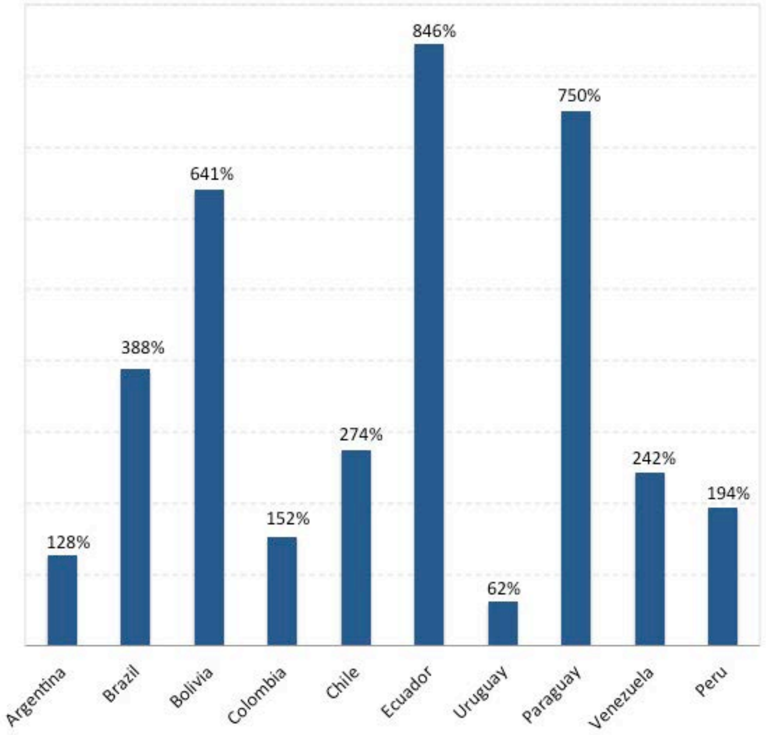


Fig. 4 Increase of %CO_2 emissions from 1971 to 2012 by South American Countries [2].

The energy situation in Chile, as Fig. 4 shows, has an increased of CO_2 emissions up to 274% from 1971 to 2012, this is due to the increasing of volumes of production, specially in mining industry which is the main industry of the country. The generation of energy in Chile is based mainly in fossil fuels, has a total installed capacity of 17 656 MW and it is divided in 4 segments from north to south. The Interconnected system of "Norte Grande" (Known in Spanish as SING) which corresponds to a 23.5% of total installed capacity, central interconnected system (Known in Spanish as SIC) which corresponds to a 75.6% of total installed capacity and Aysen and Magallanes systems, both corresponds to a 0.9%. [3].

It is important to reduce the use of traditional sources to produce energy because of the environmental impact, which can be seen in the increase of CO_2 emissions during the last forty years [4]. The first strategy to reduce the traditional sources dependence it is based on the reduction of energy consumption applying energetic saving program, focused on the reduction of energy demand and efficient energy use in houses and industry [5]. A second strategy to achieve these goals is using renewable energy sources, not only to produce energy at large scale but also to design and to use autonomous systems [6]. Nowadays, renewable energy technologies are being improved up to being quite competitive with conventional energy systems in terms, both efficiency and reliability [7], with the main advantages of reduction of traditional sources dependence and reduction of CO_2 emissions to atmosphere. Renewable energy sources also avoid security problems related to atomic energy [8], which is favorable from the social point of view, to apply renewable energy systems [9].

Renewable energies are produced from natural sources, such as eolic, solar, rainwater, waves, and geothermal [10]. For these energy sources can be applied, it is necessary to develop energy storage devices, which are as important as the development of energy sources. Today, the challenge for researchers is to store energy in the appropriate way for a late use transformed in the form required. Energy storage not only reduces the mismatch between supply and demand but also improves performance and reliability of energy systems and plays an important role in energy conservation [11]. This leads to fuel savings making a more rentable system through reduction of waste energy and capital cost. For example, storing energy would improve the performance of a power generation plant by loading level and a higher efficiency, which would lead energy conservation and generation at lower cost [12]. The different methods that exit today to store energy can be divided into two broad categories: short-term storage and long-term storage depending on the length of the storage.

For example, when the excess heat collected is stored in the summer to use it during winter, this corresponds to the concept of seasonal thermal energy storage (STES) or a long-term storage. Another classification would be according to its mechanisms for energy storage: sensible heat storage, latent heat storage and chemical reaction/thermo-chemical heat storage [7].

I.2 Mechanisms for energy storage

(a) Sensible heat storage (SHS)

When a material experience change in it internal energy due to a change of temperature, whether increasing temperature by heating or reducing by cooling, the thermal energy that can be stored is called "Sensible heat storage". The amount of sensible heat stored can be calculated according to the following equations [12]:

$$Q = \int_{T_i}^{T_f} mC_P dT$$

$$Q = mC_{p*}(T_f - T_i)$$

Temperatures T_i and T_f from the equations are represented in Fig. 5 as T_1 and T_{melt} or as T_{melt} and T_2 respectively.

In this kind of storage, the most important thermo physical properties are density and specific heat, but also other properties and parameters are important for sensible heat storage such as thermal conductivity and diffusivity, operational temperatures, cost of the materials, vapor pressure, thermal stability and also heat loss coefficient according to the volume ratio and the surface areas to transfer heat [13].

(b) Latent heat storage (LHS)

In this case, the heat is absorbed or released while the material is experiencing a phase change, this phase change can be from solid to liquid, from liquid to solid, or even just a transition from solid to solid and also the inverse process in all the cases. The storage capacity of a material to storage latent heat can be calculated according to the following equations [12]:

$$Q = \int_{T_i}^{T_m} mC_P dT + ma_m \Delta h_m + \int_{T_m}^{T_f} mC_p dT$$

$$Q = m\left[C_{p1}(T_m - T_i) + a_m \Delta h_m + C_{p2}(T_f - T_m)\right]$$

In this case, temperatures are represented in Fig. 5 as shown below: T_i = T_1, T_m=T_{melt} and T_f=T_2.

The materials that have been used more are those that change from solid to liquid phase and the thermo physical properties that they should have are as follow:

- Thermal properties; melting and crystallization point within the range of operating temperature, relatively high latent heat per unit volume and specific heat and also relatively high thermal conductivity of both solid and liquid phase.
- Physical properties; congruent melting point of the material, high density for the materials have a high energy storage density, at the operating temperature it is necessary that the vapor pressure of the material it is low and also a small volume change.
- Kinetic properties; an ideal material should have a high nucleation and adequate crystallization rates and no supercooling.
- Chemical properties; the material need to have long-term chemical stability, be compatible and non-corrosive with container material, reversible freeze/melt cycle and to ensure safety is necessary to be non-toxic, non-flammable and non-explosive.
- Finally as sensible heat storage materials it is important that phase change materials be readily available in large quantities at low cost. [14].

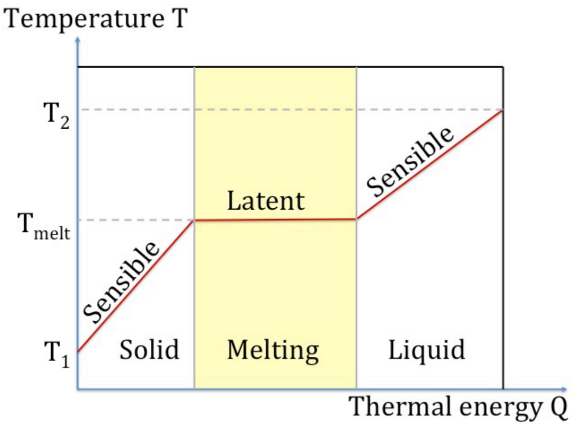


Fig. 5 Sensible and latent heat for a solid material [16]

(c) Chemical reaction/thermo-chemical heat storage

This method consists of storing energy that is released by chemical reversible reactions in one direction and absorbed when reactions go to the other way. Comparing to the other two methods, thermo-chemical heat storage present a higher energy density so less volume of material would be necessary to store the same quantity of energy by sensible or latent heat storage. However, only some tests at lab scale have been performed up to now and there are not commercial applications yet.

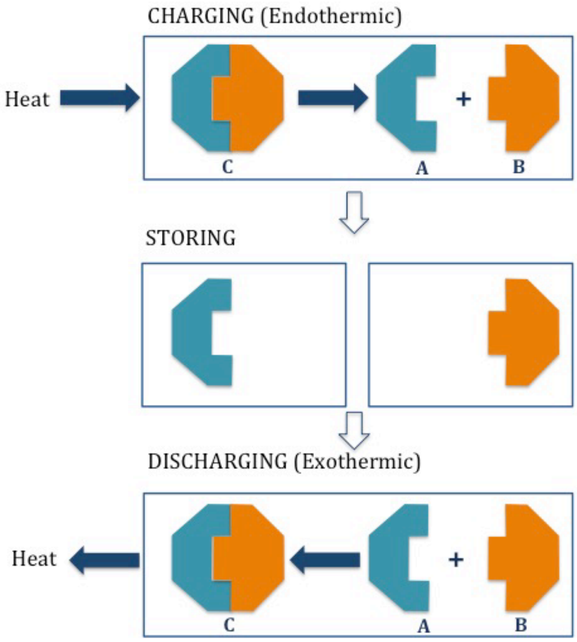


Fig. 6 Process of thermochemical energy storage cycle: charging, storing and discharging [17].

There are many substances that have been studied and tested as thermal energy storage materials at different ranges of temperature, based on LHS and SHS methods, at low temperature up to 120 °C, medium temperature from 120 °C to 250 °C and at high temperature over 250 °C. Fig. 7 shows the classification of LHS and SHS materials, some materials of sensible heat storage are being applied at industrial scale in several thermo solar plants mainly in Spain and United States, and this is the case of the solar salt, which is a mixture of 40% KNO3-60% Na_2NO_3 that melts below 300 °C. Furthermore, some PCM materials are being tested to be applied at low temperature in buildings and domestic hot water (DHW) [13-15, 18-20].

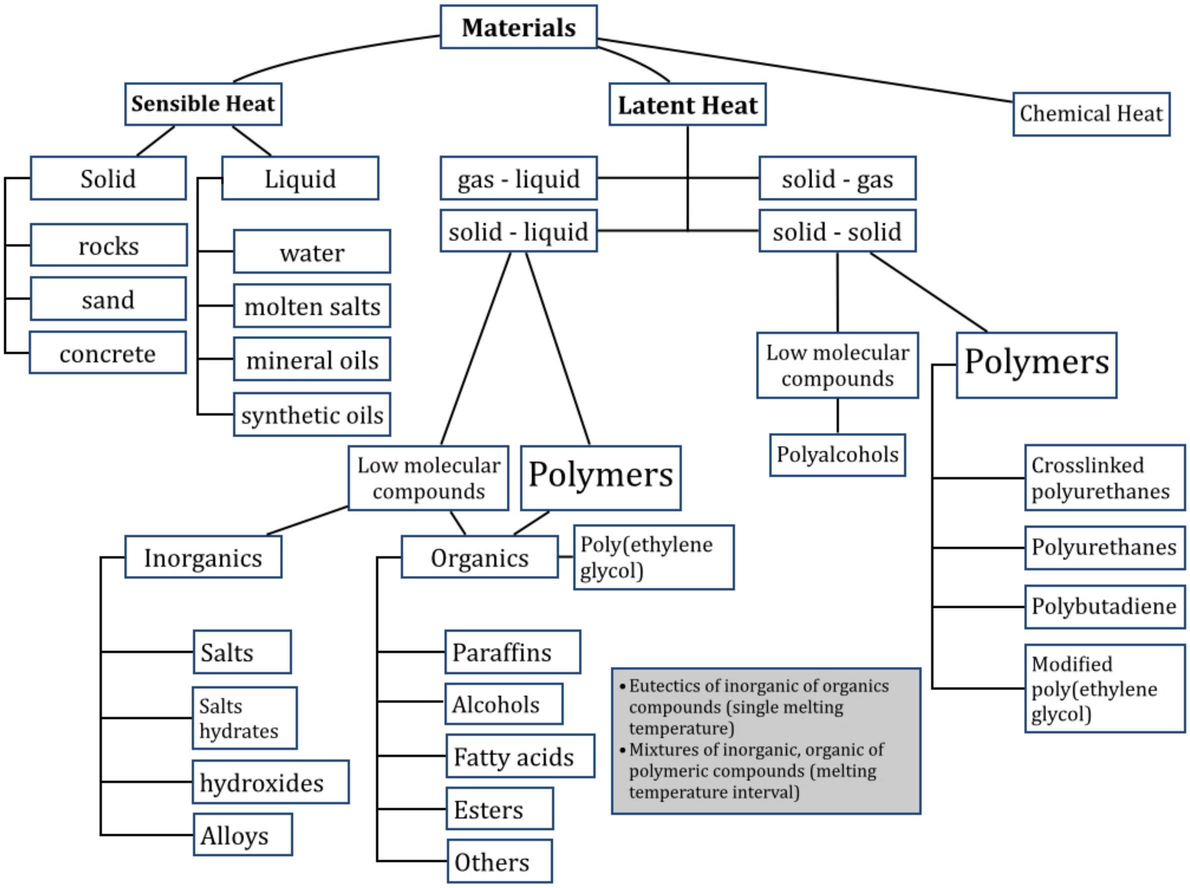


Fig. 7 Classification of Sensible heat and Latent heat energy storage materials [13-15, 18]

I.3 Concepts for thermal energy storage

The requirements for these materials are according to the system in which they will be applied, the range of temperature of the system, if it is latent or sensible heat storage, whether they are for short-term or for long-term storage systems. Based on this, the classification can be as follow:

LHS at high temperature is applied in solar power plants; the systems that this plants use are divided in active systems, which can be direct or indirect, and passive systems.

(a) Active direct systems

In these systems, the heat transfer fluid and the storage medium are the same. This reduces operational costs because of the use of expensive heat exchangers is no needed. The solar power plant that uses active direct system is the two-tank storage system (see Fig. 8)

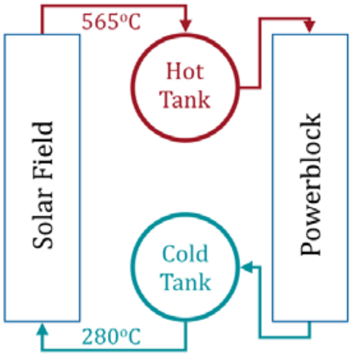


Fig. 8 Scheme of an active direct two-tanks storage system (modified from [13]).

The advantages of these systems are the separated hot and cold tanks, which reduce the risk of approach, temperatures can be increased in tanks if it is necessary because of the separated tanks.

The disadvantages are the high costs of heat thermal fluid (HTF); even that having two tanks are convenient because operational conditions can be easily modified these structure can be more expensive; difference of temperatures between tanks are relatively small; there are risks of solidification of the HTF because of the high melting point.

(b) Active indirect systems

In this case, the HTF is different than the heat storage medium. The system configurations are two, the first one it is a two tanks indirect storage system where a heat exchanger is needed (see Fig. 9)

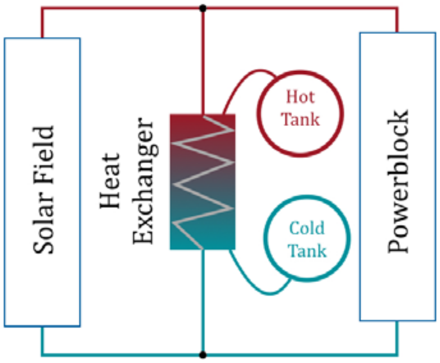


Fig. 9 Scheme of an active indirect two-tanks storage system (modified from [13]).

The energy in these systems is stored in a liquid medium, usually molten salts, which are contained in the tanks and the heat from solar field is transported by another heat fluid that usually is an oil, and transferred through the heat exchanger.

The second configuration would be similar but instead of two tanks to store energy has only one tank known as thermocline (see Fig. 10).

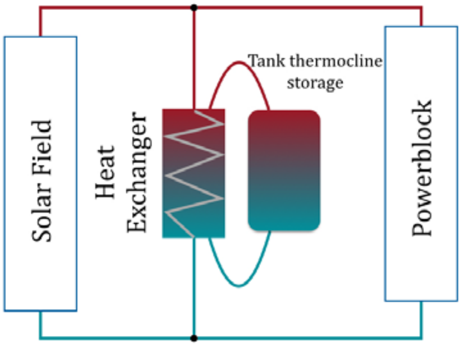


Fig. 10 Scheme of an active indirect one-tank storage system (thermocline) (modified from [13]).

The tank contains the hot and cold storage fluid, this reduces the costs because only one tanks is needed, but increases the operational costs due to is more difficult to modified operational conditions as hot and cold temperature, also it has a complex storage design and thermodynamically is an inefficient power plant.

(c) Passive systems

In these systems the heat is transferred to a storage medium, usually a solid medium like concrete, castable materials and PCMs, shown in Fig. 11.

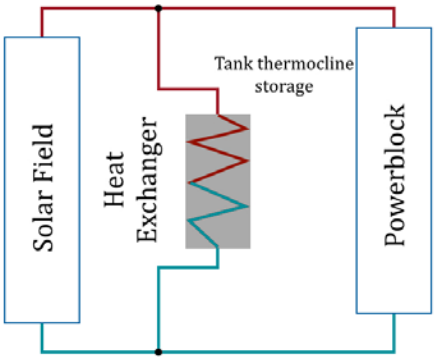


Fig. 11 Scheme of a passive heat storage system (modified from [13]).

The heat is transferred and storage to the concrete blocks through a HTF from the solar fields. The main advantage of these systems are the low costs of thermal energy storage media; there is a good contact between pipes and concrete blocks which leads a high heat transfer; facilities of handling materials of heat transfer and storage. Some disadvantages would be the high costs of heat exchanger and complex engineering required and non-stable at long-term.

There is some hot domestic water (HDW) systems that have been modeled based on a similar configuration [22]. A heat exchanger is needed as Fig. 12 shows and some external boiler, the operational range of temperatures of these systems are from 40 °C to 60 °C, and the materials that have been used to energy storage are mainly commercial PCM.

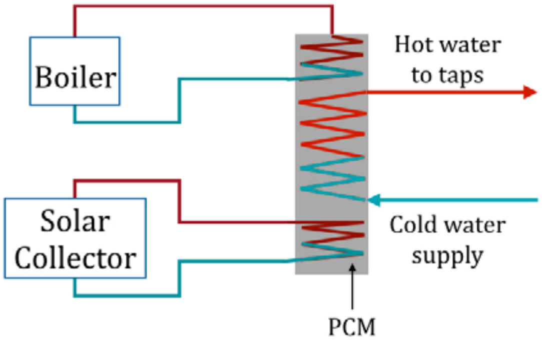


Fig. 12 Scheme of hot water systems (adapted from [22]).

Chapter II.

Hypothesis, Objectives and Structure of thesis

II.1 HYPOTESIS

Using the sun as a renewable energy source to reduce pollution and CO_2 emissions producing electrical energy or reducing the use of it, is taking more importance day by day both worldwide and within Chile. Due to Solar Energy is not continue available, is necessary to store it while solar energy is available to use it when the source is not available. For this reason, the research has as hypothesis that is possible to obtain mixtures of inorganic salts of two or more components, which will have a thermal stable behavior, with adequate melting points, heat of fusion and heat capacity to be applied as thermal solar energy storage materials.

II.2 OBJECTIVES

(a) Overall objective

To design new materials, characterize their chemical and thermal properties and test its potential application in thermal energy storage (TES) systems.

(b) Specific objectives

- To review literature related to thermal storage, phase change materials (PCMs), sensible heat thermal storage (SHTS) and phase diagrams of eutectic mixtures.

- To study the phase equilibrium of mixtures of inorganic salts by Differential Scanning Calorimetry (DSC) method.

- To select most promising materials and characterize their chemical and thermophysical properties for potential application in TES systems at lab and pilot scales

- To assess the viability of applying TES materials based on their operation temperature ranges.

II.3 STRUCTURE OF THESIS

During the PhD thesis several experimental measurements were conducted in order to characterize the thermal, chemical and thermophysical properties of four simple and double hydrated salts, which were Bischofite (>95 % $MgCl_2 \cdot 6H_2O$), Astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), Kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$) and Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). These materials are by-products and waste from non-metallic industry in the northern Chile, which precipitate in the solar evaporation ponds that are part of the process to obtain $LiCO_3$, KCl and KNO_3, as are shown in Fig. 13 and Fig. 14.

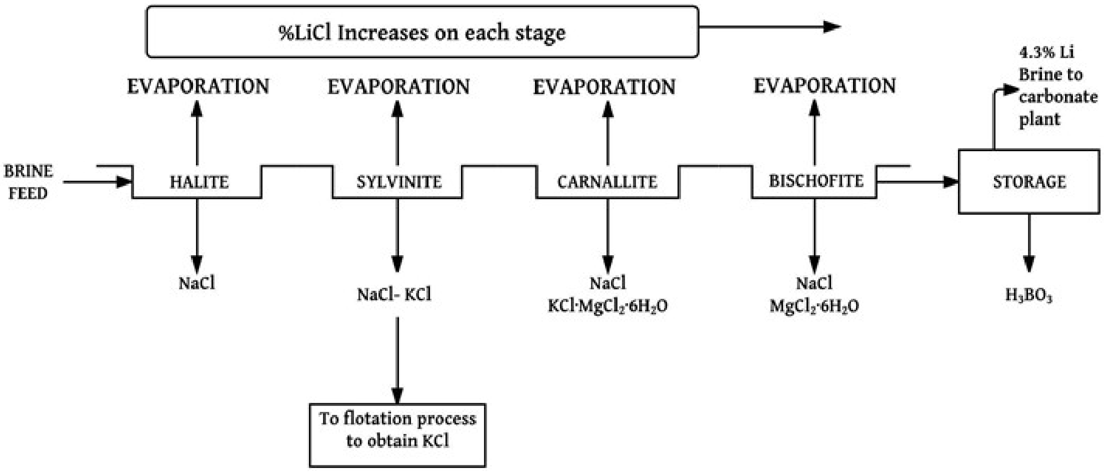


Fig. 13 Process to obtain Li_2CO_3 and KCl from salt flat San Pedro de Atacama.

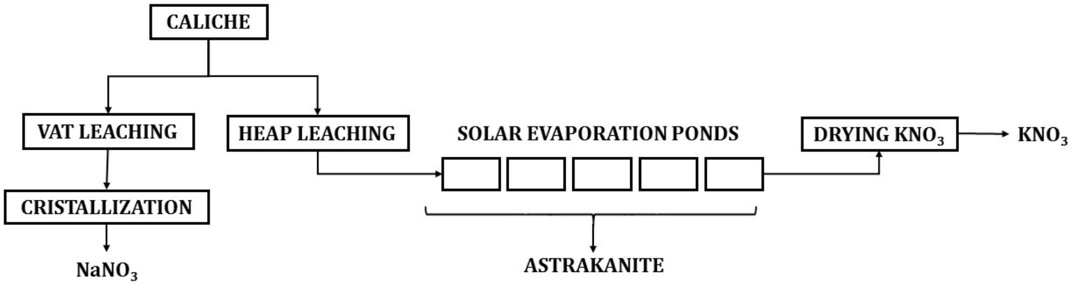


Fig. 14 Process to obtain KNO_3 from Caliche.

The salt characterization results were reported and published as journal papers, procedias and congress proceedings (some manuscripts are submitted and others still under elaboration). Fig. 15 shows the structure that had been followed to report the results obtained from the performed studies.

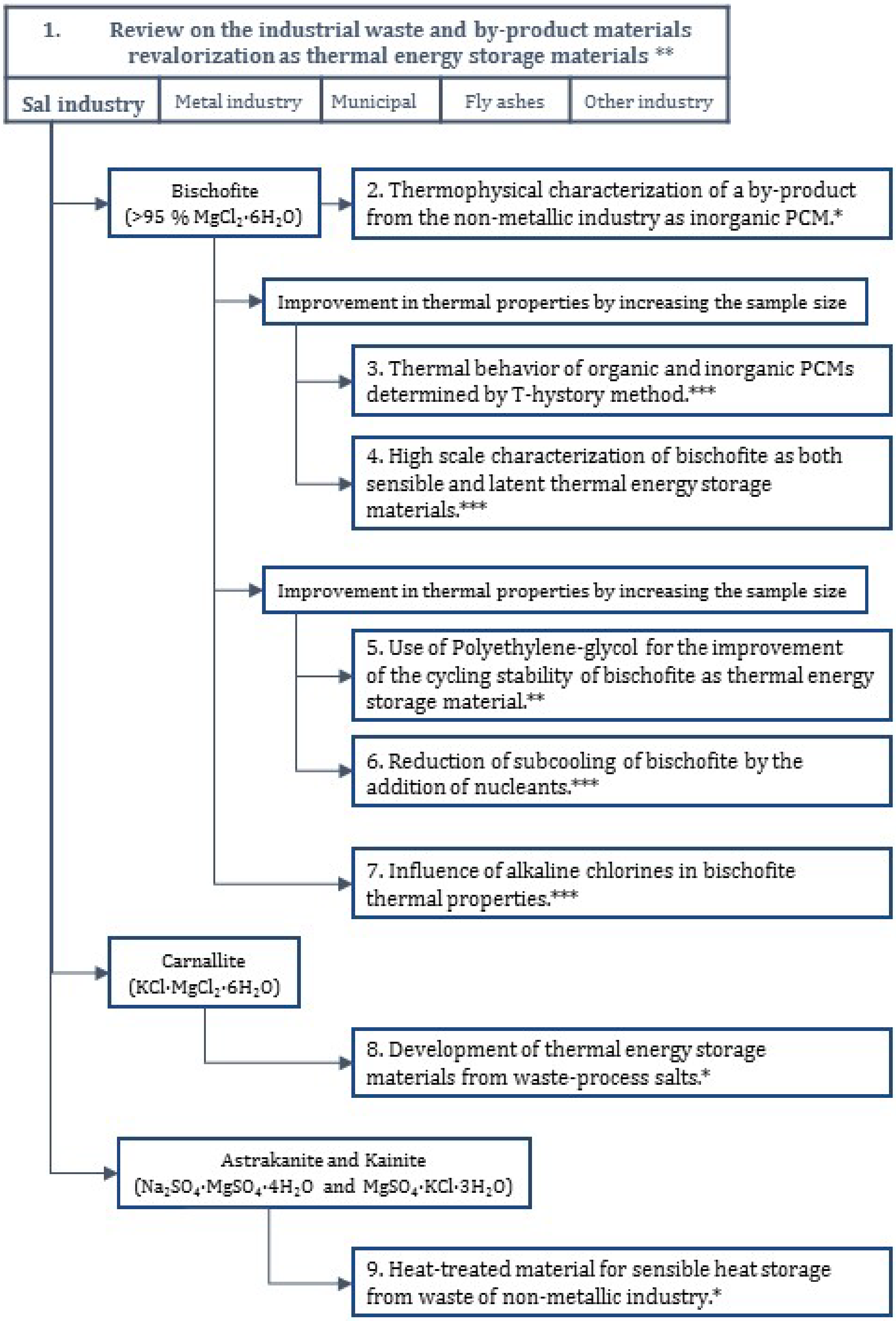


Fig. 15 Structure of thesis based on papers with results of experimental measurements.

** Paper already published.*

*** Manuscript submitted.*

**** Manuscript under elaboration.*

Chapter III.

Review on the industrial waste and by-product materials revalorization as thermal energy storage materials

III.1 Introduction

This chapter gives the information about the waste materials and by-products that have been studied and tested worldwide up to now as thermal energy storage materials. According to the amount of energy demand and supply it is necessary to implement storage energy systems to reduce the gap that exits between them; furthermore storage materials that are being used in commercial application are too expensive to make those systems profitable at large scale and efficient. Finally there are tons of waste materials and by-products, which don't have specific applications, the use of these materials will have a strong impact environmentally speaking and it is a useful way to increase their value-addition.

The scope of this review was focused mainly in these aspects:

- Materials that are being under research to be applied as thermal energy storage materials, based on low cost materials as waste or by-products.
- Different industrial waste materials have been considered as potential TES and have been characterized as such.
- To show that revalorization of wastes or by-products can be carrying out.

Bibliography shows that some industrial wastes have potential application as TES materials. Up to this time, those that have been studied come from the metallic and non-metallic industry, also asbestos containing wastes (ACW) and fly ashes, and finally municipal wastes, using glass and nylon.

The main contributions of this review are summarized below:

- Thermophysical properties
  - Characterization at small and large scale.
  - Melting temperature within the operating temperature range, for the phase change materials (PCM), at low, medium and high temperature.
  - Thermal stability within the operating temperature range for sensible heat storage materials.
  - Heat capacity of PCMs and SHS materials.
  - Small change density on phase transformation from solid to liquid and vice versa.
  - Thermal conductivity.

- Chemical properties
    - Morphological characterization.
    - Cycling stability during heating and cooling.
- Economics
    - Amounts of production by year
    - Prices of by-products materials
    - Life Cycle Assessment (LCA) performed for some materials.
    -

→ Most of wastes materials need a previous treatment before can be apply as thermal energy storage material.

→ Most of the wastes materials have potential to be applying as sensible heat storage material at high temperature (from 500 °C to 1100 °C).

→ The wastes materials from non-metallic industry have potential application, mainly as PCM at low temperature.

→ Astrakanite and carnallite which have potential to be applied as SHS materials at medium temperature, from 200 °C to 500 °C.

→ Looking for the best way to contain these materials without degradation and lost of them or without the corrosion of containers, would enable to test these materials at high scale.

Chapter IV.

Industrial mineral as thermal energy storage

IV.1 Introduction

Chapter V provides the results obtained for thermal, chemical and thermophysical characterization of hydrated salts. It is well know that inorganic materials specially hydrated salts have high latent heat of phase change in the case of Phase change materials and also relatively high values of heat capacity, this property is from the point view of both latent and sensible heat storage.

The scope of these studies was focused on different aspects:

- Morphologic and chemical composition of these wastes materials and by-products.
- Evaluation of thermal stability and decomposition temperatures wastes materials and by-products.
- As hydrated salts mainly compose these salts, thermal stability through cycles of heating and cooling were also studied.
- Thermal properties as melting point, latent heat of fusion and heat capacity were also evaluated.

Bibliography shows a wide range of inorganic materials that are being applied as both latent heat and sensible heat energy storage [12-15, 18].

IV.2 Bischofite

This section shows the characterization of bischofite by itself and also with some additives in order to improve their thermophysical properties. Bischofite is available in two qualities on the industry, standard and “A grade” quality, the quantity of production of one or another would depend on the demand of clients. The main difference between them is the content of $MgCl_2{\cdot}6H_2O$; “A grade” quality has a higher concentration of this component than standard quality, what gives a higher price per ton, ≅150 US$/ton and 40US$ US$/ton respectively, it is important to mention that the price of A grade is defined based on the price of synthetic $MgCl_2{\cdot}6H_2O$ on the market, but always lower.

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

Bischofite was extensively studied during the PhD thesis because of it abundance in this region of the country and also it low price.

The scope of this section is described below:

- To evaluate by-product from non-metallic industry to be apply as PCM at low temperature.
- Characterize their chemical properties and determine the presence of impurities of bischofite.
- Compare chemical properties with those for synthetic $MgCl_2 \cdot 6H_2O$.
- Characterize thermophysical properties as melting point, heat of fusion and heat capacity of bischofite and compare them with those for synthetic $MgCl_2 \cdot 6H_2O$.
- Determine physic properties as density and viscosity of both bischofite and $MgCl_2 \cdot 6H_2O$.
- Evaluate the cycling stability through cycles of heating and cooling of both bischofite and synthetic $MgCl_2 \cdot 6H_2O$.
- With properties determined, calculate the Energy Storage Density (*esd*) for both materials.

The results obtained at lab scale were published as:

- Svetlana Ushak, Andrea Gutierrez, Hector Galleguillos, Angel G. Fernandez, Luisa F. Cabeza, Mario Grágeda. Thermophysical characterization of a by-product from the non-metallic industry as inorganic PCM. Solar energy materials and solar cells 2015; 132: 385-91.

The main contributions of this work are as follow:

- Thermophysical properties as melting and crystallization point, and also heats of fusion and crystallization where determined for.
- Those thermophysical properties were compared with synthetic $MgCl_2 \cdot 6H_2O$.
- Phisycal properties as density and viscosity where determined for bischofite and $MgCl_2 \cdot 6H_2O$.
- Thermal stability were performed by cycles of heating and cooling for both bischofite and synthetic $MgCl_2 \cdot 6H_2O$.

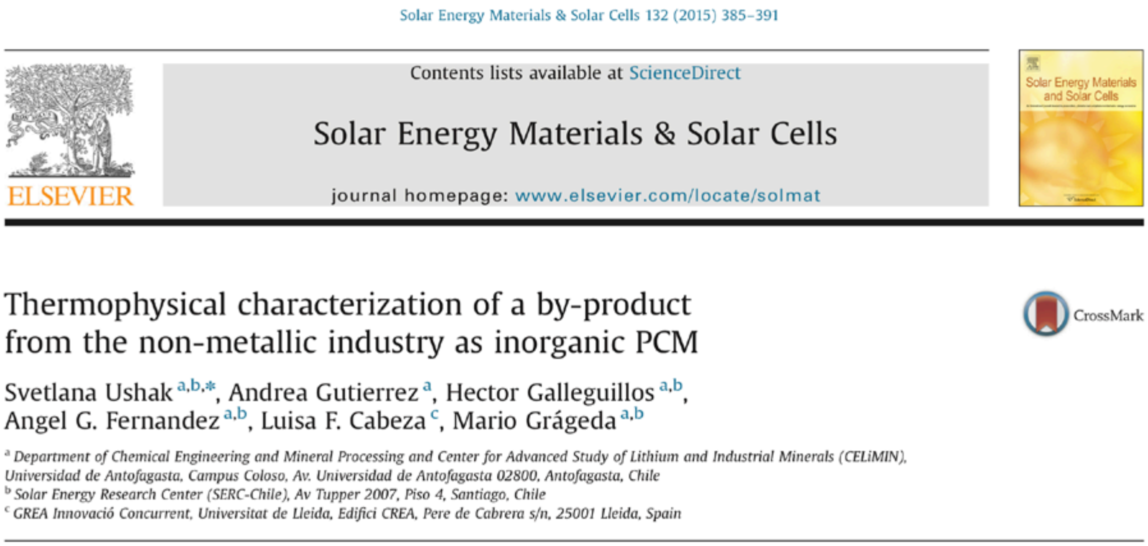
→ The melting point of bischofite and the synthetic $MgCl_2 \cdot 6H_2O$ determined were relatively close with 98.9 °C and 114.5 °C respectively, the difference is mainly due to the presence of impurities in bischofite (≅5% composition of impurities), which in this case reduce the melting point of bischofite in almost 15 °C.

→ A similar behavior was observed in the heat of fusion, where were determined 120.2 kJ kg^{-1} and 126.6 kJ kg^{-1} for bischofite and synthetic $MgCl_2{\cdot}6H_2O$ respectively.

→ The heat capacities for both solid samples were similar and close to 2.0 kJ kg^{-1} K^{-1}, so the impurities didn't have an important effect over this property. The heat capacity of melted bischofite was determined; the values for liquid bischofite increased linearly almost 50% at temperatures over 115°C.

→ Thermal stability through cycles of heating and cooling showed a subcooling of about 37°C and 29 °C for bischofite and $MgCl_2{\cdot}6H_2O$ respectively, which means that more study was needed to permit the application of these materials.

→ The evaluation of the density as a solid and liquid salt showed that the volume increased on 13% from solid to liquid phase. And also permitted to calculate the *esd*, which were 170 J cm^{-3} and 192 J cm^{-3}, remarkable similarities for a by-product salt in comparison with a synthetic salt.



Solar Energy Materials & Solar Cells 132 (2015) 385–391

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

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doi:10.1016/j.solmat.2014.08.042

IV.3 Improvement in thermal properties of bischofite by increasing the sample size

Increasing the scale of experimental methods is one of the ways to reduce the subcooling and improve cycling stability, reported by other author in previous research [23, 24]. That is why was decided to tested bischofite by itself at higher scales. The samples sizes were increased from 10 mg at lab scale to 15 g at medium scale and 225 kg at pilot plant. Summaries of the results obtained are described below:

(a) Thermal behavior of organic and inorganic PCMs determined by T-history method

Thermophysical characterization of bischofite was determined at medium scale with T-history method, using approximately 15 g of sample to evaluate it melting point and latent heat of phase change. The results obtained were close to those obtained at lab scale, a melting point of 102 °C and higher heat of fusion of 168 J g^{-1}. In addition to these measurements, some cycles of heating and cooling were performed. The results obtained indicate a stable behaviour upon cycling, since the values of melting point are identical within the limits of measuring reproducibility. Crystallization temperatures in T- History measurements were between 95°C and 98°C, which leads a subcooling from 4°C to 8 °C, much smaller than at lab scale with 37°C of subcooling.

Due to the hygroscopic characteristics of this salt, the water content by Karl-Fischer titration was determined. The measured water content was 62.68 ±0.81 as percentage by mass.

These results of T-history measurements were compared with other, performed for organic PCMs to propose them as thermal energy storage materials and a manuscript is currently being developed with a significant progress, this is the reason that this document only presents an abstract of the manuscript.

(b) High scale characterization of bischofite as both sensible and latent thermal energy storage materials

Also, thermophysical properties were determined at high scale in a pilot plant, using samples of 225 kg to test bischofite as a SHS and LHS material. With thermal properties previously determined at lab scale, as conductivity and latent and sensible Cp, made possible to calculate, such as the temperature profiles below 80 °C and the amount of energy stored. The same process was performed for LHS for the temperature range from 80°C to 120°C, the energy stored and power were also determined with the treatment of results obtained. The main results indicated that at high scale, in the case of LHS and the evaluation of bischofite as PCM, it almost does not present subcooling, as the melting point and crystallization temperatures remain constant during heating and cooling cycles. The manuscript to report these results is under developing, with an important progress.

IV.4 Improvement of thermal properties of bischofite by using additives

For bischofite can be applied at medium scale, where less than 10 kg of material is required, the use of additives to improve thermal properties is needed. On the one hand, the manuscript where are reported the results obtained for bischofite and polyethylene glycol of different molecular weights, used as a thickener to avoid phase segregation is already submitted and described below. On the other hand, the manuscript which reports results obtained for thermal property improvements with the addition of nucleants is under development, for this reason only a summarize of it is shown in this document.

(a) Use of Polyethylene-glycol for the improvement of the cycling stability of bischofite as thermal energy storage material.

Phase segregation is a common problem of hydrated salts. Usually, this produced because molecules of water are not enough to dissolve solid salt during the melting process, so they settle at the bottom of the container [12]. Some authors recommend the use of thickener agents to avoid this problem [25, 26], which can be organic or inorganic. The scope of this work is described below:

- Thermal property improvements of bischofite;
- Use of an organic material, polyethylene glycol, use in this case as a thickener additive that usually was study as a PCM by itself;
- Evaluation of long-term stability, through heating and cooling cycling of bischofite mixtures with PEG of different molecular weights.

The main contributions of this work are summarized below:

- Thermal stability comparison between bischofite and mixtures of bischofite with polyethylene glycol of different molecular weights;
- High latent heat of fusion of a specific mixture;
- High thermal stability through heating and cooling cycles;
- Reproducible phase change temperatures;
- Non-toxic and non-explosive mixtures;

- No degradation of samples after a large heating and cooling cycles.

→ The PEG 600 had more influence over thermal properties of mixture with bischofite, reducing both the melting point and heat of fusion from 98.9 and 120.2 J g-1 to 79.3C and 61.1 J g-1 respectively, this is a disadvantage for a material can be applied as thermal energy storage.

→ The mixture of bischofite with 5% of PEG 2000 was the most stable of the three tested, because the temperature of crystallization with this additive, even though are lower than those obtained for the melting points, remains stable during the cycles of heating and cooling.

→ The potential applications for these mixtures, based on the temperature of phase change (~100C), could be for indoor solar cooking or industrial waste heat (IWH) recovery.

→ Although the melting and crystallization points remain constants during the cycles of heating and cooling, more studies were performed and are reported in the next manuscript, which shows the addition of nucleants.

(b) Reduction of subcooling of bischofite by the addition of nucleants

Another disadvantage that hydrated salt present is the subcooling, which consists in have different temperature of melting and crystallization point during heating and cooling cycles, respectively. This is a big problem if a material is intent to be applied as PCM, because one of the main requirement for materials can be applied as LHS is to having a melting point within the range of operational temperature, having the same melting and solidification point and these temperatures need to be reproducible during cycles of heating and cooling. Bischofite also have this problem, with a subcooling of 37°C (see paper attached in ANNEX II), this value was obtained after 30 cycles of heating and cooling evaluated with DSC method. It also could be seen that this subcooling doesn’t remains constant through the cycles. Some authors have tested the addition of nucleants to reduce subcooling in PCM successfully. The effect of nucleants in the mixtures is to initiate the nucleation during the cooling process, so the hydrated salt can crystallize in its initial form. Literature provides the criteria that some authors are using to determine if a nucleant will be the adequate for a material or not. The criteria are shown below:

- Thermal stability: Nucleant must have a higher melting point than hydrated salt.
- Solubility in water: lower solubility in water than hydrated salts.

- Nucleant must bind water in its structure.
- Similar crystalline structure between PCM and the nucleant. This criteria was propose by us, although some other authors propose that nucleant crystal structure has to "fit well" with the PCM structure [27].

Based on the criteria mentioned above, the nucleants selected were $SrCO_3$, $Sr(OH)_2$, Li_2CO_3, $LiOH \cdot H_2O$ and CaO.

DoE software was used to design the mixtures composition of bischofite and nucleants (from 1% to 3%). Chemical data as solubility of nucleants and bischofite were collected from literature. Also, data available for crystal structure was review but confirmed with DRX analysis to determine the space group of nucleants, due to some different space group was reported for the same nucleant. Thermal properties were determined with DSC method. The best nucleant was determined based on the one that reduce more the subcooling. The subcooling reduce from 37 °C of bischofite varied depends on the nucleants added, being the results as follow: for Li_2CO_3 subcooling range obtained was from 11 °C to 28 °C, for the nucleant $LiOH \cdot H_2O$ was also high from 17 °C to 24 °C and for CaO was even higher, from 20 °C to 26 °C. The two nucleants that worked the best were $SrCO_3$, $Sr(OH)_2$ with ranges of subcooling from -0.6 °C to 20 °C and from 0.9 °C to >10°C respectively, even 20 °C is still a high value of subcooling there are compositions of mixtures $Sr(OH)_2$ (3% w/w $Sr(OH)_2$) that reduces the subcooling near to 0°C. This manuscript is also being developed with a significant progress.

IV.5 Evaluation of impurities over thermal properties of bischofite

(a) Influence of alkaline chlorines on thermal properties of a by-product salt to be applied as thermal energy storage material

Bischofite, as was mentioned above, it is a by-product from non-metallic industry that precipitates during the process to obtain KCl and Li_2CO_3, which means that to obtain bischofite remaining a constant composition, is not the main focus of the companies that produce these salts. This is why for this research was decided to evaluate the influence of alkaline chlorides impurities, which are always part of bischofite composition, on the thermal properties. The alkaline chlorines that were chose are NaCl, KCl and LiCl.

IV.6 Atrakanite and Kainite

(a) Development of thermal energy storage materials from waste-process salts

There are several by-products and waste salts from non-metallic industry in Chile, which almost don't have any application up to now. This means that their market prices are low or in some cases are even for free. On the one hand the industry is interested in finding some application for these materials so they can increase their incomes, on the other hand, as researchers we are looking for alternative low cost materials to be applied in energy storage systems, so it is possible to reduce their costs. In order to solve this issue, the scope of this work is described below:

- Characterization of two double hydrated salts, which are wastes materials from non-metallic salts.
- Study of their morphological and chemical composition.
- Evaluation of thermal stability thermal properties.

The main contribution of this work were as follow:

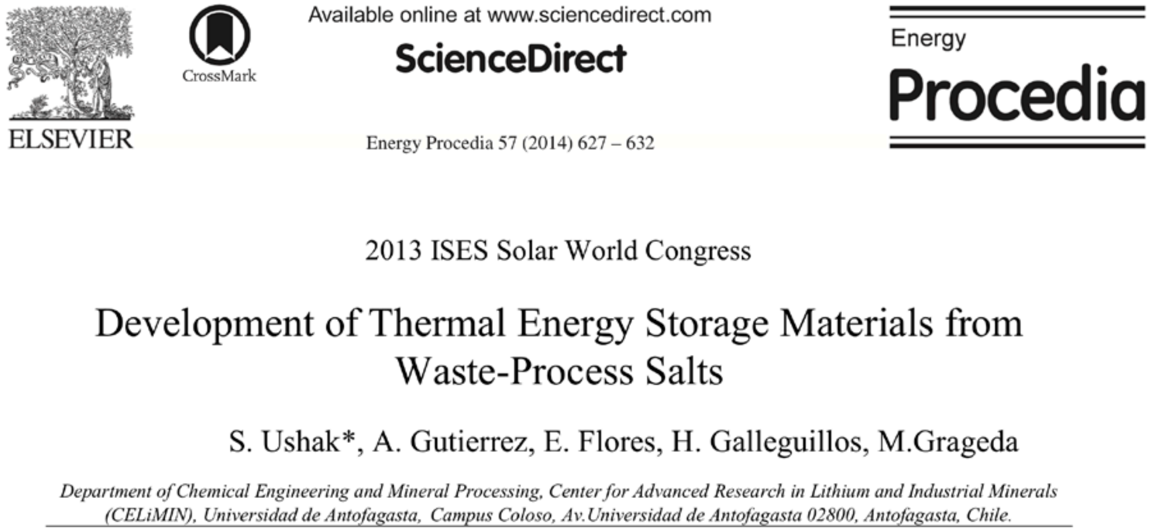
- Morphological information of both Astrakanite and Kainite and also the impurities those are present on these samples.
- Thermal phenomena those are present in the range of temperature from 0 °C to 400 °C.
- Thermal and cycling stability of anhydrous Astrakanite in the temperature range from 550 °C to 750 °C.
- Heat capacity at low temperature in a range from 0°C to 100 °C for Astrakanite and heat capacity for anhydrous Astrakanite at medium temperature from 350 °C to 500 °C.

→ Both salts astrakanite and kainite, are suitable to be used as sensible heat storage materials at low temperature, from 0 °C to 100 °C .

→ Two heat-treated salts from astrakanite also presented stable stages to be applied as thermal energy storage.

→ The first stage was from 180 °C to 280 °C to be applied as sensible heat storage material. In this range of temperature, astrakanite already lost 2 molecules of water this could be established stoichiometrically.

→ The second stage is at high temperature, from 550 °C to 750 °C, where the astrakanite had already lost the 4 molecules of water. This new anhydrous salt showed a cycling behavior of melting and solidification, so this heat-treated salt show potential to be applied as a phase change material at high temperature.



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Energy Procedia 57 (2014) 627 – 632

Energy Procedia

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Development of Thermal Energy Storage Materials from Waste-Process Salts

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doi:10.1016/j.egypro.2014.10.217

IV.7 Carnallite

(a) Heat-treated material for sensible heat storage from waste of non-metallic industry

The other by-product evaluated during the PhD was carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), which as was explained above, precipitates during the process to obtain Li_2CO_3 and KCl. The scope of this work is below:

- To evaluate thermal stability of carnallite using TGA method, within a wide range of temperature, from 50 °C to 1000 °C.
- Discuss potential application at medium temperature as sensible heat storage material.
- Determine heat capacity at low and medium temperature.

The main contributions for this work are summarized below:

- Thermal behavior of carnallite from low to high temperature.
- Thermal stability ranges for potential application as sensible heat storage as carnallite or as a heat-treated product of carnallite.
- Heat capacity of carnallitle and the heat-treated product for the thermal stable ranges of temperature.

→ Thermal stability of carnallite was evaluated in a wide range of temperature, from 50 °C to 1000 °C.

→ From 50 °C to 160 °C the salt lost 5 molecules of water, this was stoichiometrically calculated.

→ From 160 C to 400C this heat-treated salt remains stable without losing any mass, only presented a thermal phenomenon that can be a physical transition. According to this, heat-treated carnallite has potential to be applied as sensible heat storage material.

→ Further studies are currently undergoing, for this reason in this document are show only the overall results presented in a conference in October 2014.

Chapter V.

CONCLUSIONS

The study presented in this thesis was set up to find cost-effective materials that have potential to be applied as thermal energy storage materials, either as sensible or LHS materials. To evaluate this potential, thermophysical characterization of by-products and waste materials have been carry out. To improve the thermophysical properties of tested materials, on the one hand measurements at different scale size were performed, on the other hand some additives were used. The main conclusions of this study are as follows:

- The extensive literature review showed that several materials have been tested and proposed to be applying as TES materials, however, almost of them are too expensive for TES system to be cost-effective. It was also found that only few studies of waste materials or by-products applied as TES materials have been carry out.
- To provide the require tools and knowledge for the development study, was developed a review with all the information and results of the by-products and waste materials that have been characterized and tested as TES materials available up to now.
- The results obtained for bischofite show that this mineral is suitable for applications at low temperature (<120 C) as a PCM, with a melting point close to 100 C. If it is applied at large scale, there is not need for the use of additives, because bischofite showed stable behavior through cycles of heating and cooling, also non-subcooling was observed at pilot-scale study.
- On the other hand, if bischofite is going to be applied at small scale, it will be necessary to use additives, such as nucleants and thickeners, to stabilize the mixtures and their thermal properties though cycles of heating and cooling.
- The best nucleants for bischofite were Sr(OH)2 and SrCO3, because they reduced the subcooling from 37 C to -0.6 C and 0.9 C respectively, when they were added in a 3% w/w.
- The thickener that worked better was PEG 2000 added to bischofite in a 5% w/w. The results showed that this organic material avoided the phase segregation of bischofite, which allows the crystallization point to remain constant through cycles of heating and cooling.
- LiCl was the one that had more influences over them, reducing the melting point of bischofite in 17 C. If it is necessary to modify the melting point of bischofite for specific applications, LiCl would be the best option to be used as an additive.

- Astrakanite and kainite are suitable to be applied as SHS materials at low temperature (<100°C), with values of heat capacity of 1.131 J $g^{-1}K^{-1}$ and 0.985 J g^{-1} K^{-1} respectively.
- A heat-treated material from Astrakanite is suitable for applications at high temperature as PCM, in the range of temperature from 550 °C to 750 °C , showing reproducibility through cycles of heating and cooling.
- A heat-treated material from Carnallite has potential to be applied as SHS material at high temperature, in the range of temperature from 160 °C to 400 °C .

Recommendation for future work

- It is recommendable to test all potential materials presented in this PhD Thesis at different scale to evaluate the feasibility of different applications of them, from lab scale to pilot plant scale and also several cycles of heating and cooling to test the stability of these salts.
- For salts that are suitable to be applied as PCM is important to evaluate the best way to encapsulate them, taking account the applications and which properties have to be remain.
- Before TES systems designing, either with PCM or SHTS materials, is necessary to develop corrosion tests to evaluate the compatibility of TES materials with the containers materials.
- To develop a technic economical evaluation for the applications of these potential materials as TES.

Chapter VI.

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ANNEX I
MANUSCRIPT OF REVIEW COMPLETED TO SUBMITT TO PROGRESS IN MATERIAL SCIENCE

Review on industrial waste and by-product materials revalorization as thermal energy storage (TES) materials

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Abstract

Today our society must face is the satisfactory supply, dispatchability and management of the energy. Thermal energy storage (TES) has been identified as a breakthrough concept in industrial heat recovery applications. A wide variety of potential heat storage materials has been identified depending on the implemented thermal energy storage method: sensible, latent or thermochemical. Although no ideal storage material has been identified, several materials have shown a high potential depending on the mentioned considerations. Despite the amount of studied potential heat storage materials, the determination of new alternatives for next generation technologies is still open. In this regard, this paper presents the review of low cost heat storage materials with a double objective: in one hand, the implementation of improved heat storage devices based on new appropriate materials and, on the other hand, the valorisation of waste industrial materials will have strong environmental, economic and societal benefits such as reducing the landfilled waste amounts, reducing the greenhouse emissions and others.

Different industrial waste materials have been considered as potential TES materials and have been characterised as such. Asbestos containing wastes, fly ashes, by-products from the salt industry and from the metal industry, wastes from recycling steel process and from copper refining process and dross from the aluminium industry, and municipal wastes (glass and nylon) have been considered. This review shows that the revalorisation of wastes or by-products as TES materials is possible, and that more studies are needed to achieve industrial deployment of the idea.

Key words: Thermal energy storage (TES); Industrial waste; Slags; Aluminium dross, Inorganic TES

Contents

1. Introduction

1.1 Thermal Energy Storage (TES)

One of the most important challenges that current society must face is the satisfactory supply, dispatchability and management of the energy. In this frame, a successful and efficient exploitation of all the energetic resources, fossil and renewable, will be the key factor in order to reach a fair and equitative distribution of the available energy. According to the societal and industrial development previsions, the energy information administration (EIA) predicted an increase of the energetic demand on OECD and non-OECD countries of around 25 % and 88 % respectively in 2040 [1]. Predominantly the main responsible of this increase will be the emerging countries where the development of heavy industries such as steel, ceramic, glass, and others has experienced an important growth. In addition, the energy demanded by domestic and transport applications have also suffered a noticeable increase in the last years. The fossil fuel dependence usually suffered by these activities is expected to be reduced in the next decades in favour of alternative renewable technologies.

Among the different renewable energies, thermo-electric power generation in concentrated solar power (CSP) plants presents several strategic advantages when compared with photo-voltaic (PV), wind, geothermal or hydraulic. One of the most representatives is the possibility of heat storage, which allows improving the capacity factor and overall efficiency of the plant [2]. This fact makes large scale solar-thermal electricity generation particularly interesting as it allows adapting the generation to the demand (dispatchability), extending the production to non-solar irradiance periods and equilibrating the power generation avoiding undesirable production peaks [3]. In addition, thermal energy storage (TES) systems are nowadays considered as an integral part of CSP plants, which contributes to reducing the electricity costs, increasing of the annual solar-to-electricity efficiency of the plant (13.2 % vs 12.4 % without storage) and providing higher potential viability of the CSP technology [4]. In order to reach the levelized cost of the electricity (LCOE) of 6 c$/kWh predicted by DOE for 2020 [5] and according to the predictions of International Energy Agency (IEA) for the next years [6], shown in Figure 1, the investment costs of CSP plants have to decrease around 50 % from 2010 to 2020. As a consequence, the produced electricity costs would decrease in the same ratio or even faster thanks to a progressive efficiency increase. This fact makes CSP technology more competitive compared to conventional technologies.

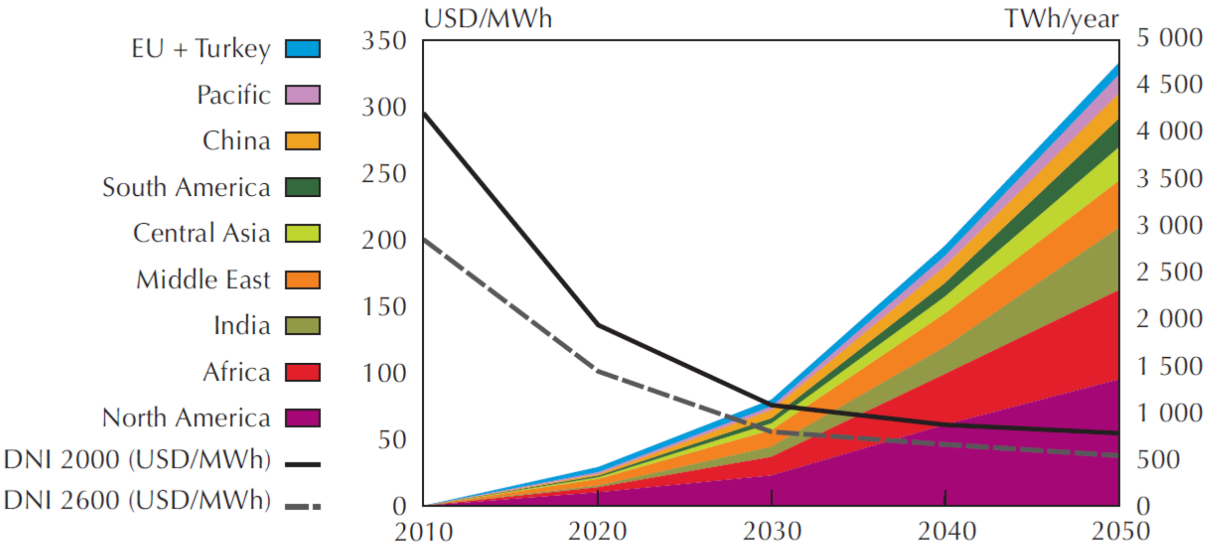


Figure 1 Expected price and CSP installed in Spain and US for the next 35 years [3].

In the particular case of a 50 MW parabolic trough CSP plant the investment costs of a TES system represents around 10 % of the total plant cost. The investment and performance of TES systems mainly depends on the storage material being in current technologies the most expensive part with around a 50 % of the total TES system [7].

A report published by ESTELA in 2013 [8] highlighted the key issues to be included in the European research programs for the next years, mainly focused on integrated TES systems in CSP plants summarized below:

- Reduce the costs of the storage (key performance indicators for 2010: 35,000 €/MWh$_{th}$, and for 2020 15,000 €/MWh$_{th}$), and increase the storage efficiency (key performance indicators for 2010: 94 %, and for 2020: 96 %) and dispatchability [9].
- Maximize storage capacity of existing designs which reduces the specific storage cost.

Up to now, and due to the variety of TES concepts reflected by different heat transfer fluids (HTF) and operating temperatures, there is not a clear leading technology for next generation of CSP plants and an strong research effort on different alternatives is still needed.

TES systems can also represent a breakthrough concept in industrial heat recovery applications. According to the report of US DOE [10], there are large heat recovery opportunities in different industrial processes. These applications require a particular research and development in order to adapt the heat production to the storage. In this regards, several industrial processes, shown in

Table 1, have revealed a strong recovery potential with the subsequent economic and environmental benefits. Some estimations [10] show that the implementation of TES systems in industrial heat recovery applications might increase the efficiency of the overall process and decrease the CO_2 emissions. In this regard, electricity and heat production are the main responsible of greenhouse gas emissions. As it may be seen in Figure 2, CO_2 emissions from energy supply (energy generation and transport) and use (final consumption) are the largest source in the EU-28 accounting for 60 % of total greenhouse gas emissions in 2011 [9]. The 4,050 TWh of solar electricity generated by CSP plants in 2050 are expected to avoid around 2.5 Gt of CO_2 emissions per year worldwide [11].

Table 1 Potential wastes heat amount and temperature of different industrial processes [10].

Industry	**Temperature range [ºC]**	**Recovery potential [%]**
Iron/steel	430 - 1700	8 – 47
Glass	427 - 1420	23
Cement	338 - 449	15
Metal casting	121 - 1150	33
Boilers	150 - 260	6

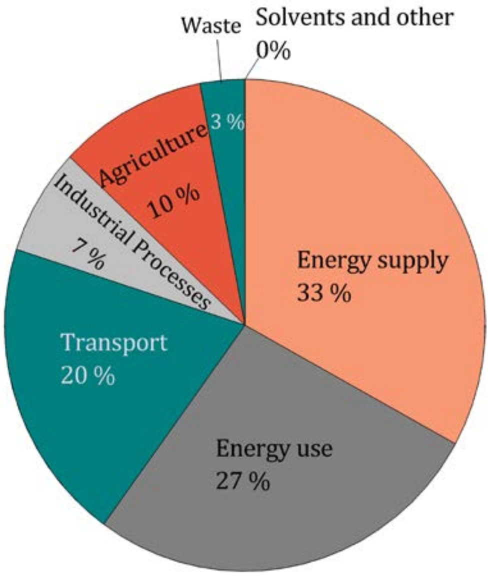


Figure 2 Share of emissions by sector in the EU-28 in 2011 [9].

In another field of industrial applications [12], TES present high potential as needed subsystem for internal industrial process optimization. Compressed Air Electricity Storage (CAES) can be given as a characteristic example of growing interest. Thanks to more than 30 years of large scale operation at Huntorf (Germany) and McIntosh (Alabama), CAES is acknowledged as a reliable alternative technology to conventional hydraulic systems. Nevertheless, if the heat of compression is lost, the efficiency is roughly limited under 50 %. Then, the integration of a TES subsystem would allow the valorisation of this heat leading theoretically to an efficiency up to 70 %. This TES unit should operate one to three full charging/discharging cycles per day in the range of 50 to 650 °C using compressed air as heat transfer fluid. Such operating parameters are obviously severe for a sensible heat based thermal energy storage material. Consequently, only high temperature refractory materials could be considered which are usually too expensive and present too high environmental footprint for such subsystem. Therefore, low - cost and environmentally friendly thermal energy storage materials (TESM) are highly needed for the future development of ACAES (adiabatic CAES) technologies.

1.2 Analysis of the TES materials currently used in commercial applications

A wide variety of potential heat storage materials has been identified depending on the implemented TES method: sensible, latent or thermochemical. The particular application also limits the suitable materials as a function of the operation temperature range, storage capacity, power and other requirements. Overall, although no ideal storage material has been identified, several materials have shown a high potential depending on the mentioned considerations.

In sensible heat storage applications, several authors have identified different attractive materials [13,14]. In this scope, according Khare et al. [15] appropriate sensible heat storage requires:

- Thermophysical properties: high energy density, heat capacity and conductivity and long term thermal cycling stability.
- Chemical properties: chemical stability, non-toxic, non-explosive, low potential reactivity with the HTF and the container material.
- Mechanical properties: good mechanical stability, low coefficient of thermal expansion, high fracture toughness and high compressive strength.
- Economic properties: cheap and abundant materials with low cost of manufacturing into suitable shapes.
- Environmental aspects: low manufacturing energy requirement and CO_2 footprint.

Among the large number of materials identified for sensible heat storage applications, two of them present a particular interest: water and different molten salt mixtures. The first one fully meets the necessities of a low temperature storage with a high storage capacity and economic viability. At higher temperatures, the most extended material in sensible heat storage applications are different molten salt mixtures: 60 % wt $NaNO_3$ + 40 % wt KNO_3 (the most common solar salt), Hitec heat transfer salt (7 % wt $NaNO_3$ + 53 % wt KNO_3 + 40 % wt $NaNO_2$), Hitec XL (12 % wt $NaNO_3$ + 46 % wt KNO_3 + 42 % wt $Ca(NO_2)_3$), Morton Solar Salt, etc. Current commercial heat storage applications are mainly based on these materials, which has led to a noticeable maturity level of this sensible storage technology. Anyway, sensible heat storage presents several limitations that next generation storage applications need to overcome. In this frame, the operation temperature range of the salts is limited between 250-265 ºC, which implies an important storage capacity limitation together with the need of continuous heat supply to the salts in order to avoid their freezing. In addition, their low thermal conductivity value, around 0.5 W m^{-1} K^{-1}, leads to a poor heat transfer coefficient, which implies the use of complex and expensive heat exchange devices.

The nitrate salts used in CSP are mainly (roughly 60 %) natural products for which Chile is acknowledged to be the worldwide leader for centuries. According to the related literature [16], the peak of production was 3 Mt/year in 1910 and only 0.8 Mt/year in 2007. If the current molten salt TES is applied to the expected CSP market growth [17], 9 to 20 Mt would be needed every year, definitely more than the actual production already shared by the needs in fertilizers and the chemical industry. Alternatively, synthetic nitrate salts could be used as TESM but this would lead to an increase in the Greenhouse Gas (GHG) content of 52 % [18]. Moreover, the extensive mining of those salts in the Atacama area has led to 132 Mt of wastes and 100 ghost mines over 417 km^2 of desert. This highlights the fact that even if a material is made of natural resources, its environmental impacts are not obviously negligible.

Latent heat storage method has also identified as a very promising concept in the heat storage frame. Although the number of commercial applications based on phase change materials (PCM) is currently very limited, latent heat storage presents several advantages when compared with sensible, among them, larger storage energy density and constant or quasi-constant operation temperature. Several authors have identified a wide variety of PCM [19-22]. In this case, a high phase transition latent heat, thermal conductivity and density are desirable. Depending on the application, the transformation temperature is the other critical aspect of the suitable materials. The most interesting potential materials studied by the moment are paraffin, sugar alcohols or salt mixtures. Among the mentioned PCM, the main limitations are two: in one hand a low thermal conductivity value (between 0.5 to 5 W m^{-1} K^{-1} [19]) and a low operation temperature. Proposed in the 80´s, metals and metallic alloys have also been identified as very attracting materials because of their high thermal conductivity value, constant operation temperature and high operation temperature [23-25]. In particular, Mg-Zn and Mg-Zn-Al alloys have revealed a very interesting behaviour within the frame of high power and fast thermal response applications but associated with a prohibitive cost.

Thermochemical heat storage has been reported as a very interesting heat storage alternative because of its high potential storage energy density. However, the maturity level of these technologies is still in a preliminary state and a strong research effort is needed in order to become a real and viable alternative.

In order to clarify the level of development of the different storage systems Tamme et al. [26] provided in 2011 the maturity status of TES, pointing out that these technologies with the greatest potential to increase the energy density of the system were also these with less maturity level. As it may be seen in Figure 3, even if their energetic density is quite low compared with other media, sensible heat storage materials are currently the more commercially developed ones.

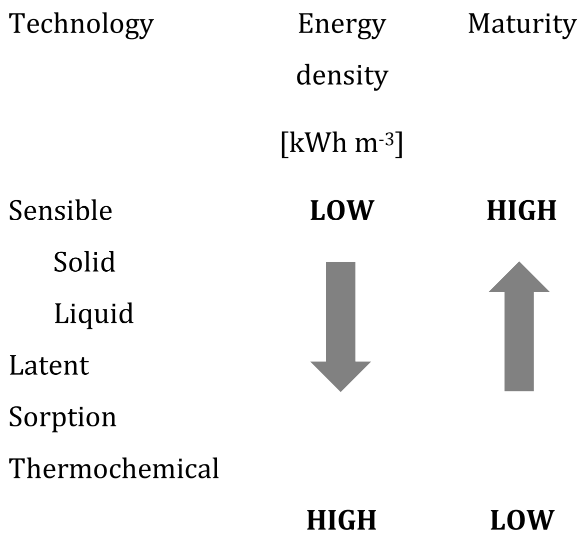


Figure 3 Maturity status of different TES technologies [26].

Despite the amount of studied potential heat storage materials, the determination of new alternatives for next generation technologies is still open. In this scenario higher operation temperature levels, up to 800-1000 ºC, larger storage capacities, improved chemical and mechanical stability, optimized environmental footprint and a low cost will be mandatory.

Almost all these properties related with the heat storage materials have to be well-known before the design and construction of a new TES system. On the other hand, environmental aspects are the less considered ones on the selection of a storage material. In order to evaluate the environmental impact of a given storage system Life Cycle Assessment (LCA) technique was used by Oro et al. [27]. LCA is a technique to assess the environmental aspects and potential impacts associated with a product, process or service. In particular, it takes into the inventory of relevant energy and material inputs and environmental releases to evaluate the potential environmental impacts associated to them. The work presented by Oro et al. analysed and compared the impact of the manufacturing and operation of three storage technologies based on liquid sensible heat (two tanks with molten salts), solid sensible heat (concrete) and latent heat (molten salts) materials. The analysis shown that the system based on two tanks of molten salts has the higher impact per kWh stored due to the specific equipment to withstand higher temperatures in the facility. On the other hand, even though the energy stored by the system based on concrete was the lowest one, the global impact per kWh stored was also the lowest due to the construction simplicity.

However, the critical issue in order to obtain an economically viable storage is to reduce the cost of the storage material. Aligned with this statement, one of the aims of this work is the review of low cost heat storage materials. In particular, the valorisation of industrial by-products and waste materials has revealed a high potential in the heat storage frame. In addition, this goal shows a double objective: in one hand, the implementation of improved heat storage devices based on new appropriate materials and on the other hand, the valorisation of waste industrial materials will have strong environmental, economic and societal benefits such as reducing the landfilled waste amounts, reducing the greenhouse emissions and others.

1.3 Low cost industrial waste and by-product materials

As explained before, among the most important improvements needed to overcome current storage limitations are the operation temperature range, storage capacity and total storage cost [8]. An overall enhancement of these issues might lead to an important competitiveness increase of solar-thermal power generation. In short, if the CSP technology wants to be a real alternative to power generation in the next decades, the total levelized cost of the produced electricity should follow the evolution shown in Figure 4 [5]. According to this prediction, the total cost of the plant should be reduced in 2020 a 51 % and a 42 % in parabolic trough and tower plants respectively, being the cost of the TES system around a 10 % of the total CSP plant [8]. Despite other possibilities of reducing the TES cost, the cost of the storage material represents an important fraction of the total amount. This makes the search of new low cost storage materials a critical activity in order to reach a cost-effective thermal storage alternative.

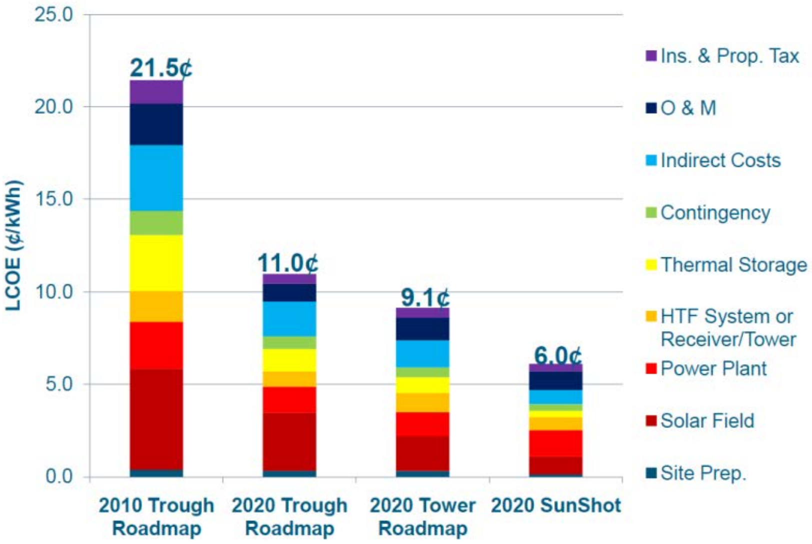


Figure 4 Roadmap of the total levelized cost of electricity in parabolic trough and tower plants from 2010-2020 [5].

In addition, the availability of the storage material in an enough amount is also a key factor to allow the scheduled CSP growth on the next years. Lack in the availability or even a conflict on the final use of the TES material may lead to variability on the price and risks the development of solar power.

In this frame, as indicated by several authors, the valorisation of industrial waste by-products as heat storage materials has shown a very high potential in order to reduce the cost of the storage [28]. Several waste materials have been considered and analysed, mainly for sensible heat storage. Among them wastes coming from asbestos (Cofalit®) [29,30], coal fly ashes [31,32], municipal solid waste incinerator (MSWI) fly ash [33], concrete [34] and slag from metallurgic industry [35] has revealed a high suitability for innovative heat storage solutions. This alternative presents several important advantages which might improve the efficiency and cost effectiveness not only of CSP industry but also of the industrial processes producing these by-products themselves. Among the benefits on CSP, the valorisation of industrial waste materials for storage could represent an important cost reduction of the cost of the material. This could help to match the storage cost reduction planned by Tamme [26]. In particular, some waste materials allow high temperature heat storage (up to 1200 ºC), depending on the particular thermal energy storage concept implemented. This is also an important added value to this type of materials. In the industrial area, the valorisation of waste products can also represent a viable alternative to reduce the environmental footprint of factories. In addition, currently, industry has to cover any suitable treatment of the produced wastes, which usually implies an important economic effort in order to inertise, landfill or perform any other procedure necessary to guarantee the satisfactory treatment of the by-products. In this work, different wastes from industry are reviewed in order to obtain a successful thermal energy storage concept.

2. Industrial waste materials used in TES

2.1 Asbestos Containing Wastes (ACW)

2.1.1 Definition of the waste material (origin)

Asbestos has been used worldwide during the XXth century in various well known industrial and domestic applications, leading to an estimated amount of 174 Mt/year consumption. Obviously, this already high amount of matter is only a fraction of the total inventory of Asbestos Containing Wastes (ACW). In the case of France, 250,000 t of ACW are produced every year, among which only 6000 t are industrially inertised while the rest is stored in landfills waiting for further treatment. Most of the countries have banned its use since 1995 and the containing already made asbestos containing materials are submitted to severe rules for dismantling and treatments. The health impacts of those materials are due to the micro fibrous structure of the Asbestos. Therefore, the rather unique industrial treatment approach allowing a full inertisation is necessary based on the melting of the material leading to the irreversible suppression of the fibrous structure.

2.1.2 Treatment technologies

As already mentioned, only melting based processes allow a full inertisation of the ACW. As such a treatment is necessary made at high temperature, around 1400 °C, the process is highly energy consuming and leads to a significant GHG and embodied energy amount of the obtained ceramic. Therefore, as demonstrated by the involved authors [29], only high temperature TES applications such as CSP or ACAES can really offer advantageous environmental pay back justifying the waste treatment.

Practically, those melting treatments involve plasma torch or microwave heating sources in semi batch reactors. The ACW are fed under sub-atmospheric atmosphere (avoiding any Asbestos fibre release to the surrounding environment) in the reactor containing a melted pool of matter. Semi batch withdrawal of the matter is poured within cast steel moulds and left for cooling under ambient atmospheric conditions. Then, within those current industrial operating conditions, several structural organization of the material are observed in the ingot [36]. The characterization of those structures have led to the selection of the best one regarding TES applications. Then, specific operating conditions of cooling (active or passive) were defined leading to moulded ceramic modules made of a unique proper structure of fine isotropic micron size crystals. This manufacturing approach was validated at both laboratory and industrial scale.

Complementary work was done with success to develop hybrid concentrated solar assisted process allowing significant reduction in the energy consumption of the treatment.

2.1.3 Thermophysical properties, characterization & compatibility studies

Both the glass and the ceramic made from melted ACW were characterized in terms of thermo physical properties of interest for TES applications. Original and valuable characterizations were made on their thermo mechanical properties under thermal cycling and high temperature to assess their ability to sustain thermal stress and fatigue. The obtained basalt-like ceramic presents stable values of its properties in the range of those already known for rocks of similar compositions. Even if the ACW initial composition can be seen as highly fluctuating, the main major involved compounds (O 32 % wt, Ca 31 % wt, Si 23 % wt, Fe-Mg-Al 13 % wt) control the various properties. As illustrated in the X-Ray Diffraction (XRD) diagram of Figure 5, the glass crystallizes at a temperature of about 900 °C to form a ceramic made of Wollastonite, Akermanite and Augite. As highlighted in the same diagram, the structure of the obtained ceramic is very stable under successive thermal cycling between room temperature and 1000 °C. This result demonstrates the ability of the recycled ACW ceramic to sustain high temperature thermal cycling.

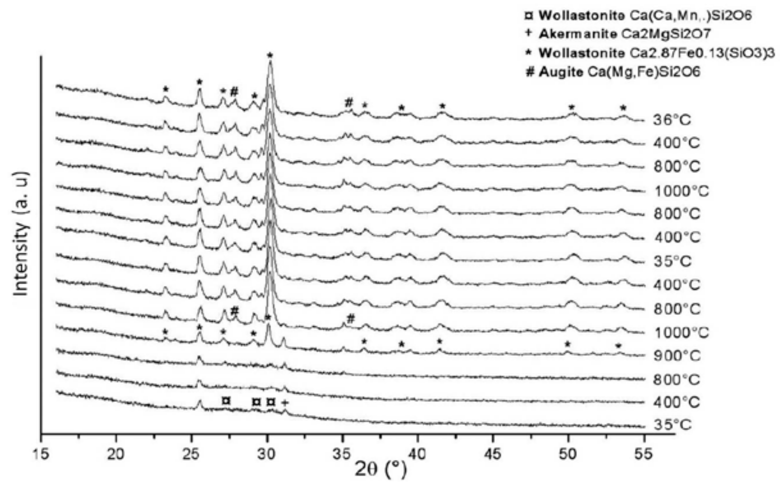


Figure 5 XRD diagrams of the ACW glass and ceramics under thermal cycling [29].

The characterization of the ACW ceramics from room temperature up to 1000°C led to the following range of values: 3120 kg/m^3 in density, 0.800 to 1.034 kJ kg^{-1} K^{-1} in thermal capacity, 2.1 to 1.4 W m^{-1} K^{-1} in thermal conductivity, 8.8 10^{-6} K^{-1} in coefficient of thermal expansion. The behaviour of the Young modulus was studied using an original ultrasonic pulse echography from room temperature up to 1000°C. The results, illustrated in Figure 6, highlight the refractory behaviour of those ceramics and then their ability to sustain severe thermal cycling operating conditions. Those assessments were confirmed by extreme thermal cycling made between 500 and 1000°C under concentrated solar flux with cooling and heating rates of 100, 300 and 2500°C min^{-1}.

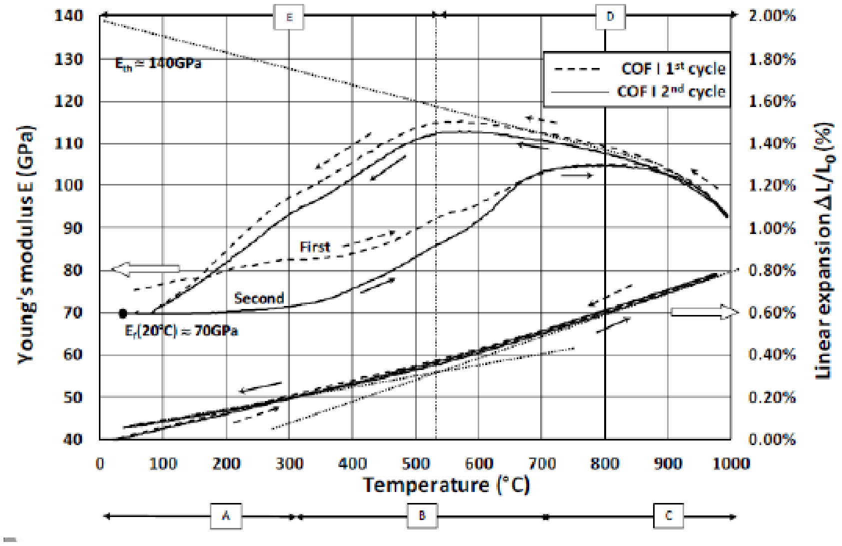


Figure 6 Young modulus and linear expansion of the ACW ceramics under thermal cycling [37].

The compatibility of the ACW made ceramics has been studied for various heat transfer fluids (HTF) of interest currently used in TES applications: molten salts, hot air, compressed hot air, oil, hot water and atmospheric steam. The tests were achieved by direct contact between ceramic samples and the HTF under real operating condition range (temperature, pressure, time) for several thousands of hours. Characterizations (scanning electron microscope (SEM), differential scanning calorimetry (DSC), X-Ray diffraction (XRD), etc.) were made regularly in order to follow the possible degradation or modification of the ceramics and eventually of the HTF. Concerning the molten salts, among the various corresponding families, only the nitrates present a good compatibility with the Cofalit [18,30,38]. Therefore, the recycled ceramic can be used under direct contact with the so-called solar salt $NaNO_3/KNO_3$ in thermocline units. The Cofalit can be also used under direct contact with hot air, up to 1100°C, even under concentrated solar radiation and severe thermal cycling without change [39]. Under compressed hot air, a HTF of particular interest for ACAES and future gas turbine CSP tower systems, the Cofalit presents a structural change from Wollastonite to Augite leading to an increase of 29 % in its thermal conductivity [12]. Tests with oil, hot water and atmospheric steam were successful even if additional tests are highly needed with pressurized steam.

2.1.4 Storage application modelling analysis

The applicability of those ceramics to large scale TES application was studied numerically in the particular case of the ACAES process [12]. Performances of cumulated charge/discharge cycling on a sub TES unit composed of stacks of flat plates were calculated for various configurations (plate thickness, inter plate distance) and operating conditions. The simulations were achieved under non dimensional approach leading to numerous results highlighting the most relevant ones and the possible potential of improvements. While the basic studied configuration led to possible geometrical configuration in agreement with the expected performances, advanced systems could be developed using more complex geometries (such as static mixers made of stacked corrugated plates) and/or more conductive ceramics. Complementary studies will be achieved following those approaches but specific heat transfer coefficient correlations on complex geometries would be needed.

2.1.5 Lab scale experiences

The ACW ceramics were tested in TES lab scale units in the form of granular packing (oil as HTF) and in the form of shaped packing (Figure 7: plates and corrugated plates using hot air as HTF).

Hundreds of thermal cycling under operating conditions of ACAES (50 to 650°C), linear CSP (200 to 400°C) and central receiver CSP (400 to 800°C) were achieved. During those experiments, the thermal behaviour of both the material and the TES unit were recorded. The TESM was characterized at the end of the experiments for comparison with the initial ceramic. No changes of structure or properties were noticed between raw and cycled modules.

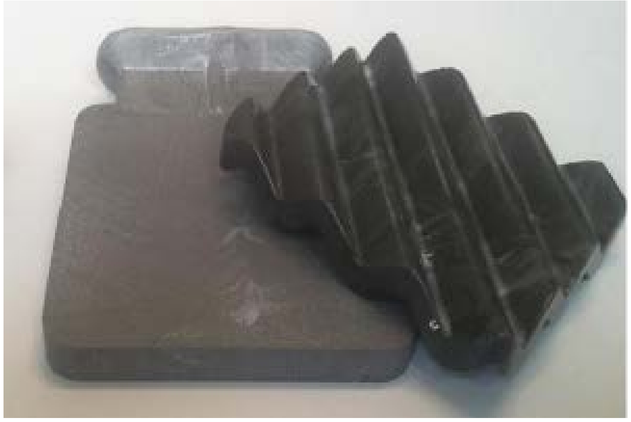


Figure 7 Flat and corrugated plates of ACW ceramics tested under hot air up to 800°C [36].

Due to their thermal inertia, conventional TES test units can be usually operated under rather limited range of heating/cooling rates. Therefore, in order to assess the limit of use of the Cofalit ceramics, a high heating rate dynamic solar facility was used [39]. This device is composed of a 2 m ID vertical axis parabola lighted by a two axis heliostat and controlled by graphite blades in between. The upper surface temperature of the sample (in pink in Figure 8) is followed by a pyrometer and controlled by the graphite blades positions. Repeated thermal cycling of heating rates ranging from 100 to 2500 °C min^{-1} can be achieved. The temperature at various depths in the sample below the surface is measured by thermocouples. As all possible cracks would lead to an induced thermal resistance, the recorded signal assesses the whole behaviour of the material. Moreover, the phase lag and the delay between the curves allow a direct estimation of the thermal diffusivity under thermal cycling at high temperature. Using this device and up to 2500 °C min^{-1}, the Cofalit samples were able to sustain the fatigue tests between 500 and 1000 °C without failure.

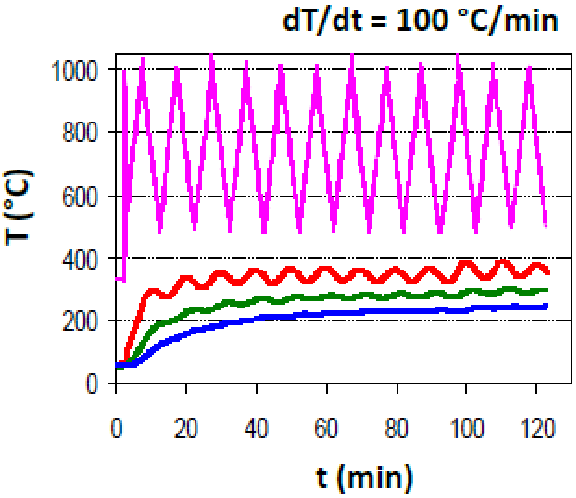


Figure 8 Thermal cycling of a Cofalit cylinder (25 mm ID, 200 mm length) under concentrated solar flux, temperatures at 0, 10, 25 and 40 mm from surface [39].

2.2 Fly ashes

2.2.1 Definition of the waste material (origin)

Fly ashes are micron-size particles present in gaseous effluents produced by industrial combustions such as coal fired power plants or municipal solid wastes incinerators (Figure 9(a)). Those particles are mainly composed of SiO_2, Al_2O_3 and CaO, and can consequently be used as primary materials for ceramic manufacturing. While coal fired power plant fly ash (CFA) are mainly amorphous, spherical and contain low amount of pollutants, the municipal solid waste fly ash (MSWFA) are rather crystallized, needled shaped and contain critical pollutants such as dioxins (Figure 9(b)).

(a)

(b)

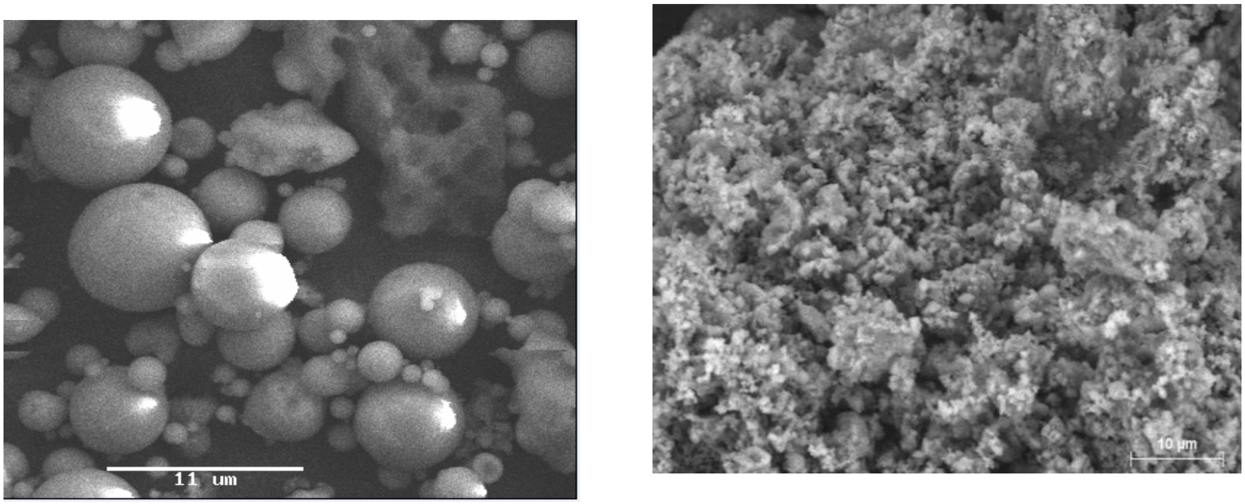


Figure 9 SEM picture of Coal Fly Ash particles (a), SEM picture of MSWI Fly Ash particles (b). [32]

Both are collected from the industrial gas effluents by electrostatic filters and available in the form of light powder similar to regular cement. In some countries less concerned by environmental issues, those fly ashes are even not harvested and induce major health impacts. Most of them are stored in waste disposal leading to land investment and potential pollutant release. Another part is recycled in concrete or in the construction of roads.

2.2.2 Treatment technologies

Municipal solid waste incinerator fly ash (MSWIFA) has been treated by Europlasma/Inertam by plasma torch melting at 1400°C. At the outlet of the reactor, the molten product is currently quenched and laminated to produce glass plates of about 2 mm in thickness. Those glass plates have been used as primary material for direct characterizations and for subsequent crystallization followed by characterizations. Thanks to the crystal structure, all pollutants such as heavy metals are fixed within the material and no lixiviation effect was detected. Then, the final ceramic can be considered as stable and inert material.

Thermophysical properties of the obtained glass and ceramics were measured, leading to the following range of values (from room temperature up to 1000°C): 2962 to 2896 kg m^{-3} in density, 0.714 to 1.122 kJ kg^{-1} K^{-1} in thermal capacity, 1.16 to 1.59 W m^{-1} K^{-1} in thermal conductivity, $8.7 \cdot 10^{-6}$ K^{-1} in coefficient of thermal expansion.

The thermal behaviour of the obtained glass (dash line) or ceramic (continuous line) from room temperature up to 1100 °C, are illustrated in Figure 10. The glass presents a glass transition at about 650 °C and a crystallization peak at 900 °C while the ceramic is highly stable within the whole temperature range. This illustrates the fact that the glass can be used as TESM in storage systems operated below 600 °C while the ceramic can be used in all temperature range below 1100 °C. The variation of the thermal capacity with temperature of the ceramic is illustrated in Figure 11. This behaviour was observed with all recycled ceramics made of melted inorganic wastes such as Asbestos, Fly Ash or metallurgic slag. Even if the compositions of those wastes are different, the main compounds (SiO_2, Al_2O_3, CaO) are responsible for the observed values of the measured properties within similar ranges.

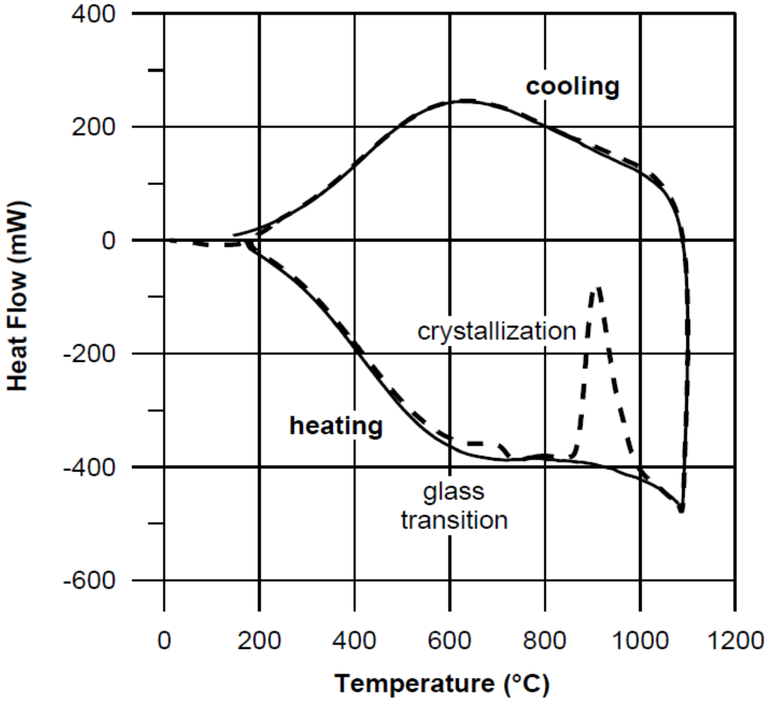


Figure 10 DSC characterization of MSWI FA made products, (dash line) from glass, (continuous line) from ceramic [32].

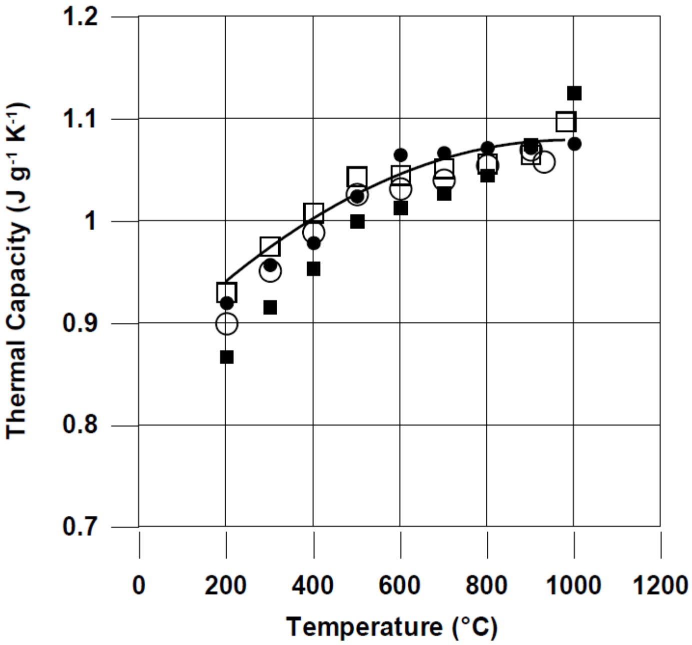


Figure 11 Thermal capacity of the MSWI FA made ceramics [32].

The CFA have been provided by the EDF Company. Those fly ash are in the form of spherical particles of few 10 µm already known to be more amorphous than MSWIFA and with less pollutant. Those fly ash have been molten using a lab scale solar parabola (1.5 to 2 kW), the molten product quenched under air and the obtained glass beads crystallized in an electric oven at 1100 °C during 20 h. The obtained ceramic is a Mullite $Al_6Si_2O_{13}$, a very valuable and well known refractory ceramic. Nevertheless, the viscosity of the molten CFA is too high to allow an easy moulding for the production of shaped storage modules. Additional $CaCO_3$ (up to 20 % wt) to the initial CFA before melting led to proper composition for the modules elaboration. While preliminary experiments were done with synthetic $CaCO_3$, similar work was achieved with egg shell recycled $CaCO_3$ with success. In both cases, the Mullite ceramic is replaced by the Anorthite, another valuable refractory ceramic. According to the fact that egg shells are considered today as highly dangerous wastes from the food industry, this successful mix of CFA and egg shell can be considered as an illustration of the possibility to manage the properties of the final product by use of several wastes. The obtained ceramics have been characterized, from room temperature up to 1000 °C their main properties range are : 2600 kg m^{-3} in density, 0.735 to 1.300 kJ kg^{-1} K^{-1} in thermal capacity, 1.3 to 2.1 in thermal conductivity, $4.0 \cdot 10^{-6}$ K^{-1} in CTE. Those ceramics can be used as sensible heat TESM up to 1000 °C.

As CFA are in the form of rather regular micron size spherical amorphous silica particles, the treatment can be done by sintering (compression under heat) instead of melting. This approach has been already tested with success by the PROMES CNRS laboratory and the Tellus Ceram Company at lab scale. Up to 100 % CFA containing modules were produced in the form of plates or cylinders and are still under characterizations. This approach could lead to the production of shaped storage modules using less energy than with the melting technique.

2.2.3 Availability/Yearly production & cost

As municipal solid waste incinerators are still under extended development in Europe, the corresponding wastes present a wide potential of material of about 1.6 Mt/year (EU 15). As an order of magnitude, a MSWI such as the Calce unit near Perpignan-France produces 6,634 tons of fly ash every year for a treatment of 186,000 tons of municipal wastes. The same unit produces 30 MW of electricity from the combustion heat which could be considered in the energy balance of the fly ash needed treatment by melting.

As the world production of CFA is estimated to be around 750 M tons per year (42 Mt/year in EU 15), those wastes present a huge potential. Moreover, they are produced by the companies already involved in power production which are those that will also need thermal storage unit in the future. Therefore, those material considered today as environmental and economic constrains can be viewed by those companies as highly valuable primary materials.

In both cases, all Fly Ash are produced from MSWI or Coal combustion worldwide in huge amounts and then can be considered as particularly strategic in the context of the global energy transition. Moreover, their potential of economical valorisation and development of corresponding industrial activity could encourage all countries to harvest those wastes from fumes instead of discharging them to the environment.

2.3 Salt industry

2.3.1 NaCl

A by-product from the potash industry is chosen to test its suitability as thermal energy storage material [40]. It was identified by X-Ray Diffraction (XRD) as crystalline sodium chloride (NaCl).

The original shape of this salt is granulated (Salt A). However, the main drawback of that shape is the air gaps between the grains which decrease its thermal conductivity. For that, different ways to shape and compact the material were considered. In other thermal storage materials, authors propose metal additives, metal fins or graphite to increase it [40], but these solutions represent an increase of the system cost. So, a cheaper option was considered: the addition of water to eliminate air gaps and to achieve a continuous solid form of the salt by evaporating it later. The suitable mixture of salt and water found had an addition of 17 % of water (Salt B).

At the laboratory, thermal conductivity, specific heat capacity and density were measured. Thermal capacity is obtained by multiplying density and specific heat capacity (Cp·ρ). These are the important parameters to determine the suitability of a material to store sensible heat. After the laboratory characterization of these by-products, their properties are listed and compared to other sources (Table 2). It can be seen that NaCl has different properties depending on the source.

Table 2 Main properties of NaCl as sensible heat storage solid material found in the literature and experimentally [40]

Material	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	Specific heat capacity ($kJ\ kg^{-1}\ K^{-1}$)	Density ($kg\ m^{-3}$)	Thermal capacity ($kJ\ K\ m^{-3}$)	Price (€/kg)
NaCl [13, 40]	7	0.850	2160	1836	0.15
NaCl [42]	10.4 - 11.7	0.850 – 0.870	2120 - 2210	1802 - 1923	< 0.01
Salt A (original NaCl)	0.33	0.738	1384	1021	-
Salt B (water-shaped NaCl)	2.84	0.738	2050	1513	-

Moreover, both by-products were tested at higher scale. 59 kg of Salt A and Salt B were thermally cycled from 100 to 200 ºC.

The thermal energy storage tank design were the salts were tested (Figure 12) is based on the concept of a shell-and-tube heat exchanger, consisting of a vertical tube bundle with four tubes through which the HTF is circulated and a housing surrounding the tubes serves as storage material container. Its main characteristics are: 0.05 m^3 capacity, dimensions of 0.35 x 0.35 x 0.41 m, and 0.002 m thickness A316 stainless steel walls.

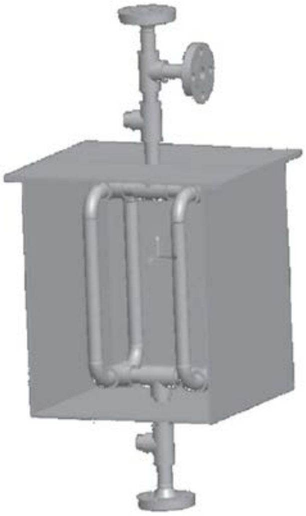


Figure 12 Interior TES tank design used for the NaCl testing at pilot plant scale [40].

Four experiments varying the length of the charge and the discharge from 4 to 8 h and the heat transfer flow from 1 5o 3 m^3 h^{-1} were performed to calculate: thermal conductivity, thermal diffusivity, energy delivered and accumulated by the salts and cycle performance. Thermal conductivity and diffusivity results are shown in Figure 13.

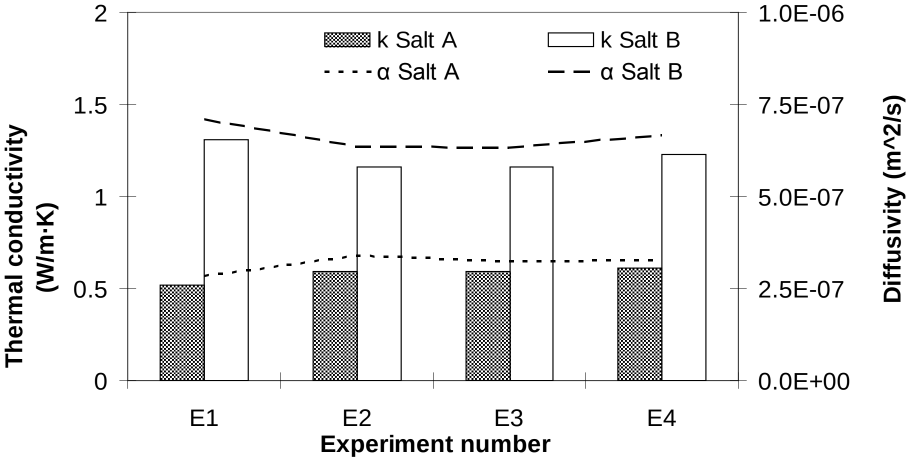


Figure 13 Thermal conductivity (k) and thermal diffusivity (α) for E1, E2, E3 and E4 experiments using both salts [40].

These analyses show that Salt B (water-shaped) represents a better option as storage material than Salt A due to the reduction of air gaps inside the solid. Moreover, using the data achieved at the laboratory, thermal capacity was calculated and compared with other solid materials found in the literature and similar values to other sensible heat storage materials like concrete and silica firebricks were observed. Thus, NaCl represents an interesting competitor because of its thermal properties, its behaviour in a real scale plant and especially because of its price (from 5 to 100 times cheaper than other solid material candidates for sensible heat storage).

2.3.2 Bischofite

Inorganic materials, especially salt hydrates, are the most important group of TES as PCMs, and they have been studied for several researchers. This group of materials has attractive properties, as high energy storage density, relatively high thermal conductivity, only slightly toxic, not very corrosive, and compatible with plastics [13,21,41,43-45]. Although salt hydrates are sufficiently inexpensive, non-metallic industry has vast quantities of waste materials or by products, which don't have or have limited applications. Some researchers have been studied these materials to be applied as TES.

In the north of Chile, the presence of the mine industry is tremendously important; one of the main products of non-metallic industry is the potassium chloride. During the production process of this salt in "Salar de Atacama" are obtained several by products and even waste materials, one of this is bischofite, which has as main component $MgCl_2 \cdot 6H_2O$ with some impurities. Nowadays bishofite has few applications, in Europe the main application is for de-icing of roads. In Chile, its uses this salt to compact and improve the mining roads, because of its hydroscopicity. The demand in Chile exceed the 100,000 tons per year, within an approximately price of 40 US$/ton on its low quality variety and the purified bischofite price is closed to the $MgCl_2 \cdot 6H_2Om$ but always lower, around 155 US$/tons. Other countries has also the presence of this salt, in similar processes, this is the case of Israel and The Netherlands [43].

The physical and thermal properties of bischofite were determinate. The chemical analysis showed the main components of bischofite (Table 3) and the mineralization (Table 4) determined that the quantity of $MgCl_2 \cdot 6H_2O$ in bischofite is nearly 95 %, moreover according to the mineralization this salts presents the existence of two hydrated salts, carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and $Li_2SO_4 \cdot H_2O$.

Table 3 Chemical analysis results of bischofite [43].

Element	**Average concentration range [%]**	**Concentration used in this study [%]**
Sodium, Na	0.321 – 0.360	0.360
Potassium, 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 Mineralization resulting of a bischofite sample [43].

Compound	**[%]**
NaCl	0.90
KCl	0.20
$MgCl_2·6H_2O$	94.80
$KCl·MgCl_2·6H_2O$	1.80
$Li2SO_4·H_2O$	3.20

The thermal properties of this salt are near to the synthetic $MgCl_2·6H_2O$, with a melting temperature of T_{onset}=98.9 ºC and T_{onset}=114.6 ºC respectively (Figure 14). Also the heat of fusion value is similar 120.2 kJ kg^{-1} and 126.6 kJ kg^{-1} respectively; the differences are because of the presence of impurities in bischofite.

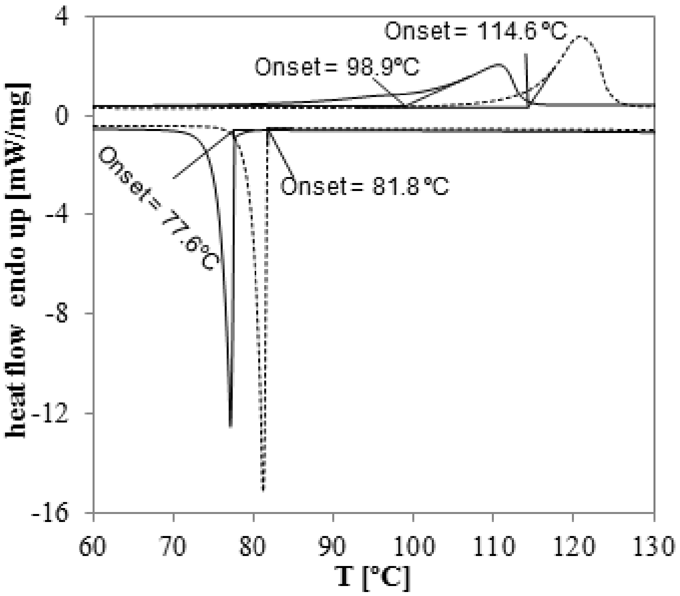


Figure 14 DSC measurement curves for one cycle of heating and cooling of bischofite (continuous line) and $MgCl_2·6H_2O$ (dotted line) [44].

Bischofite shows good thermal stability [43], with a mass loss of 0.4 % compare to $MgCl_2·6H_2O$ which doesn't present mass loss, within the temperature range from 30 ºC to 140 ºC measured at aluminium crucibles with lid. Furthermore, about long term cyclic stability, bischofite showed a very good behaviour related to melting point and heat of fusion (see Table 5), but it's variable in the cooling process: the temperature of crystallization don't remain constant during the cycles, this is a normal behaviour in hydrated salts, due to most of them present segregation phases or poor nucleation during the solidification process [22, 46].

Table 5 Thermal properties of bischofite after cycles of heating and cooling [43]

Sample	Cycle N°	T_m [°C]	$\Delta_F H$ [kJ kg^{-1}]	T_C [°C]	$\Delta_C H$ [kJ kg^{-1}]	ΔT [°C]
Bischofite	10	100.9	116.2	64.5	117.4	36.4
	20	101.1	116	70.1	117.8	31.0
	30	102.2	115.5	58.7	115.8	43.5
$MgCl_2·6H_2O$	10	114.5	133.5	88.8	129.5	25.7
	20	114.6	133.1	83.2	129.4	31.4
	30	114.4	136.9	85.2	132.3	29.2

This study also determined physical properties as viscosity, heat capacity, density as a function of temperature and energy storage density (esd), showed in Table 6, demonstrating that bischofite (by-product) present similar properties than synthetic $MgCl_2 \cdot 6H_2O$, even though with the presence of impurities.

Table 6 Physical properties of bischofite and $MgCl_2 \cdot 6H_2O$ [43].

Compound	**Cp** **[kJ kg^{-1}K^{-1}]**	**ρ** **[kg m^{-3}]**	**µ** **[mPa s]**	**esd** **[kJ m^{-3}]**
Bischofite	1.6 - 2.1$^{(25\text{-}60)°C}$ 1.7-3.0$^{(115\text{-}125)°C}$	1686$^{30°C}$ 1598$^{40°C}$ 1513$^{50°C}$ 1481$^{115°C}$	22.9-13.8$^{(110\text{-}150)°C}$	178 016
$MgCl_2 \cdot 6H_2O$	2.1 - 1.95$^{(25\text{-}60)°C}$	1517$^{25°C}$ 1422$^{128°C}$	16.7-12.4$^{(120\text{-}140)°C}$	180 025

Gutierrez et al. [44] studied the addition of different molecular weight PEG to improve cycling stability of bischofite during heating and cooling cycles, improving the thermal performance of the mixture when applied as phase change material. The results obtained are show in Table 7. According to this research the mixture of bischofite + 5 %PEG 2000, was the most stable due to the crystallization temperature remains within the variation range of 7 °C during the cycles of heating and cooling.

Table 7 Temperatures and heats of fusion and crystalisation for mixtures of bischofite with PEGs of different molecular weights [44].

Sample	**Cycle num**	**T_m [°C]**	**$\Delta_F H$ [kJ kg^{-1}]**	**T_C [°C]**	**$\Delta_C H$ [kJ kg^{-1}]**	**ΔT [°C]**
Bischofite+5 %PEG 600	10	99.4	96.6	59.4	82.4	40
	20	99.4	112.7	62.9	75.0	36.5
	30	99.4	113	60.5	97.0	38.9
Bischofite+5 %PEG 2 000	10	97.7	75.0	62.7	76.8	35.0
	20	98.7	78.3	69.5	81.2	29.2
	30	100.6	83.8	66.9	86.3	33.7
Bischofite+5 %PEG 10 000	10	99.7	85.6	60.0	81.8	39.7

	20	104	92.5	70.1	89.0	33.9
	30	105.5	98.2	64.6	97.7	40.9

Thermophysical properties presented by bischofite are suitable for use as PCM at medium temperature, around 100 ºC, but is necessary to reduce the subcooling of the mixtures.

2.3.3 Astrakanite and Kainite

With the aim of testing other wastes usually present in thee non-metallic industry as thermal energy storage materials, the potential of two double hydrated salts were evaluated [45]: synthetic astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) and waste kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$). The samples were characterized by scanning electron microscopy, SEM-EDX. According to these study astrakanite has crystals separated, with rhombohedra shape, and the presence of impurities was not detected, however, the discarded salt, kainite presents agglomeration. TGA and DSC studies were performed to evaluate the use of the anhydrous phase of astrakanite as a solid TES media at high temperatures. The TGA results showed no weight loss between 320 ºC and 750 ºC. DSC results (Figure 15) revealed that the anhydrous phase of astrakanite presents a reversible melting – solidification behaviour in the range from 570 °C to 680 °C, but it is necessary to perform deeply studies.

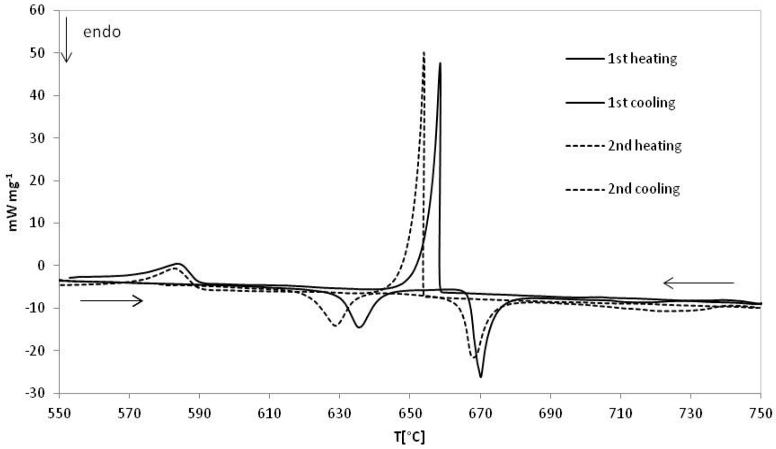


Figure 15 DSC cyclic study of high- temperature phase of astrakanite sample[45].

Heat capacity obtained for astrakanite, kainite and anhydrous phase of astrakanite are show in Table 8. The heat capacity for astrakanite is from 0.9 to 1.2 kJ $kg^{-1} \cdot K^{-1}$ and for kainite is from 0.8 to

1.0 kJ kg^{-1}K^{-1}, for the temperature range from 0 °C to 100 °C, and for the anhydrous phase of astrakanite at high-temperature, it is from 1.2 to 2.1 kJ kg^{-1} K^{-1}.

Table 8 Heat capacity of Astrakanite and Kainite as a function of temperature [45]

Compound		**Cp** **[kJ kg^{-1} K^{-1}]**
Astrakanite	Hydrated salt	0.9-1.2 $^{(0\text{-}100)°C}$
	Anhydrous phase	1.2-2.1$^{(150\text{-}500)°C}$
Kainite	Hydrated salt	0.8-1.0$^{(0\text{-}100)°C}$

Astrakanite and kainite, waste process-salts from the non-metallic mining industry in northern Chile, are suitable to be used as heat storage materials at low temperatures, from 0 ºC to 120 ºC. After evaluation of heating and cooling cycles, it was found as well that the anhydrous phase of astrakanite can be used as a solid TES material at a high temperature range, 350 ºC to 530 ºC.

Metal industry

2.4.1 Definition of the waste material

Steelmaking is one of the worldwide most extended heavy industries with larger development level. Far from reducing the total steel production, in the last 10 years the total produced steel amount has experienced an increase of around 5 % every year [48]. In addition, the steel consumption has also been increased in the same ratio.

However, this production activity implies the generation of one of the largest by-product of the high temperature manipulation, extraction and refining of metals: Steel slag. This material of the metallurgic industry is generated, essentially, during the melting process of the iron ore and about 10 to 20 % of slag is produced per ton of steel. When the final casting is obtained, the liquid steel slag is easily removed from the liquid steel by density difference and cooled down for solidification. The mentioned process, which is particular of each steelmaker, generates different types of steel slag depending on the furnace technology used, the ore or scrap composition, particular additives introduced in the steelmaking process or the cooling conditions of the slag. In general, slag is a partially vitreous by-product of smelting ore due to separating of the metal fraction from the worthless fraction. It can be mainly considered as a mixture of metal oxides. However, slag can contain metal sulphides and metallic components in the elemental form as well as heavy metal traces, such as chromium, molybdenum or vanadium. Since these substances can be leached to some extent from the slag, possible environmental hazards cannot always be excluded. Moreover, steel-industry slag is alkaline, producing water leachate with a basic pH of approximately 11. Even if slag are from now on officially classified as non-hazardous waste in Europe, dumping slag should not be considered as a long-term solution of waste management and new market should be identified to recycle 100 % of this material.

The European Slag Association [49] classified the slag in different families depending on their nature: Granulated Blast furnace Slag (GBS), Air-cooled Blast furnace Slag (ABS) both coming from the production of iron by thermochemical reduction in a blast furnace, and obtained under different cooling conditions; Basic Oxigen furnace Slag (BOS) formed during the solidification of the steel in a basic oxygen furnace and generated by addition of limestone and/or dolomite; Steelmaking Electric Arc Furnace Slag for Carbon and Stainless steel (EAF C and EAF S respectively) formed during the melting of the scrap in an electric arc furnace; and Steelmaking Slag (SMS) which includes slag from the steel production process to the subsequent treatment of crude steel. Each one of these slag families is identified with the corresponding CAS number.

The main furnaces used in EU27 are Basic Oxygen Furnace (BOF) with 58.2 %, Electric Arc Furnace (EAF) with 41.4 %, and Open Heart Furnace (OHF), with 0.3 % [50].

2.4.2 Treatment technologies

The legal status of the ferrous slag (their classification as either waste, product, or by-product) has been discussed worldwide for more than 25 years. Even though, according to the Waste Framework Directive 2008/98/CE – Article 5, steel slag may be currently classified as a by-product because it is produced as an integral part of the production process and its use is certain without any further processing [49].

The effect of the slag on human health and environment was specially investigated during last years. Numerous toxicity and ecotoxicity tests were performed and, on the basis of their results, it could be concluded that slag is not hazardous [49].

For this reason additional treatment processes are not needed for ferrous slags. In fact, treatment technologies developed for slags are related with the posterior application of this by-product. In this frame, for an optimal use of ferrous and steel slag the existence of accorded standards, which include the relevant requirements, depending on the field of use, is necessary. Currently, these standards are focused on the use of slags as construction material or aggregate or as fertilizer [49], but most of the European countries have developed their own directives and regulations as a basis for marketing by-products or secondary raw materials. According to these normative the treatment of each slag will vary depending on its slag family. The main general treatments for each slag family are listed in Table 9.

Table 9 Different treatment processes for the ferrous slag [49,50].

GBS	Rapid quenching of the molten slag with high pressure, high volume water sprays, grinding of the granulated slag to cement fineness
ABS	Crushing and screening of the air cooled slag
BOS	Crushing and screening of the slag that has been air cooled and watered
EAF C	Crushing and screening of the slag that has been air cooled and watered
EAF S	Crushing and screening of the slag that has been air cooled and watered

The EU Commission agreed that industrial operations such granulation, pelletisation, foaming, proper solidification connected with a specified heat treatment and separation, crushing sieving (screening) and milling (grinding) are also examples of slag processing [49]. In addition, it was remarked that no negative environmental impact has ever been reported when slag is used in accordance with the requirements of the relevant regulation.

Different treatment methods of steel slag are related to the energetic losses derived from this by-product in the steel industry, around a 6.4 % of the total energy input [51]. The necessity to improve the energetic efficiency of the steel production plants forced the sector to develop new technologies and treatments to recover the wasted heat of the hot slag. These technologies were reviewed by Barati et al. [52] being classified in three categories: recovery as hot air or steam; conversion to chemical energy as fuel or thermoelectric power generation.

An innovative treatment technology, which could facilitate the integration of slag in the mentioned valorisation applications and also could open new potential valuable markets for this material, was introduced by Syuhada [53], from Krakatau Steel. This treatment methodology consists on the atomization of liquid EAF S slag directly at the end of the steelmaking process. It permits to obtain spherical glassy pebbles of this material (PreciousSlagBalls®) with a diameter from 0.2 cm to a few cm. This treatment present two important advantages, on one hand it avoids any further moulding or shaping of the solid slag, which represents a high energy demanding process, as it takes the liquid slag directly from the steel production. On the other hand, the flexibility to obtain different diameters of slag balls is an important feature which favours the ulterior use on different applications, from their use as fertilizer to the design and construction of innovative thermal energy storage solutions based on slag packed bed concepts.

Summarizing, no specific treatment methodology is currently necessary for steel slag. However, the ulterior application of this material could lead to different treatment technologies in order to optimize it for the particular application.

2.4.3 Short overview related with the revalorization of waste materials

Up to now, the revalorization of this material as an added value product represents the main solution to manage this by-product [54,56]. Different researchers have suggested the use of slag for very different applications in several areas depending on the particular composition. In Europe, in 2010 around a 76 % of the total produced slag was revalorized in different fields (Figure 16).

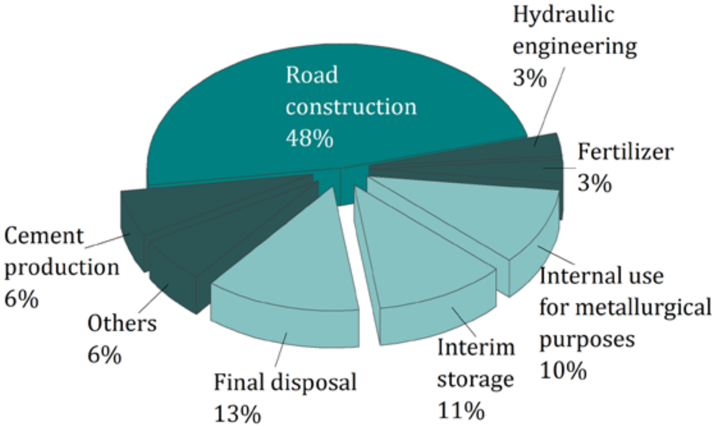


Figure 16 Use of slags from ferrous metal industry in Europe in 2010 [49].

One of the usual applications of slag, due to their high durability and strength, is road construction [55,57]. Their high bulk density and abrasion together with the rough texture make slag a very suitable material for construction purposes. Slag also presents a high binder adhesion and frictional or abrasive resistance, making possible their use as aggregates in surface layers of pavement and asphaltic layers. The second most extended application of this material is the cement and concrete production [58-64]: its addition as arid aggregate represents one of the biggest current alternative to the reutilization of slag.

The use of slag as potential material for ceramic glass production has also been proposed in references [65,66]. On the other hand, based on the porous structure of steel slag, Shi et al. [67] and separately Chamteut et al. [68] have extensively studied the possibility of their use in waste water treatment. In this frame, several contamination types have been successfully eliminated, for example by mercury or arsenic adsorption. Some authors [66, 67] also suggest the CO_2 capture and flue gas desulfurization by using slag. Finally, the use of the slag in agriculture as fertilizer is another extended application due to the high mineral content of slag, mainly CaO, SiO_2 and MgO [49].

The European Slag Association reported a complete and wide range of application fields for the different types of slag (Table 10).

Table 10 Typical slag applications practiced in Europe [49].

	As aggregate for	For the manufacture of
GBS	Bituminous and hydraulic bound mixtures Unbound mixtures Waste water treatment Embankments and fill Railway ballast Roofing Ground stabilization	Stone wool Glass (blended with other components) Fertilizer
ABS	Bituminous and hydraulic bound mixtures Unbound mixtures Embankments and fill Ground stabilization Sand blasting	Cement and other hydraulic binders Concrete Stone wool Glass (blended with other components) Fertilizer
BOS	Bituminous and hydraulic bound mixtures Top layers for high skid resistance Unbound mixtures	Cement and other hydraulic binders Stone wool Glass (blended with other components)

	Dams (road construction and noise protection) Waste water treatment Embankments and fill Railway ballast Sealing in surface layers to protect deposits roofing Armour stone Ground stabilization	Fertilizer
EAF C & EAF S	Bituminous and hydraulic bound mixtures Top layers for high skid resistance Unbound mixtures Dams (road construction and noise protection) Waste water treatment Embankments and fill Railway ballast Sealing in surface layers to protect deposits roofing Armour stone Ground stabilization	Cement and other hydraulic binders Stone wool Glass (blended with other components)

(a) 2.4.4 Availability/Yearly production & cost

Steel slags represent, in mass, between 15 to 20 % of the total production of the steelmaking process [70]. According to Elliot et al. [48] in 2014, around 1500 million tons of steel were produced. The total produced steel slag at global scale was close to 250 million ton. As a consequence, the appropriate treatment of this by-product is a challenging issue, which has to be solved successfully. In Europe, where around 16 % of the worldwide steel production is carried out [51], about 76 % of slag is re-used in different applications. The remaining 24 % is landfilled (13 %) and stored in the steelmaking plant (11 %).

Recent data published by U.S. Geological Survey, Mineral Commodity Summaries estimated the price of slag increased from $17.6 per ton in 2005 to $23.0 per ton in 2009 [71] quite cheaper than the common storage materials used until the moment as molten salts.

2.4.5 Revalorization as TES material: strengths and weaknesses

International Energy Agency (IEA) established thermal, chemical, mechanical and economic requirements for TES materials, among others inexpensive, available in large quantity without conflict of use, stable up to 1000 °C, compatible with heat transfer fluids and non-toxic.

Thermophysical properties of ferrous slag, detailed later, indicate very appropriate values for the use of this material in thermal energy storage applications according the IEA criterions. In addition, slag shows an extended thermal stability range, up to 1200 ºC, limited by the melting process of this material. This allows a high operation temperature, suitable for a wide range of heat storage applications, from thermo-solar power generation to industrial heat recovery. On both applications, the potential implementation of a ferrous slag based packed-bed storage solution could be successful. On one hand, on the CSP frame, the substitution of large amounts of molten salt by this low-cost by-product in a single storage tank could lead to a substantial cost reduction of the storage system, and hence, of the produced electricity. This concept is not only valid for current storage technologies based on molten salt up to 565 ºC, it can also be suitable for next generation power plants where the operation temperature will be higher, up to 800-1000 ºC. In addition, slag does not need any further treatment in order to be used as heat storage material, and can be directly obtained and conformed from the EAF [54,73].

On the other hand, the main drawback using slag as TES material may be the compatibility between the by-product and the HTF or the container material. Positive results may permit a direct contact between the slag and the fluid, which the subsequent elimination of sophisticated heat exchangers.

Overall, TES systems based on slag as thermal storage material represents a low-cost breakthrough solution both to the CSP heat storage and to the industrial waste heat recovery.

2.4.6 Thermophysical properties, characterization & compatibility studies

A complete characterization of slags is necessary to evaluate their suitability to be used as TES material. Different authors analysed the composition and thermophysical properties of this by-product showing very promising results that would make it suitable to be used in thermal energy storage applications.

Mineralogical characterizations of different slag types were presented by de Brito et al [73] revealing the major and minor substances found in each slag type with the corresponding crystallographic structures, although no data about the composition was provided (Table 11).

Table 11 Mineralogical composition of different slag [73].

Country	Type of slag	Minerals identified	Ref.
Spain	EAF-slag	Wustite/plustite, magnesioferrite/magnetite, hematite, larnite, brendigite/merwinite, gehlenite, birnessite/groutellite (manganese oxides)	[75]
Italy	EAF-slag	Fine fraction: glauchronite $(CaMn)_2 \cdot SiO_4$, iron manganese oxide (FeMnO) Medium: calcite ($CaCO_3$), glaucochronite $(CaMn)_2 \cdot SiO_4$, iron manganese oxide (FeMnO), magnetite (Fe3O4), portlandite (Ca(OH)2)	[76]
Sweden	LDF-salg	Mayenite, ($Ca_{12}Al_{14}O_{33}$), free MgO. β-Ca_2SiO_4, γ-Ca_2SiO_4, $Ca_2Al_2SiO_7$.	[77]
	BOF-slag	Larnite, β-Ca_2SiO_4, solild solution of (Fe,Mg,Mn)O, solid solution of (CaMg)O	
	EAF-slag, S1	Merwinite, $Ca_3Mg(SiO_4)_2$, γ-Ca_2SiO_4, solid solution of spinel phase $(Mg, Mn)(Cr, Al)_2O_4$	
	EAF-slag, S2	β-Ca_2SiO_4, wustitute-type solid solution ((Fe, Mg, Mn)O), $Ca_2(Al, Fe)_2O_5$, Fe_2O_3	
Singapore	Kirschsteinite based EAF-slag	Kirschsteinite ($CaFe_2+(SiO_4)$), Mg-wustite	[78]
Spain	EAF-salg, S1 and S2	Major: gehlenite [$Ca_2\ Al(Al,Si)_2\ O_7$], larnite (Ca_2SiO_4) Minor: bredigite [$Ca_{14}Mg_2(SiO_4)_8$] manganese oxides (Mn_3O_4, MnO_2), magnesioferrite ($MgFe_2O_4$), magnetite (Fe_3O_4)	[79]

Calvet et al. [30,35] presented an experimental characterization of as received and re-melted EAF S slag (as received slag melted and solidified again to obtain a desired shape) coming from steel production process. In these publications the TGA results shown no mass loss between 300 °C and

1200 °C under Argon, and a small mass gain when dry air is used as purge gas due to the oxidation of metal iron (3.15 %) still contained in the waste.

The heat capacity of black slag samples was measured in the 200-750 °C temperature range and showed values between 0.600 and 0.800 kJ kg^{-1} K^{-1}, as shown in Figure 17. Thermal conductivity was measured with the laser flash method and is decreasing with temperature from 1.7 W m^{-1} K^{-1} at 50 °C to 1 W m^{-1} K^{-1} at 900 °C (Figure 18). This relatively small value imposes to increase the heat exchange surface between the HTF and the TES material to obtain satisfactory heat transfer in the future storage system.

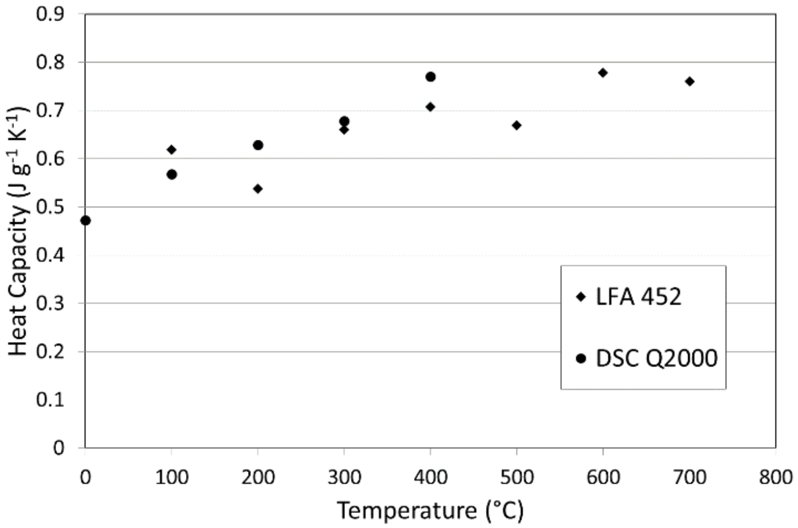


Figure 17 Heat capacity of a sample of as-received black slag as function of temperature from room temperature up to 700 °C measured with Netzsch LFA 452 and DSC TA Q2000 [35].

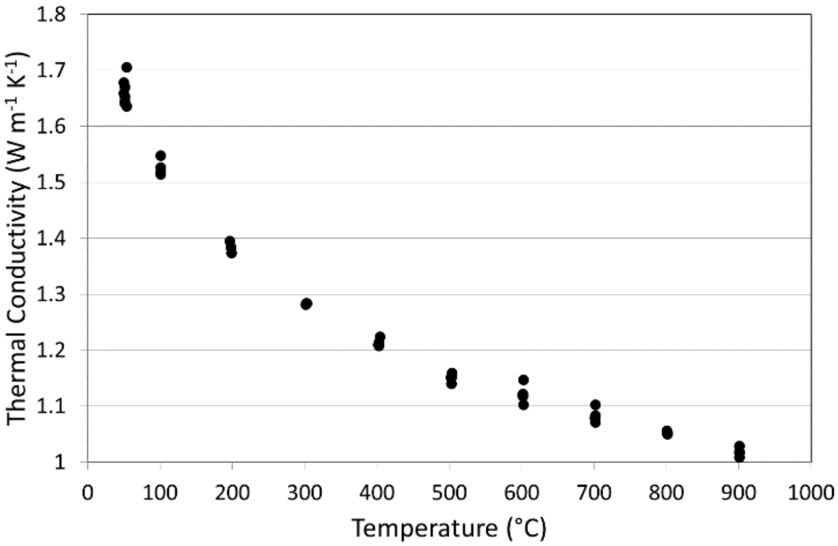


Figure 18 Thermal conductivity of the re-melted sample as function of temperature from room temperature to 900 °C [35].

Figure 19 reports the composition of the slag, which was measured together with the density, melting point, thermal stability, heat capacity and thermal conductivity.

Thermophysical properties were also reported by Gil et al. [74]. In this publication the skeletal and bulk density for both re-melted and as received slag was measured. The authors completed the characterization of Calvet including values of density, heat capacity, thermal diffusivity and thermal conductivity of re-melted slag.

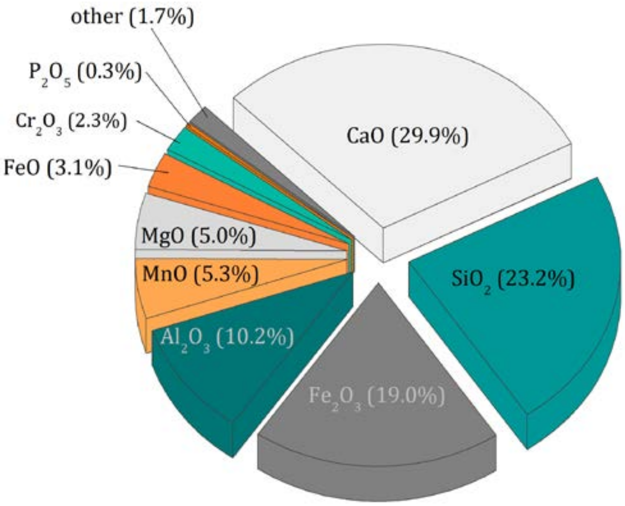


Figure 19 Chemical composition of slag analysed by Calvet et al. [35].

Ortega et al. [80] compared the thermophysical properties of two EAF slag coming from different steelmaking companies (named Slag1 and Slag2). The main difference between the materials was the cooling conditions applied after the steelmaking process: one of them was cooled down rapidly, 3-4 hours, by using water while the second one was cooled down in open air during 2-3 days.

Thermal stability experiments were conducted by thermogravimetric analysis in the range of 200-1000 ºC and chemical stability was studied using a chamber furnace at 1000 ºC and testing the samples during 500 hours under air atmosphere. The results shown both slag are thermally stable at least up to 1000 ºC and any chemical reaction was detected. The authors also measured the slag density at room temperature and their heat capacity and thermal conductivity at 350 ºC concluding that the results revealed slag as suitable candidate to be used as TES material.

The results reported in Ref. [35,74] are summarized in Table 12 were slight differences in the thermophysical values are observed. This might be related to the heterogeneous nature of this material. Overall, the authors concluded that according to the results obtained, both slag can be considered as potential TES material candidates.

Table 12 As received and re-melted slag thermophysical properties reported by different authors ($^{1)}$ Archimedes method; $^{2)}$ Helium pycnometer; $^{S1)}$ Slag 1; $^{S2)}$ Slag 2; $^{v)}$ vitrified slag n.a. = not available; n.r. = not reported; r.t. = room temperature).

Property		As received slag	Temp range [ºC]	Re-melted slag	Temp range [ºC]	Ref
Density	kg/m^3	2876 $^{1)}$ 3170 - $^{2)}$ 3510 $^{S1)}$ 3430 – $^{S2)}$ 4110	r.t. r.t. r.t. – 350	2989 $^{1)}$ 2860 - $^{2)}$ 3600 n.a.	r.t. r.t. --	[35] [74] [80]
Melting temperature	ºC	1200 n.a. n.a.	-- -- --	n.a. n.a. n.a.	-- -- --	[35] [74] [80]
Heat capacity	$kJ\ kg^{-1}\cdot K^{-1}$	from 0.6 to 0.8 from 0.66 to 0.86	300 – 750 200 – 650	n.r. from 0.68 to 0.96 $^{v)}$ from 0.72 to 1.2	-- 200 – 650	[35] [74] [74]

		$^{S1)}$ 0.865 – $^{S2)}$ 0.837	r.t. – 350	n.a.	200 – 650 --	[80]
Thermal diffusivity	m^2/s	n.a. n.a. n.r.	-- -- --	n.r. from $8 \cdot 10^{-7}$ to $5 \cdot 10^{-7}$ n.a.	-- r.t. - 925 --	[35] [74] [80]
Thermal conductivity	W/m·K	n.a. n.a. $^{S1)}$ 1.47 – $^{S2)}$ 1.51	-- -- r.t. – 350	From 1.7 to 1.0 Around 1.7 n.a.	r.t. – 900 120 – 650 --	[35] [74] [80]
Thermal stability	ºC	Air Argon n.a. Air	r.t. – 1200 r.t. – 1200 -- 200 – 1000	n.a. n.a. n.a. n.a.	-- -- -- --	[35] [35] [74] [80]

A chemical compatibility analysis has also been reported by Mills [81] who presented a study of the slags reactivity with the container, the metal and the atmosphere. These studies, mainly focused on the reactivity of the slag with the typical elements used during the production of the steel, may be considered a first approach on the knowledge of compatibility of this by-product with other materials.

The reaction between the slag and the container is only described and few recommendations about the alloying metals to be used in the container are presented. Slag and metal reactions were softly studied in order to determine unwanted reactions in continuous casting. Regarding to the atmosphere, Mills analysed the formation of different oxides depending on the oxygen, nitrogen and moisture concentrations.

A more complete compatibility study by Ortega et al. [82] presented results of slags in contact with three different HTF: synthetic oil (Syltherm 800), molten salts (Solar Salt) and air. The target was to analyse the level of reaction of two different slag with these fluids in real working conditions (CSP plants) at 400 ºC, 500 ºC and 1000 ºC respectively.

The experiments were performed putting in contact a sample of slag with the correspondent fluid in a sealed crucible with controlled atmosphere during 500 hours. After this period the samples were analysed by XRD measurements and under scanning electron microscopy and thermochemically characterized. The results revealed that some structural modifications in the slag occur when working with air at 1000 ºC as HTF. These modifications were also observed in previous works by the same author [80] who concluded after these transformations, which occurs during the first hours/cycles, the material obtained is totally stable. Regarding the Solar Salt and Syltherm 800 results, no mayor transformations have been observed neither un the fluids nor in the slags, concluding that the slag are fully compatible with both HTF at the tested temperatures.

2.4.7 Storage application modelling analysis

The thermophysical properties revealed by the slag make this material very attracting for several thermal energy storage applications. However, as usual with novel TES materials, prior to the construction of any storage device based on steel slag, a strong modelling and design effort is still needed. In this sense, three different simulation areas are of special interest: modelling of the thermophysical properties of slag, basic design and modelling of heat storage concepts and devices, and thermomechanical modelling of the storage.

On the first step, the modelling of the thermophysical properties of steel slag, Mills [81] and references therein has developed different models and calculations in order to predict the most relevant thermophysical properties of the slag. In particular, numerical fits, neural networks, structural, thermodynamic and molecular dynamics models were used and developed. These techniques permitted to obtain an accurate description of the liquidus and solidus temperatures, heat capacity, enthalpy, thermal expansion, density, viscosities, electrical conductivity, surface tension and thermal conductivity.

Regarding the second modelling stage, basic design of heat storage devices, very limited information can be found in the literature related to steel slag based TES concepts. In this frame, CIC Energigune has identified the solid packed-bed arrangement of EAF slag pebbles as the most promising concept to use this material in heat storage applications [80,82]. Packed bed storage is a well-known and mature technology implemented in diverse TES applications [83-85]. From this starting point, several storage solid materials and heat transfer fluids (molten salts, thermal oil and air) have been modelled as potential TES device candidates in a thermocline-type storage [4,87].

Moreover, the underlying basis of packed bed modelling is also well developed and validated in different works.

For the particular case of EAF slag in packed bed arrangement, Ortega et al. [82] have performed Computational Fluid Dynamic (CFD) simulations establishing the optimization of the operation mode of the storage unit as a function of the inlet/outlet temperature tolerance of the system, oriented to potential new generation CSP plants. In their calculations they also estimate the overall efficiency of the storage system, determined between 58-93 % depending on the transient or stationary operation of the system. The optimization of the slag pebble diameter and its impact on the overall behaviour was also analysed. As a conclusion, the authors obtained very promising results, which guarantee the viability of EAF slag as storage material in packed bed arrangement.

2.4.8 Lab scale experiences

The slag have been moulded in form of plates (Figure 20(a)) and corrugated plates (Figure 20(b)) by PROMES CNRS Laboratory to be assembled (Figure 20(c)) and use in a small scale TES system using air as heat transfer fluid in direct contact with the storage material by [35]. Tests consisted on 25 cycles of 6 hours each one, with temperature variation from 100 ºC to 700 ºC and the results shown the re-melted slag was stable after more than 25 thermal cycles.

This test has validated the approach of using slag as TES material at laboratory scale. More complex geometries such as corrugated plates will be tested for comparison on their performances related to thermal storage.

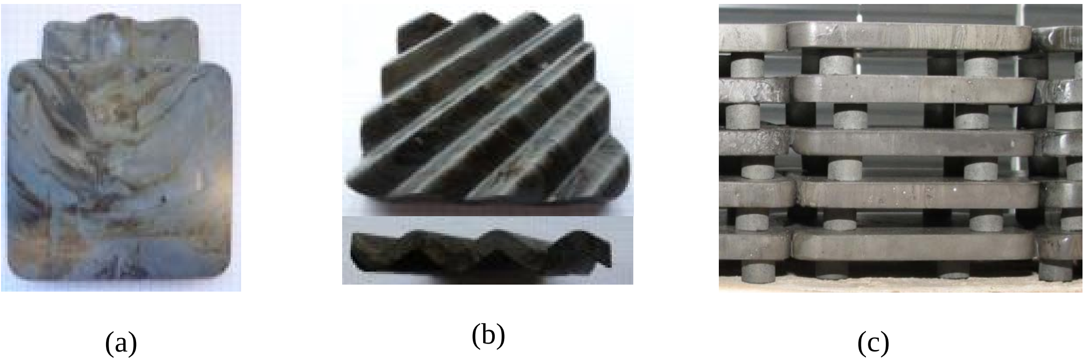

(a) (b) (c)

Figure 20 Pictures of (a) a single shaped slag plate (b) one corrugated plate made of slag, (c) assembled plates tested in direct contact with hot air [35]

Other metal industries

2.5.1 Waste from recycling steel process

Barreneche et al. developed in 2012 an elastomeric matrix made with EPDM filled with Electrical arc furnace dust (EAFD) and PCM [88-90]. Their composition is listed in Table 13.

Table 13 Composition of the material of EPDM matrix [88,89]

PCM	12 (% wt)
EPDM	16.7 (% wt)
EAFD	71 (% wt)
Zn stearate	0.3 (% wt)

The PCM used to manufacture the new materials was RT-21 commercialized by Rubitherm. This PCM has 21 °C as melting point and its phase change enthalpy is 100 kJ kg^{-1}.

On the other hand, EAFD is a brown powder containing heavy metals and it is classified as hazardous waste in most of the industrialized countries, requiring a treatment previous its landfill. For this reason, the process of incorporating EAFD as a filler into a polymer matrix, in order to obtain a composite formulation that can yield a mouldable heavyweight sheet useful for increase acoustic insulation in constructive systems is a feasible method to valorise this waste and to achieve one way to encapsulate/stabilize PCM.

Furthermore, the obtained results were compared with the results obtained for a commercial material characterized following the same assays and experiments. Thus, the advantages and inconveniencies presented for EPDM matrix may be shown and compared with the other two materials studied (TEXSOUND and EVA/EXACT).

Tensile strength test was done at room temperature conditions (around 20 °C) and the results of the mechanical properties average are listed in Table 14 as well as the thermophysical characterization and thermal conductivity values obtained.

Table 14 Mechanical and thermal properties of dense sheet materials under study [88,89].

		EPDM	EVA/EXACT (1:3)	Texsound
Maximum strength: σmax	(MPa)	2.0 ± 0.1	3.4 ± 0.2	0.4 ± 0.0
Maximum elongation: εmax	(%)	437	37.5	575
Melting Temperature	(°C)	22.4 ± 0.1	21.5 ± 0.5	No phase change
Melting Enthalpy	(kJ kg-1)	18 ± 0	12 ± 1	
Effective thermal conductivity: εeff	(W/m·K)	0.21	0.18	0.24

The thermal performance of this dense sheet has been already tested in start-stage in an experimental set-up located in Puigverd de Lleida (Figure 21). The material has been added in order to increase the thermal inertia of internal walls. The two cubicles were provided with an internal wall in order to simulate two different environments. Each area is equipped with a heat pump which located in the environment far from the dense sheet was programmed to operate between two different set points of 28 ºC and 18 ºC in cycles of 12 hours. The thermal response of the environment close to the dense sheet is evaluated.

Figure 21 Experimental set-up located at Puigverd de Lleida (Spain).

2.5.2 Waste from copper refinement process

By-products coming from the copper industry (BPC) are promising materials to be used as STES material [92,93]. Navarro et al. have evaluated the BPC stabilized in Portland cement properties as sensible heat TES by using design of experiments (DOE). The energy density (r_{en}) of these formulations, calculated by thermophysical characterization and bulk density, follows the Eq. 1 where *BPC* is the percentage in weight of the waste and percentage in weight of water is H_2O.

$$r_{en} = 4.41 + 0.11 \cdot \mathrm{BPC} - 0.047 \cdot \mathrm{H_2O} + 0.057 \cdot \mathrm{BPC} \cdot \mathrm{H_2O} \qquad (1)$$

Therefore, the energy density of the final compound is increased by increasing variables (BPC content and water ratio). However, the mixing process is more difficult when BPC percentage is higher than 77 % wt difficult. Moreover, the thermal conductivity of the samples under study does not depend on the BPC content and it is accounted around 1 W m^{-1} K^{-1}. The optimum formulations to be used in TES applications were those with a composition close to BPC content of 77 % and a water ratio of 0.57 %.

On the other hand, some slag from Cooper as well as from steel recycling process were evaluated and compared by Navarro et al. in 2012. The properties of these wastes were introduced in a material selection software and the evaluation of the selection were published [93]. This study demonstrated that several wastes (WDF, IB, Cofalite and WRutF) are cost effective materials to be used as sensible heat TES for an application such as concentrated solar plants, solar cooling, etc.

2.5.3 Dross from the aluminium industry

Aluminium industry is producing as well some waste called dross. Generally, in the aluminium process, dross represents more than 4 % of the total primary aluminium production and 20 % of the secondary aluminium production. In 2013 the yearly world production of primary and secondary aluminium raises up to 70 million metric tons despite the global economic crisis. This production generates between 1.5 and 2.5 million tons of dross that were landfilled.

In the United Arab Emirates (UAE), each year Emirates Global Aluminum (EGA) is producing around 2.3 Million tons of aluminium, generating large amount of Al dross. These wastes are for now stored on site as landfilling is totally forbidden in the UAE. Finding new solutions of waste management become then crucial. Al Naimi et al. [94,100] have studied the composition and thermal stability of as-received Al dross samples provide by the EGA Company. The selected samples in this work were aluminium white dross (AWD) (see Figure 22 (a)) and aluminium pot skimming (APS) (see Figure 22(b)) from primary aluminium process.

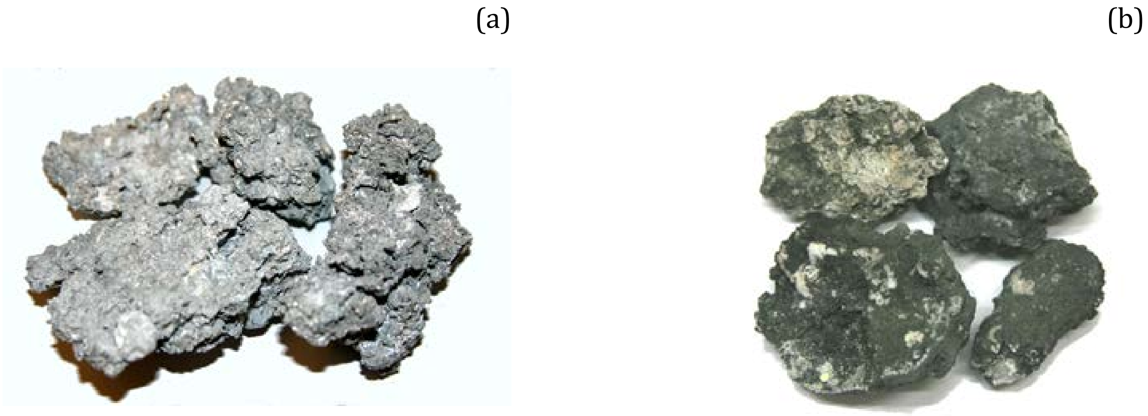


Figure 22 Pictures of (a) aluminum white dross (AWD); (b) aluminum pot skimming (APS) as-received samples [94]

In aluminium production, the process of reduction of alumina (Al_2O_3) consumes the carbon anodes which creates a layer of carbon dust plus some bath contents such as alumina (Al_2O_3) and cryolite (Na_3AlF_6) floating at the surface of the molten bath. This layer which is skimmed beforehand tapping the molten metal is the APS.

AWD is generated in casting operations and floats at the surface of the molten aluminium. Table 15 is presenting the chemical elements of the 2 samples measured with an X-Ray fluorescence (XRF), Niton XL3 XRF from Thermo scientific. Due to the limitation of the instrument, light elements (with atomic number (Z=16) and lower) could not be detected. The mass fraction of the light elements is contained in Bal* in the table. More than 80% of APS is contained in Bal * which was expected as APS is composed mainly of carbon as previously detected by EDS in the same work. Around 28% of aluminium is still contained in AWD. This is the reason to reprocess it in secondary aluminium production. The 67 % in Balance in the table can be explaining by the Oxygen not detected by the XRF tool previously detected with EDS.

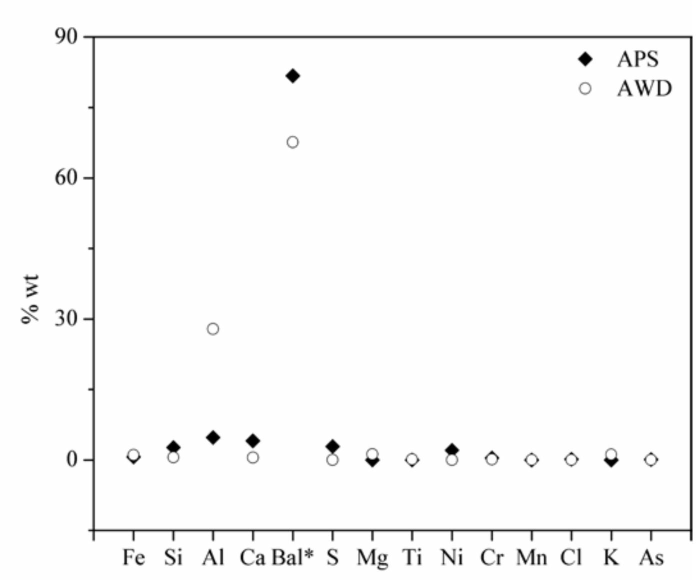
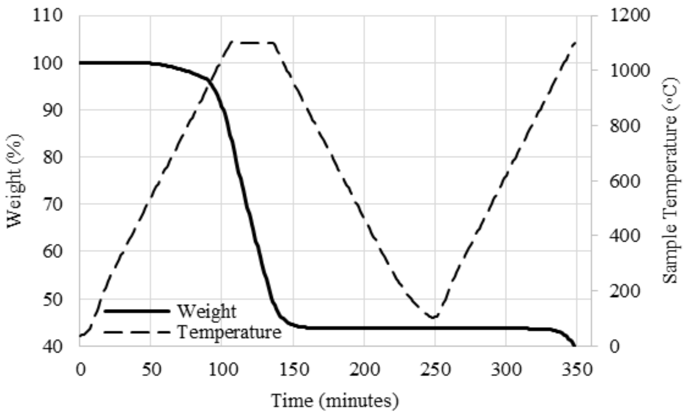


Figure 23 XRF Analysis of APS and AWD samples [100]

The thermal stability of the 2 samples were studied with a simultaneous thermal analyser (STA) 449 F3 Jupiter from Netzsch Company. Figure 23 shows the mass of the samples (in percent) versus time during thermal cycles from room temperature to 1100 °C. The APS sample starts to decompose around 500 °C and is then not suitable for higher temperature applications. On the other hand the mass of the AWD is increasing of around 10 % and is stabilized after the first cycle. This is due to the oxidation of the large amount of aluminium still contained in the material (27 %). Generally this AWD is reprocessed to extract as much as aluminium metal as possible from it. This step generates a new waste called aluminium black dross (ABD) which is currently under study at the Masdar Institute and is a new promising candidate for TES applications.



(a)

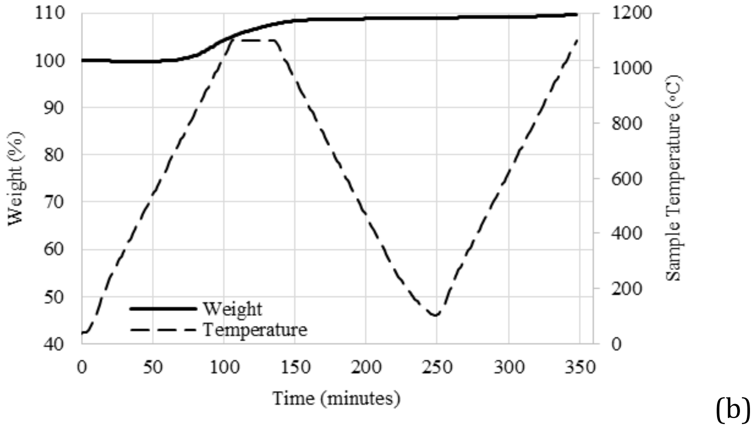


Figure 24 TGA curves of (a) APS and (b) AWD as-received samples [100].

2.4 Other industries

Three wastes and thirteen by-products from different industrial sectors (H_3PO_4 production process, biodiesel production, biomass pyrolysis and fibre production) were analysed in [95,96]. In order to analyse the suitability of these materials as latent thermal energy storage materials, measurements have been accomplished with DSC Netzsch F3 Maia. Sample mode without correction or baseline, heating rate between 0.5 and 2 K min^{-1} and sample mass around 20 mg was used to obtain first results in enthalpy –temperature curves.

Once the measurements were performed, four candidates were found. In Table 16, the source, the phase change and the potential of these candidates is shown.

Table 15 Candidates for latent thermal energy storage materials [95,96]

Candidate	Source	Phase change	Potential
Paraffin 1	Repsol (oil and gas industry)	from 20 to 45 ºC	≥ 200 kJ kg^{-1}
Paraffin 2	Repsol (oil and gas industry)	from 26 to 60 ºC	≥ 200 kJ kg^{-1}
Fibre 1	Fibre production	from $^{-}$15 to 0 ºC	≥ 200 kJ kg^{-1}
Fibre 2	Fibre production	from $^{-}$25 to $^{-}$5 ºC	150 – 200 kJ kg^{-1}

Municipal waste

2.7.1 Glass

Discarded waste glass is one of the major contributors of solid waste. It has become a significant burden on the landfills through-out the world. United Nation estimates the volume of yearly disposed glass waste to be 14 million tons [97]. For that, the feasibility of using soda–lime waste glass powder for latent heat storage application was investigated in [98].

n-Octadecane has a melting and freezing temperature close to the range of human comfort zone (16-25 ºC). For that, n-Octadecane was loaded into glass powder (GP) by using vacuum impregnation method. The surface morphology, chemical compatibility, phase change behaviour, thermal stability and reliability were determined. The maximum mass percentage of n-octadecane retained by GP was found to be 8 %. The melting and freezing temperatures of the composite PCM were found to be 26.93 ºC and 25.03 ºC while the latent heat of melting and freezing were 18.97 kJ kg^{-1} and 18.95 kJ kg^{-1} (Figure 24).

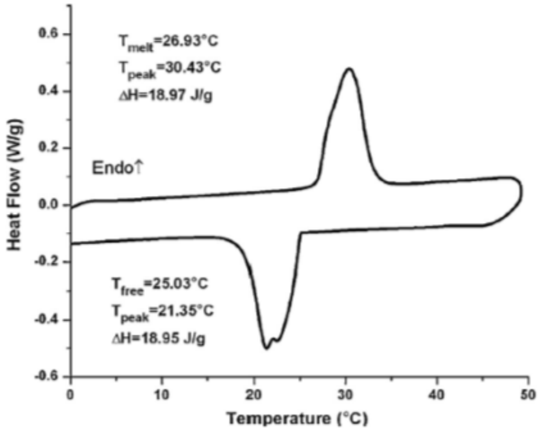


Figure 25 DSC curve of n-octadecane-GP composite PCM [98]

TGA and thermal cycling results confirmed that the composite PCM is thermally stable and reliable. It can be concluded that the composite PCM can be used for thermal energy storage applications in buildings. Its usage will provide sustainable solution to reuse the waste glass.

2.7.2 Nylon

Nylon fibres and crushed natural dolomite aggregates were used by Ozger et al. [99] to prepare a Portland concrete mix serving as a blank common Portland. For this study they manufactured concrete specimens with a 0.35 w c^{-1} ratio to study the effects of synthetic fibre reinforcement, and investigated their mechanical and thermal properties. The formula they obtained composed by Portland limestone cement, recycled nylon fibres, and dolomite aggregates as raw materials was a high-performance concrete thermal storage material using. These fibres come from post-consumer textile carpet waste. The fibre-reinforced concrete suffered less drying shrinkage than the plain concrete, and this is always beneficial because it coincides with a more limited formation of microcracks in the cement paste and a more durable material. The behaviour of the fibre-reinforced concrete (FC) appeared to be slightly more ductile than the plain concrete and the heat capacity and conductivity at 300 ºC of the FC were 0.63 kJ kg^{-1} K and 1.16 W m^{-1} K^{-1}. The better thermal behaviour of the fibre-reinforced concrete was thanks to the hygroscopic nature of the fibres. The FC exhibited a good thermal stability up to 450 ºC and the porosity produced by the melted fibres will improve the protection against thermal cracks.

3. Summary and conclusions

Table 16 shows a summary of the materials presented in this paper, together with the main parameters to consider for their use in TES applications. All materials studied so far that can be found in the literature would require an industrial validation, and only a few of them have been tested at pilot plan scale. It is also interesting to see that again only a few of them have their cost reported, but on the other hand, life cycle assessment has been carried out for about half of the materials studied. Finally, the literature shows that most of them would need to undergo a treatment prior to their reuse as TES material.

Table 16 Summary of the materials presented in this review.

Material	Industrial validation is required	Pilot plant studies	Cost estimated	Life cycle assessment (LCA)	Waste treatment before TES	Reference
Asbestos containing wastes	Yes	Performed	No reported/published	Performed	Yes	[12,29-31]
Vitrification waste	Yes	Non-Performed	No reported/published	Performed	Yes	[28]
Fly ashes	Yes	Non-Performed	No reported/published	Performed	Yes	[32-33]
Bischofite (low quality)	Yes	Non-Performed	40 US$/ton	Performed	No	[43]
Bischofite	Yes	Non-Performed	150 US$/ton	Performed	No	[43]
Bischofite+PEG	Yes	Non-Performed	No reported/published	Performed	Yes	[44]
Astrakanite and Kainite	Yes	Non-Performed	No reported/published	Non-Performed	No	[45]
Slag	Yes	Performed	Published*	Performed	Yes	[49,54-70]
EAF slag	Yes	Non-performed	No reported/published	Non-performed	Yes	[74,80-82]
PCM dense sheet	Yes	Non-performed	No reported/published	Non-performed	Yes	[88-90]
BPC cement	Yes	Non-performed	No reported/published	Non-performed	Yes	[91,92]
Low cost PCM	Yes	Non-performed	No reported/published	Non-performed	Yes	[95,96]
Waste glass	Yes	Non-performed	No reported/published	Non-performed	Yes	[97-99]
Nylon fibres reinforced cement	Yes	Non-performed	No reported/published	Non-performed	Yes	[99]

* depending on the reference

Different industrial waste materials have been considered as potential TES materials and have been characterised as such. Asbestos containing wastes, fly ashes, by-products from the salt industry and from the metal industry, wastes from recycling steel process and from copper refining process and dross from the aluminium industry, and municipal wastes (glass and nylon) have been considered.

All studied wastes and by-products have been thoroughly chemically characterized and most of them are today categorized to be landfilled or reused. This review also shows that some of this materials already undergo required treatments before landfilling, therefore, when considered as TES material the cost of this pre-treatment does not need to be included in the TES material as is, since it needs to be carried out to the original waste anyway. When possible, the review also presents a short overview related to the revalorization of the waste material or by-product, for example in slags from the metal industry.

It is important to highlight that all the wastes and by-products listed in this paper have an availability or year production high enough to be considered in the TES industry without fear of shortage. The cost is usually very difficult to have and has been reported in very few cases. Finally, as expected all of the wastes and by-products considered have their own strengths and weaknesses when considered to be revalorized as TES materials.

It is very interesting to notice that all the materials have been well characterized with a good thermophysical characterization and most of the cases with compatibility studies. Most cases, only lab characterization has been carried out, and only a few times pilot plant test and modelization can also be found in the literature.

This review shows that the revalorisation of wastes or by-products as TES materials is possible, and that more studies are needed to achieve industrial deployment of the idea.

Acknowledgements

The work is partially funded by the Spanish government (ENE2011-28269-C03-02, ENE2011-22722 and ULLE10-4E-1305). The authors would like to thank the Catalan Government for the quality accreditation given to their research group GREA (2014 SGR 123) and research group DIOPMA (2014 SGR 1543). The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° PIRSES-GA-2013-610692 (INNOSTORAGE). Laia Miró would like to thank the

Spanish Government for her research fellowship (BES-2012-051861). The work at CIC Energigune was supported by the Department of Industry, Innovation, Commerce and Tourism of the Basque Country government through the ETORTEK CIC Energigune-2013 research program. Research at Masdar Institute is supported by the Government of Abu Dhabi to help fulfill the vision of the late President Sheikh Zayed bin Sultan Al Nayhan for sustainable development and empowerment of the UAE and humankind. Researchers of PROMES address all their gratitude to the French government for the funding of their work through the ANR SESCO and SACRE projects within the ANR SEED program. They also acknowledge the support of the CNRS, the University of Perpignan Via Domitia and the EUROPLASMA/INERTAM company. The work at the University of Antofagasta was supported by FONDECYT (grant N° 1120422), CONICYT/FONDAP Nº 15110019, and the Education Ministry of Chile Grant PMI ANT 1201. Andrea Gutierrez would like to acknowledge to the Education Ministry of Chile her doctorate scholarship ANT 1106 and CONICYT/PAI N°7813110010.

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ANNEX II

PAPER PUBLISHED IN SOLAR ENERGY MATERIALS AND SOLAR CELLS.

Solar Energy Materials & Solar Cells 132 (2015) 385–391

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

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

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ARTICLE INFO

Article history:
Received 15 January 2014
Received in revised form
31 May 2014
Accepted 27 August 2014

Keywords:
Bischofite
Phase change material
Thermal energy storage
Solar energy
Latent heat
By-product salt

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 115 °C to 125 °C and the Cp showed linear increase from 1.71 kJ/(kg K) to 3.01 kJ/(kg K). The thermal stability test (30 heating/cooling cycles) of bischofite and $MgCl_2 \cdot 6H_2O$ shows subcooling of about 37 K and 29 K, 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 $MgCl_2 \cdot 6H_2O$. This study established that bishofite 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.

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

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http://dx.doi.org/10.1016/j.solmat.2014.08.042
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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 t 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] (Tables 1 and 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 40 °C.

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 $K\alpha 1$ ($\lambda = 1.5406$ 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

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

Reference	Cycle no	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]	165 [6–8,11,13]			–
		116 [6–8,11]	167 [3,7]	–	–	
		117 [3,6–8,12–16]	168.6 [6–8,12,15]			
Pilar et al. [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. [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. ** [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/m^3]	Density liquid [kg/m^3]
References without cycling the PCM	1569 (20 °C) [6–8,12,15] 1570 (20 °C) [6–8,11]	1442 (78 °C) [6–8,11,20] 1450 (120 °C) [6–8,12,15]

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 determined 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. Standard 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 115 °C to 125 °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):

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

Relatively liquid densities of bischofite were determined pycnometrically. The samples were melted for 90 min 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.

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

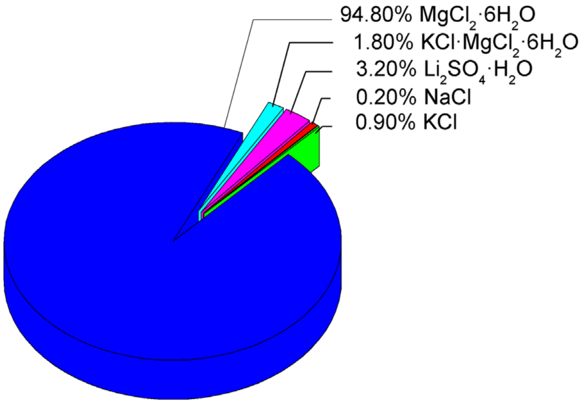

Fig. 1. Mineralization resulting of a bischofite sample.

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.

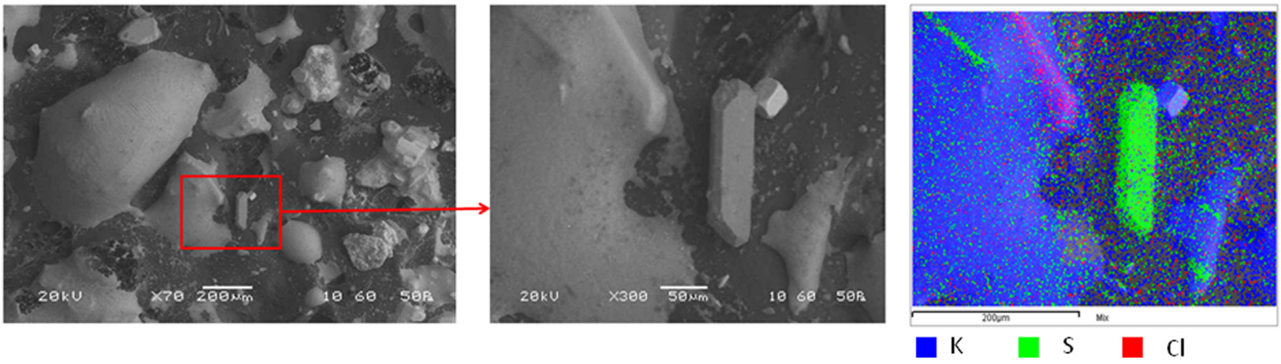

Fig. 2. SEM image of bischofite at: from left to right × 70, x300, and mapping: K (red), green (S), blue (Cl). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

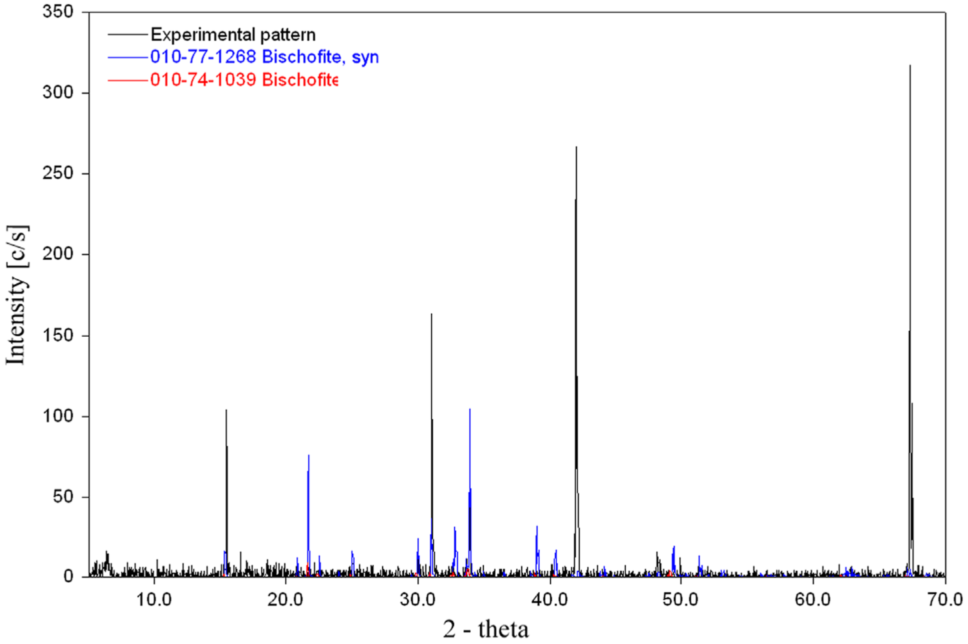

Fig. 3. XRD pattern of bischofite.

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 $T_{onset}=98.9\ ^{\circ}C$, $T_{peak}=116.6\ ^{\circ}C$ and a heat of fusion of 120.2 kJ/kg, whereas $MgCl_2 \cdot 6H_2O$ has a sharp peak with onset temperature of 114.6 °C 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 130 °C with 100% of the initial sample mass.

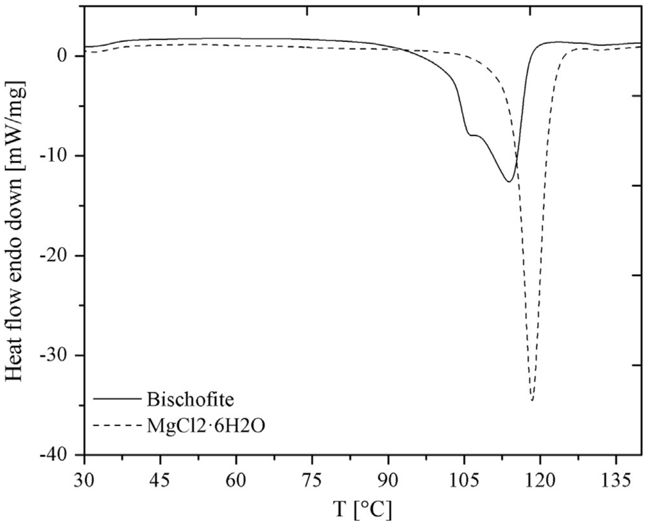

Fig. 4. DSC measurement curves for one heating cycle of bischofite and $MgCl2 \cdot 6H_2O$.

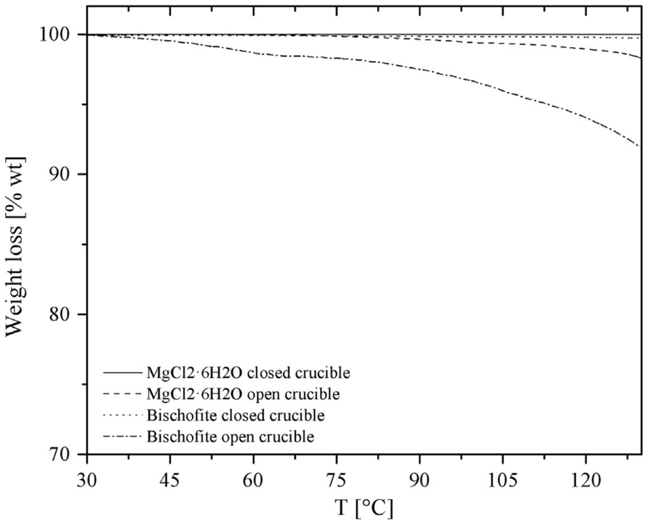

Fig. 5. Thermal stability of bischofite and MgCl2 · 6H_2O.

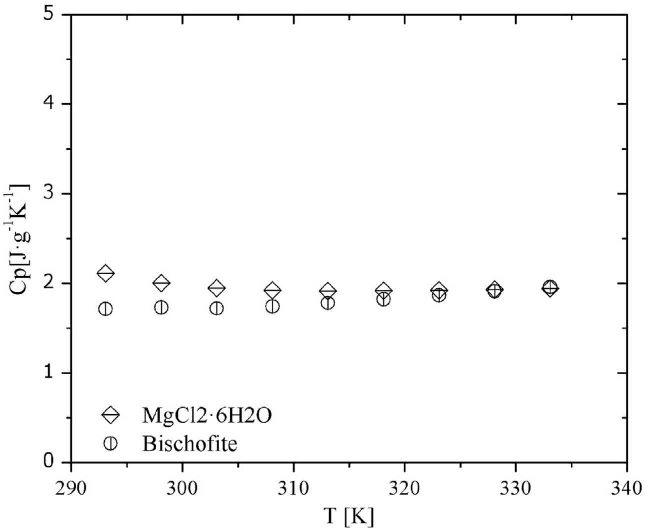

Fig. 8. Temperature dependence of heat capacity for solid samples.

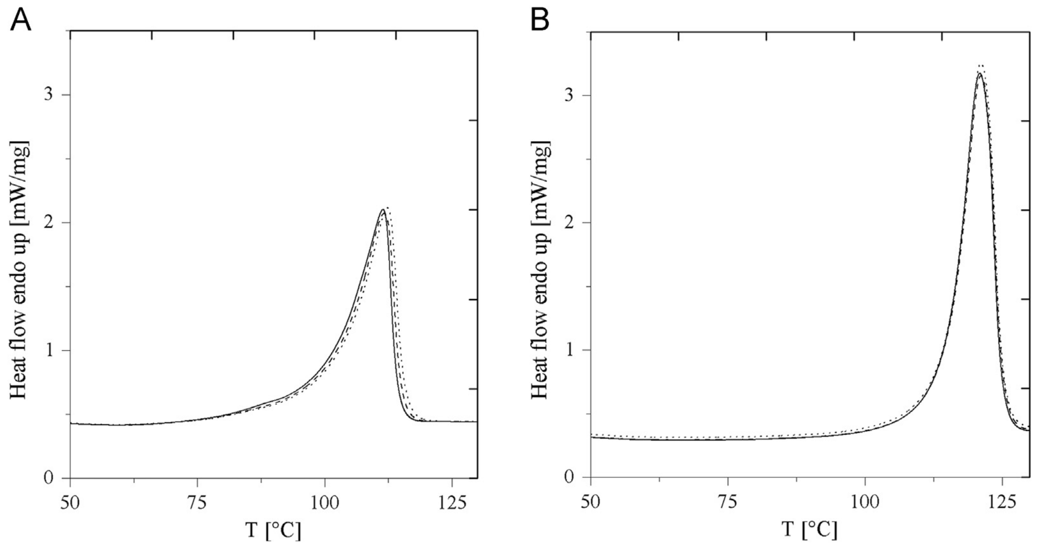

Fig. 6. DSC heating curves after various cycles, for (A) bischofite and (B) MgCl2 · 6H_2O. · · · · · · · · · · · · · 10, – – – – – · 20, and – · – · -30 cycles.

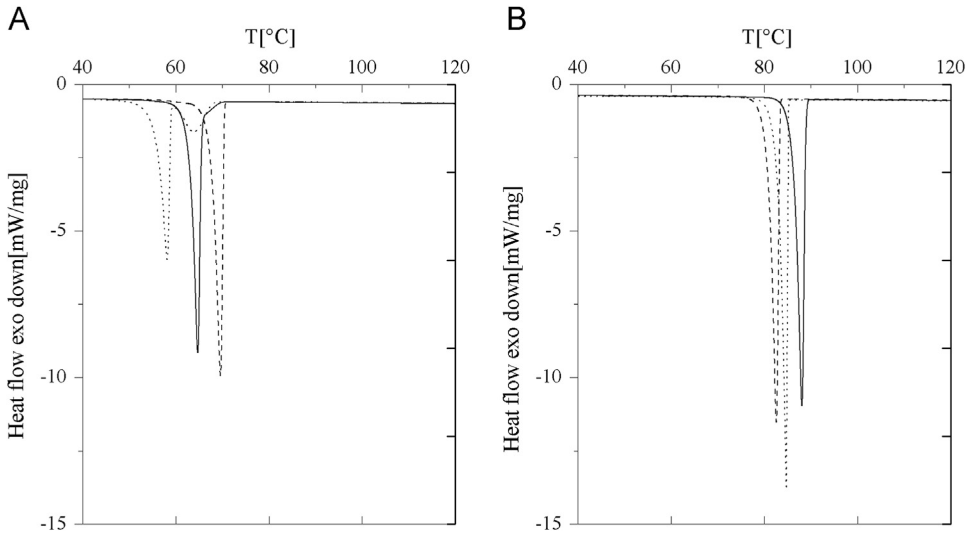

Fig. 7. DSC cooling curves after various cycles, for (A) bischofite and (B) MgCl2 · 6H_2O. · · · · · · · · · · · · · 10, – – – – – · 20, and – · – · -30 cycles.

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 90 °C. Bischofite shows about 2% mass loss at 50–60 °C and at 80 °C starts to loose mass gradually, showing an 8% mass loss at the end of the experimentation, at 130 °C.

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 $MgCl2 \cdot 6H_2O$ (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 37 K and 29 K for bischofite and $MgCl2 \cdot 6H_2O$, 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.

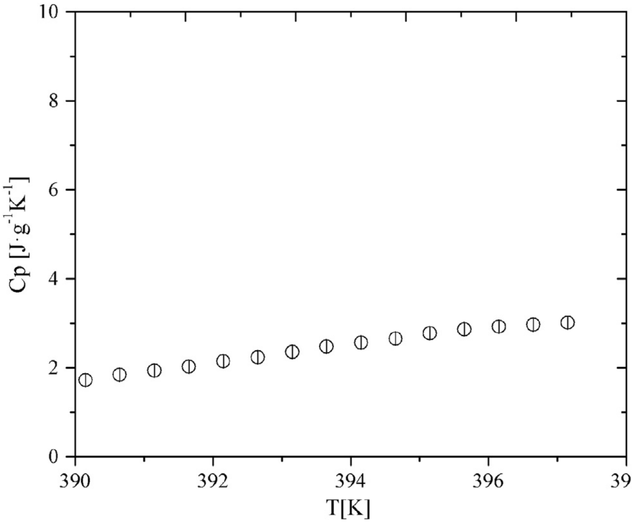

Fig. 9. Temperature dependence of heat capacity for liquid bischofite.

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

T [°C]	Bischofite	$MgCl_2 \cdot 6H_2O$	Phase
30	1686	–	Solid
40	1598		
50	1513		
115	1481	–	Liquid
128	–	1422	

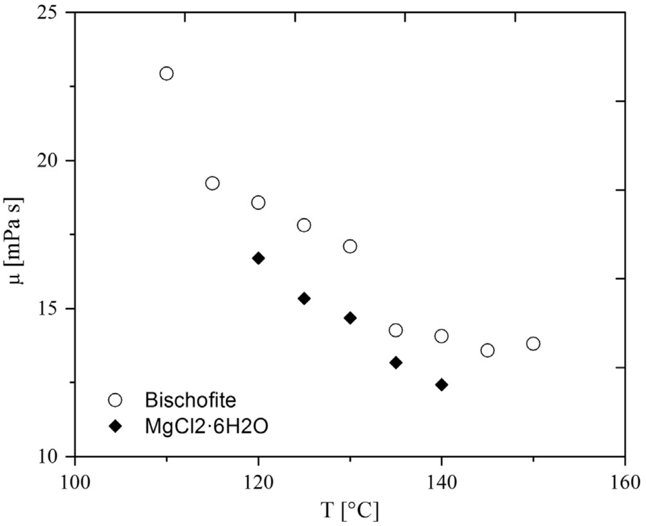

Fig. 10. Temperature dependence of dynamic viscosity for bischofite and $MgCl2 \cdot 6H_2O$.

Table 5
Summary of melting and crystallization temperatures, heat of fusion, and esd for bischofite and $MgCl_2 \cdot 6H_2O$.

Sample	Cycle no.	T_F [°C]	$\Delta_F H$ [J/g]	T_C (°C)	$\Delta_C H$ [J/g]	ΔT [°C]	esd [J/cm^3]
Bischofite	10	100.9	116.2	65.4	115.2	35.5	170
	20	101.1	116.0	70.1	115.5	31.0	
	30	102.2	115.5	58.7	115.8	43.5	
$MgCl_2 \cdot 6H_2O$	10	114.5	133.5	88.8	129.5	25.7	192
	20	114.6	133.1	83.2	129.4	31.4	
	30	114.4	136.9	85.2	132.3	29.2	

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 115 °C to 125 °C, with values from 1.71 to 3.01 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 115 °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 mPa s and for $MgCl_2 \cdot 6H_2O$ was 0.87 mPa s. The results are shown in Fig. 10.

As expected, the viscosity decreased with increasing temperature. Values of molten bischofite viscosity decrease from 22.9 to 13.8 mPa s in a temperature range from 110 °C to 150 °C. For $MgCl_2 \cdot 6H_2O$ values range from 16.7 to 12.4 mPa s in a temperature range from 120 °C to 140 °C.

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 °C. It was proven that subcooling have the value of 37 K 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 25 °C to 150 °C, where T_{fus} and ΔH_{fus} were 98.9 °C and 120.2 kJ/kg for bischofite, and 114.5 °C and 126.6 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 115 °C to 125 °C and the Cp showed linear increase from 1.71 kJ/(kg K) to 3.01 kJ/(kg K). The thermal stability test (30 heating/cooling cycles) of bischofite and $MgCl_2 \cdot 6H_2O$ shows subcooling of about 37 K and 29 K, 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 100 °C. 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

The authors would like to acknowledge the collaboration of the company SALMAG. The authors acknowledge to FONDECYT (grant no 1120422), CONICYT/FONDAP no 15110019, and the Education Ministry of Chile Grant PMI ANT 1201 for the financial support. This work was partially funded by the Spanish project ENE2011-22722. Dr. Luisa F. Cabeza would like to acknowledge the Generalitat de Catalunya for the quality recognition 2014-SGR-123. Andrea Gutierrez would like to acknowledge to the Education Ministry of Chile her doctorate scholarship ANT 1106 and CONICYT/PAI no 7813110010.

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ANNEX III
MANUSCRIPT SUBMITTED TO APPLIED ENERGY

Use of polyethylene glycol for the improvement of the cycling stability of bischofite as thermal energy storage material

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Abstract

Bischofite is a by-product of the non-metallic mining industry. It has been evaluated as phase change material in thermal energy storage, but it shows little cycling stability, therefore in this paper the mixture of bischofite with an additive was studied. Since polyethylene glycol (PEG) is a PCM itself, in this paper PEG (with different molecular weights) is used as additive in a PCM (bischofite) to improve its thermal behaviour. Results show that adding 5% PEG 2 000 to bischofite gives a more cycling stable PCM without affecting its melting temperature neither decreasing significantly its heat of fusion. This research shows that mixing an inorganic PCM with an organic additive can be a good option to improve the thermal performance of the PCM.

Keywords: Bischofite, phase change material (PCM), latent heat, thermal energy storage (TES), polyethylene glycol (PEG), cycling stability

1. Introduction

The use of fossil fuels and coal as main source of energy to produce electricity in northern Chile and also the non-existent production of hydropower water resources is a serious environmental impact, generating an urge to find substitutes towards sustainable energy sources. The high-energy consumption of this part of the country is directly related to the mining and industrial processes, which require continuous operation of energy. This is why renewable resources can be an alternative, as a complement to the main sources of energy [1]. Moreover, due to the favourable climatic conditions, the use of solar energy is seen as the right way to go. The use of solar energy brings immediately the need of thermal energy storage (TES) for system optimization. The use of latent heat in TES is very attractive due to its simplicity compared to thermochemical storage and to its higher energy density compared to sensible heat [2].

Bischofite is a mineral that precipitates in the evaporation ponds during the potassium chloride production process in Salar de Atacama (north of Chile), in a quantity of about 1.3 million tons per year. Bischofite has a few practical applications and only about 8% of the produced bischofite is marketed today: 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. On the other hand, the main component of this waste is $MgCl_2 \cdot 6H_2O$ with some impurities.

Moreover, $MgCl_2 \cdot 6H_2O$ is a well-known potential phase change material (PCM) in TES for applications such as recovery of waste heat from the industry or use of solar energy in the industry and in solar cooling [3-12]. This is why the authors of this paper have considered the use of bischofite as PCM.

In a previous paper the authors characterized bischofite as PCM [13]. Bischofite has a composition of nearly 95% $MgCl_2 \cdot 6H_2O$, with $Li_2SO_4 \cdot H_2O$, $KCl \cdot MgCl_2 \cdot 6H_2O$, NaCl, and KCl as main impurities. When applied in an energy system, bischofite should not be purified to have an economic potential for commercialization. Bischofite has a melting temperature of T_{onset}=98.9ºC, a heat of fusion of 120.2 kJ/kg, and an energy storage density of *esd*=170 MJ/m^3. That paper showed that the principal drawback found for bischofite to be used as PCM is its subcooling (37 K), which is not only high but also not constant in the cooling process of the different cycles (Figure 1).

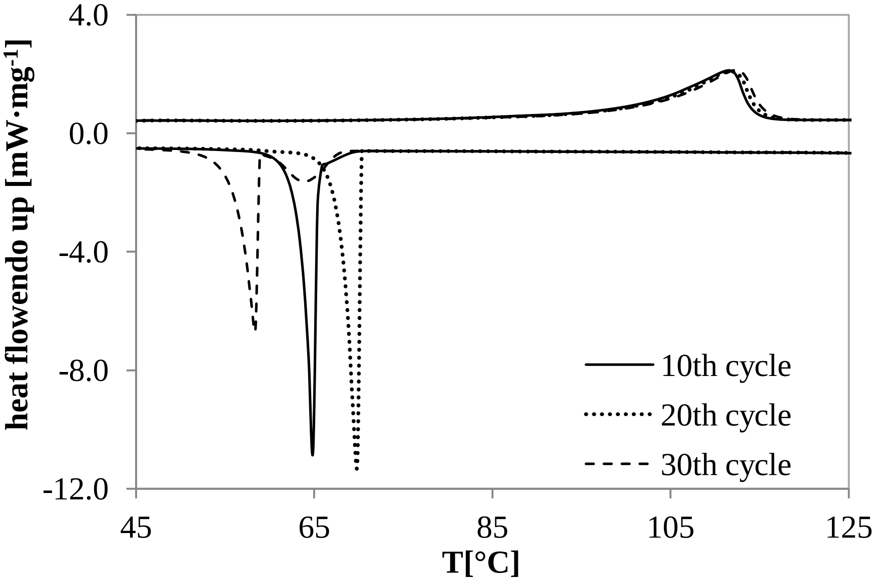

Figure 1. 10th, 20th and 30th DSC heating and cooling curves of bischofite [13].

Poly(ethylene glycol) (PEG) has been used as PCM by itself [14], but in this research we propose PEG as additive for bischofite. PEG was chosen because of its good chemical and thermal stability, expecting it could give the salt hydrate a better thermal and cycling performance, without reducing significantly its heat of fusion; moreover, this material is considered “green” because of its biodegradation and non-toxicity [25].

A PCM needs to be stable after a number of repeated melting/freezing cycles known as cycling stability [26]-27].This stability include thermal, chemical and physical properties, which should remain constant or almost constant after a cycling stability test. Cycling stability can be studied in an oven or with DSC. On the other hand, thermal stability ensures that the PCM is stable at a constant established working temperature. It can be studied in an oven or with TGA [28].

The aim of this paper is adding PEG to bischofite to improve its cycling stability during heating and cooling cycles, improving the cycling performance of the mixture when applied as phase change material. The main novelty of this paper is the use of PEG as additive to improve cycling stability of PCMs and not as PCM itself. Moreover, this paper shows the advantage of using an organic material to improve the properties of an inorganic PCM.

2. Materials and methods

2.1 Materials

The bischofite used in this research had a composition that about 95% $MgCl_2 \cdot 6H_2O$ and almost 5% of impurities as NaCl, KCl and $Li_2SO_4 \cdot H_2O$ and $KCl \cdot MgCl_2 \cdot 6H_2O$. PEG from MERCK of different molecular weight as PEG 600, PEG 2 000 and PEG 10 000 were used as thickener additive to improve thermal stability. Previously, bischofite was subjected to a drying heat treatment at 40 °C for 12 h, and then the samples were left in a desiccator.

Bischofite was analyzed alone and with 5% w/w of the three differents molecular weight PEG (Table 1). Previously other percentages were tried, but lower quantities of PEG in the bischofite did not give any significant change to the material, and higher quantities did reduce considerably the heat of fusion of the mixture without improvement in the subcooling.

Table 1. Samples composition of bischofite mixtures with PEG

Sample	Composition (% w/w)
I	Bischofite
II	Bischofite (95%) + PEG 600 (5%)
III	Bischofite (95%) + PEG 2 000 (5%)
IV	Bischofite (95%) + PEG 10 000 (5%)

2.2 Methods

Thermal stability analysis was determined with TGA/DSC METTLER TOLEDO, in a temperature range of 30 °C to 125 °C with heating rates 5 °C min^{-1} and 10 °C min^{-1}, under purified nitrogen atmosphere with a flow rate of 30 mL min^{-1}. Standard aluminium pan with lid (40 μL) were used. To determine the phase change temperatures and the latent heat of fusion a DSC 204 F1 *Phoenix* ® NETZSCH with N_2 atmosphere (volumetric flow 20 mL min^{-1}) was used. Melting temperature and heat of fusion were measure in a range from 25 °C to 140 °C. Crucibles of aluminium with 40 μL volume capacity were used. Similarly, this DSC was used to cycle between 40 °C and 120 °C the samples to determine their stability through cycles.

3. Results and discussions

3.1 Thermal properties

Some thermophysical properties available in literature for PEG of different molecular weights used are shown in Table 2, where it can be seen that melting temperatures are below 70 °C and the range of heat of fusion is from 108.6 kJ kg^{-1} to 188.7 kJ kg^{-1}.

Table 2 Thermo physical properties of PEG used as additives in this research.

Compound	Melting temperature (°C)	Heat of fusion (kJ kg^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Density (kg m^{-3})	Ref.
PEG 600	17 – 22	127	0.19 $^{(liquid\ 38°C)}$	1126 $^{(liquid\ 25°C)}$ 1232 $^{(solid,\ 3°C)}$	[2]
PEG 2 000	51.7-57.8	108.6	-	-	**¡Error! No se encuentra el origen de la referencia.**
PEG 10 000	66.6	188.7	-	-	[14]

As indicated in Table 2, PEG 600 is liquid at room T (<25 ° C) and have high heat of fusion. PEG 2000 and PEG 10 000 are solid at ambient T and they melt, mixed with bischofite, during the heating process; PEG 10 000 has a heat of fusion nearly twice higher than PEG 2000. The results of the melting temperatures in all mixtures of bischofite with three different molecular weight PEG´s are similar, around 98 °C, except for the mixture of bischofite + 5% PEG600 (**Table 3Table 3**) which has a melting temperature of 79.3 °C.

Table 3. Melting temperature and heat of fusion of bischofite and its mixtures with different PEG.

Sample	**T_F [°C]**	**ΔH_F [kJ·kg^{-1}]**
Bischofite	103.8	117.4
Bischofite+5% PEG600	79.3	61.1
Bischofite+5% PEG2000	98.8	108.8
Bischofite+5% PEG10000	96.5	86.4

Table 3 also shows the results of heat of fusion for the mixtures, which are within the range from 61.1 kJ kg^{-1} to 108.8 kJ kg^{-1}. It can be seen that the addition of PEG 2 000 does not affect significantly the heat of fusion for bischofite sample. Furthermore, the addition of PEG 600 and PEG 10 000 adversely affects the value of heat fusion, decreasing the values by 48% and 26%, respectively.

3.2 Thermal stability

The results of TGA (thermal stability) are shown in Figure 2.

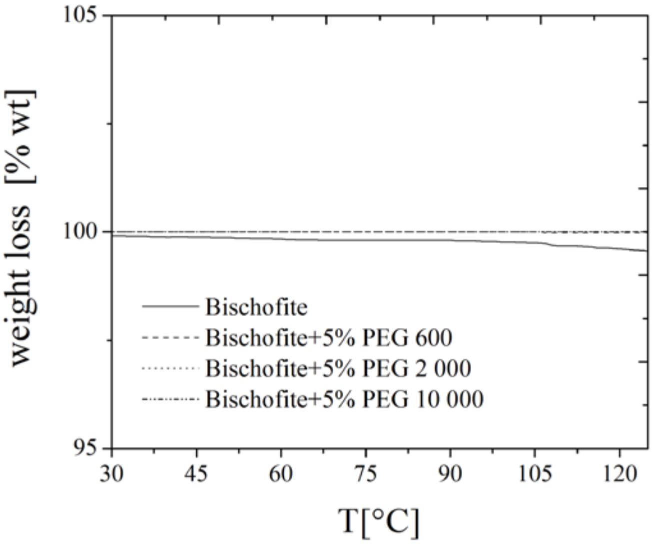

Figure 2. Thermal stability of bischofite and its mixtures with different PEG as a function of temperature

They show that the samples are thermally stable. With a detailed analysis four curves can be seen. The most unstable curve corresponds to bischofite, with a loss weight of 0.4% respect to the initial weight; the other three samples do not show differences because none of them lost mass, reaching 130 ºC with 100% initial weight.

3.3 Cycling stability

The cycling stability of samples was studied during 30 heating and cooling cycles. In Figure 3, the 10th, 20th and 30th heating cycle of samples I, II, III and IV are shown.

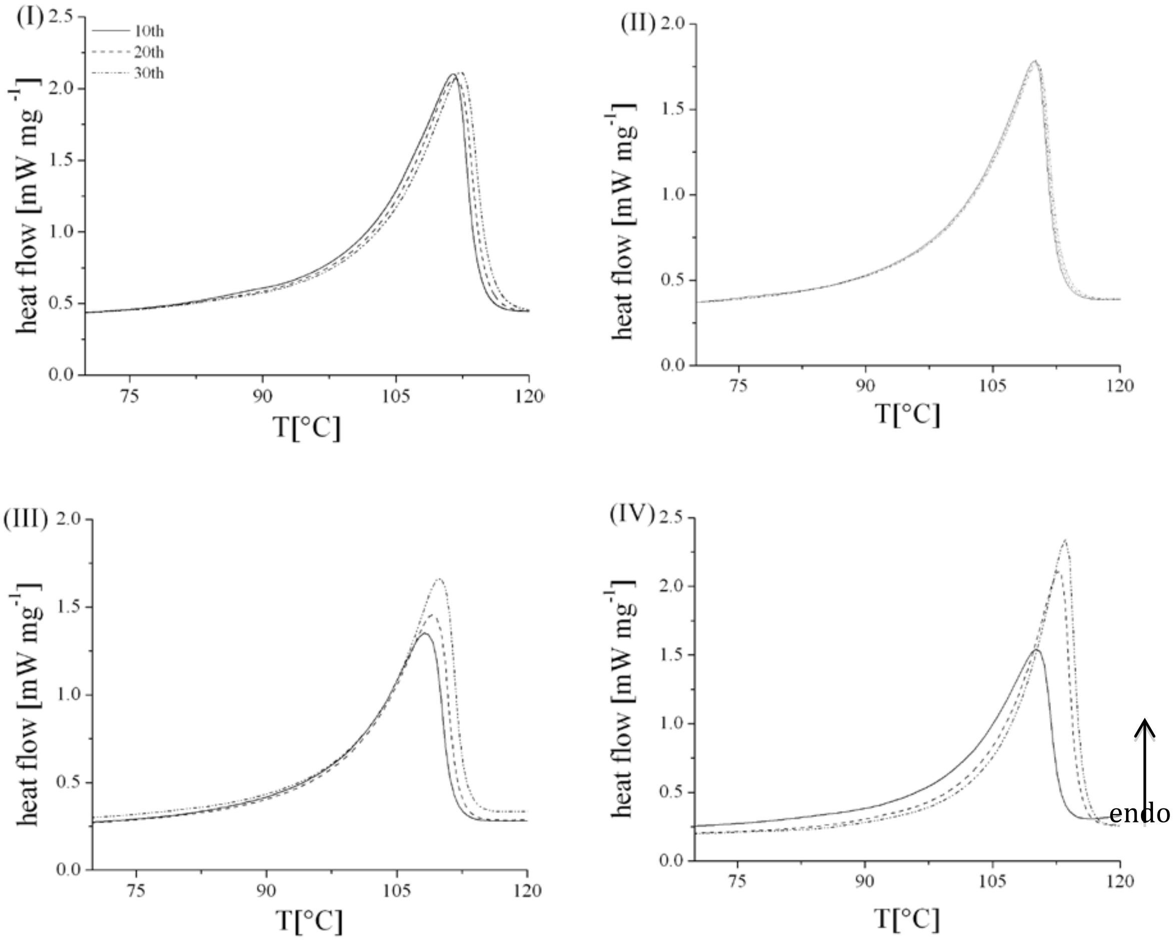

Figure 3. 10th, 20th and 30th DSC heating curves. (I) bischofite, (II) bischofite+5% PEG600, (III) bischofite+5% PEG2000 and (IV) bischofite+5% PEG 10 000.

Curves are stables during cycles, with similar melting temperatures reaching after 30 heating cycles. Especially, sample II (Bischofite+5% PEG 600) (Figure 3 (II)), where it only one curve is seen because the four curves are overlapped. The less regular sample is the bischofite+5% PEG 10000 (Figure 3 (IV)), since when the heating cycles temperature increases, the heat of fusion increases too.

For samples I, II, III and IV, melting temperatures were: for 10th cycle, 100.9°C, 99.4°C, 97.7°C and 99.7°C, respectively; and for 30th cycles were 102.2 °C, 99.4°C, 100.6°C and 105.5°C for the same samples.

The cooling cycles are shown in Figure 4, for the 10th, 20th and 30th cycles of all samples.

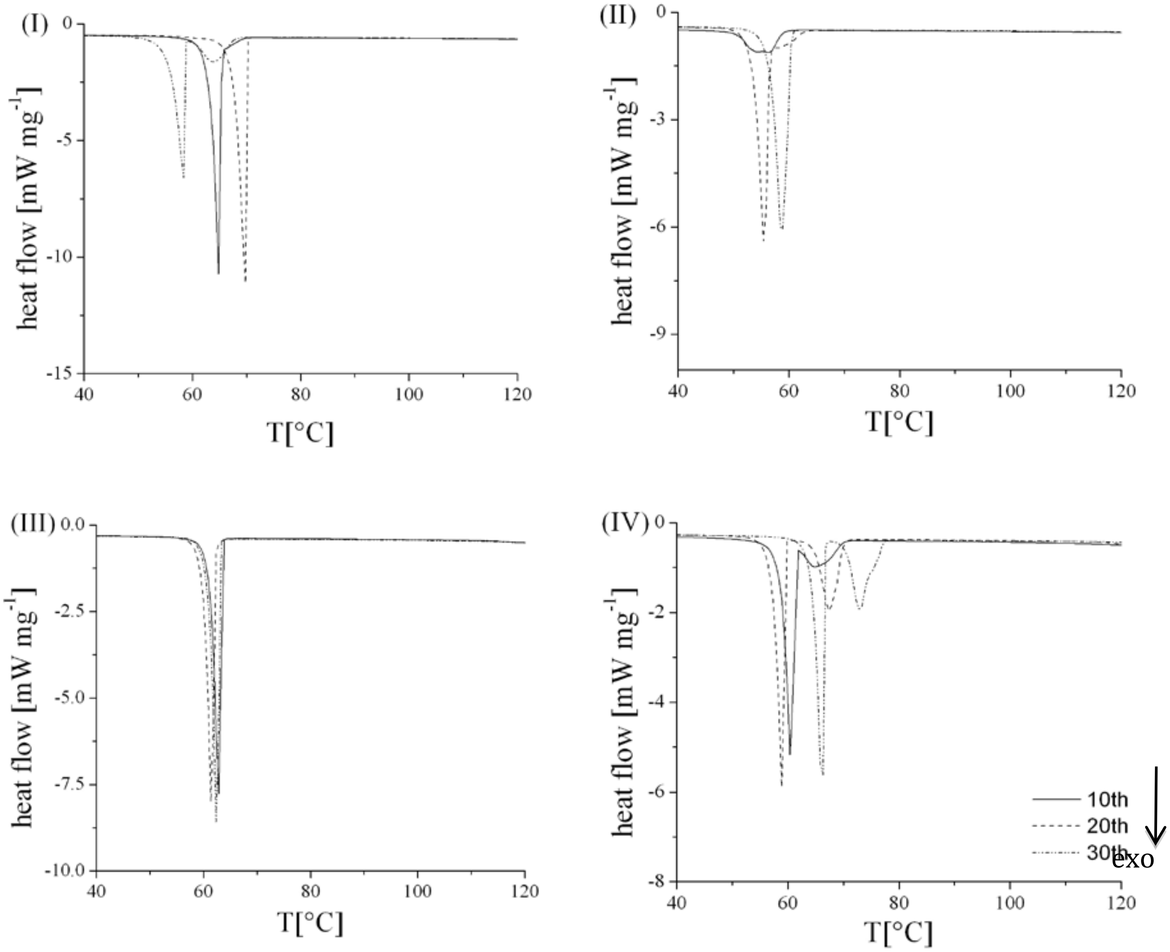

Figure 4. 10th, 20th and 30th DSC cooling curves. (I) bischofite, (II) bischofite+5% PEG600, (III) bischofite+5% PEG2000 and (IV) bischofite+5% PEG 10 000.

For samples I, II and IV, freezing temperatures present fluctuating values during the tests. The T_{cr} (on set values) varies with increasing cycles: for example, for 10th cycle, freezing temperatures were 65.4°C, 58.9°C and 69.9°C, respectively for samples I, II and IV; and for 30th cycles were 58.7 °C, 60.5 and 66.7°C. Bischofite has two peaks during cooling step, from the cycle 27 (not shown in Fig. 4) similar to cycle 30 (indicated in Fig. 4), probably due to the segregation of the impurities in the mineral. This effect was observed in previous work and described in [13]. Also, the most unstable sample, as in for the heating cycles, is the bischofite+5% PEG 10 000 (Figure 4 (IV)); the presence of two separated peaks during each cooling step is observed, due to the melting of mixture components by separate: bischofite and PEG 10 000, which probably indicates that these materials are immiscible

The mixture which presents the best behavior from the point of view of cycles of heating and cooling stability, remaining constant the crystallization temperature, is bischofite with the addition of 5% of PEG 2 000. This mixture (sample III) presents a stable behavior during 30 cycles of this experiment, remaining constant the values of heats of fusion and crystallization and close to those thermal characteristics of bischofite without additives (sample I). For this mixture (sample III), the values obtained of ΔH_F and of ΔH_{cr} are within the range from 83.6 to 108.8 kJ kg^{-1} and from 81.1 to 86.3 kJ kg^{-1}, respectively; the T_F are 97.7, 98.7 and 100.6 °C (cycle 10, 20 and 30) and T_{cr} are 63.6, 62.3 and 61.8 °C (cycle 10, 20 and 30). One of the disadvantages that bischofite presented was the subcooling of 37°C [13]. Similar results were obtained in this study with a ΔT=35.5°C. Furthermore, the addition of PEG it didn't reduce the subcooling. Samples II, III and IV exhibit this thermal phenomenon, around 40.5, 34.1 and 29.8 °C, respectively.

Although the addition of PEG 2 000 improves the cycle stability of bischofite, specially in crystallization process, the problem of subcooling is still present. Future studies are required to find nucleating agents, to mitigate this problem.

3.4 Possible applications

The potential for use a material as PCM is detemine mainly because of its values of heat of fusion (>100 kJ/kg) and melting temperature.

Farid et al. [30] indicated that for practical uses, the PCM`s should have a melting temperature within the practical range of operation, have a minimum subcooling and be chemically stable, nontoxic and non-corrosive. As well, they must have a low cost. In this sense, the mixtures studied in the present work have a T_F around 100 °C, and a potential application would be as a thermal energy storage material for indoor solar cooking [12] or for industrial waste heat (IWH) recovery in the processes that are listed in Table 4 [32], where the exhaust gas temperature could be stored for later use.

Table 4 Exhaust gas temperature of different industrial processes.

Process	Exhaust gas temperature °C
Drying, baking and curing ovens	90 – 230
Cooling water from annealing furnaces	70 – 230
Cooling water from internal combustion engines	70 – 120

Exhaust gases existing recovery devices in gas-fired boilers, ethylene furnaces, etc	70 – 230
Conventional hot water boiler	60 – 230

Even though is difficult to estimate the price of these mixtures with the data available up to now if applied as PCM for TES, it is possible to determine the advantages over the synthetic salts, linking the prices of these materials with the thermal properties determined in this study for bischofite and for other hydrated salts reported in previous studies [13, 32-33]; according to this, to storage 1 MJ of energy with hydrated salts as PCM below 100 °C would cost 1.28 US$ for bischofite, 12.4 US$ for $MnSO_4 \cdot 7H_2O$ and 15.0 US$ for $Mn(NO_3)_2 \cdot 6H_2O$.

4. **Conclusions**

Thermophysical properties for mixtures of bischofite with three different PEG (PEG 600, PEG 2000 and PEG 10 000) were determined to stabilize the thermal properties during cycles of heating and cooling. The results obtained for bischofite alone are similar to those reported in a preview research. For the new mixtures with different molecular weight PEG, the melting temperatures and heats of fusion measured were in the temperature range from 25 °C to 140 °C. The results obtained were T_F 79.3 ºC and ΔH_F 61.1 J g^{-1} for sample II (bischofite+5%PEG600), T_F 98.8 ºC and ΔH_F 108.8 J g^{-1} for sample III (bischofite+5%PEG2000) and T_F 96.5 ºC and ΔH_F 86.4 J g^{-1} for sample IV (bischofite+5%PEG10000). The cycles of heating and cooling were measured in the temperature range from 40 °C to 140 °C. The most stable sample was bischofite+5% PEG 2000 with a constant subcooling of about 36 ºC.

The addition of PEG 2000 did not change the melting temperature of bischofite neither did decrease significantly its heat of fusion. This research has shown that PEG is a good additive to improve cycling stability of PCM. This research also shows that mixing an inorganic PCM with an organic additive can be a good option to improve the thermal performance of the PCM.

Acknowledgments

The authors would like to acknowledge the collaboration of the company SALMAG. The authors acknowledge to FONDECYT (grant N° 1120422), CONICYT/FONDAP Nº 15110019, and the Education Ministry of Chile Grant PMI ANT 1201 for the financial support. This work was partially funded by the Spanish project ENE2011-22722. Dr. Luisa F. Cabeza would like to acknowledge the Generalitat de Catalunya for the quality recognition 2014-SGR-123. Andrea

Gutierrez would like to acknowledge for her doctorate scholarships to the Education Ministry of Chile (ANT 1106) and CONICYT/PAI N°7813110010.

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ANNEX IV
PAPER PUBLISHED IN ENERGY PROCEDIA

Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 57 (2014) 627 – 632
Energy Procedia

2013 ISES Solar World Congress

Development of Thermal Energy Storage Materials from Waste-Process Salts

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Abstract

TES is a technology that has been taken more importance in the last decades because of the increasing demand of clean energies, to avoid environment polluting by energy production from fossil sources. For that reason has been developed many materials for energy storage so far, but many of them are still much expensive and produce lesser energy than conventional fuels.

In this research the potential use of waste-process salts, coming from the non-metallic mining industry in northern Chile, as heat storage materials were studied. The cost of these salts is low, and it corresponds to the transport cost to the application place mainly. The stability and thermophysical properties of two hydrated double salts, astrakanite and kainite, were determined by thermogravimetry and differential scanning calorimetry techniques. That information was useful to establish the range of application for these waste-salts as materials for sensible energy storage. The results proved that both salts are suitable for using as heat storage materials at low temperatures, 0ºC to 120ºC. Also it was found that the anhydrous phase of astrakanite can be used as solid TES material at higher temperatures, 350ºC to 530ºC.

Selection and/or peer-review under responsibility of ISES

Selection and/or peer-review under responsibility of ISES.
Keywords: Thermal energy storage, solar energy ,hydrate salts, waste-salts, heat capacity

Introduction

The increasing energy demand, because of the global economy growth, has motivated the research in more efficient and clean technology for the use of energy for domestic and industrial purposes. The storage technologies are the main development so far and they have the aim of storing energy at high or low temperature for later consumption. The main types of energy storage are: Solar energy storage for

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Selection and/or peer-review under responsibility of ISES.
doi: 10.1016/j.egypro.2014.10.217

heating day overnight, summer heat storage for use during the winter, winter ice storage for cooling rooms in summer and heat storage cold or electrically generated during off-peak hours for consumption in peak hours [1]. TES is associated with solar energy commonly because of the peak hours of power used do not coincide with the hours of sunlight usually, e.g. the increasing energy consumption is given after sunset. Therefore the energy storage can help reduce these problems to deliver the stored energy in peak periods such as at night or on cloudy days [2].

In general, there are three types of thermal energy storage systems: chemical reaction, sensible heat and latent heat. Storing heat produced by reversible chemical reactions is chemical TES. The sensible TES uses the energy released or absorbed when the temperature decreases or increases. According to the physical state of the sensible storage medium, they are classified as solid (rocks, ceramics, plastic foams and others) and liquid media (water, oil, molten salts, etc.). Latent TES medium has the ability to store or release the same amount of heat than the energy associated with the phase change heat, usually from solid to liquid and liquid to solid states [3].

The North of Chile has a unique potential for developing and implementing clean energy technology. On the one hand, the climate represents an opportunity for developing clean technologies, based on the use of solar energy. On the other hand, the large reserves of salts found in the Atacama salt lake and other salt lakes have potential applications as thermal energy materials. Therefore the aim of this investigation is to evaluate the potential of two double hydrated salts to be used as thermal storage materials. These salts are waste materials from the extraction processes of the non-metallic industry in northern Chile. The samples were characterized by scanning electron microscopy, SEM-EDX. TG and DSC were performed to the salts to determine their stability range and heat capacity. Finally the thermal properties and cost of these salts were compared with the common materials used for thermal storage in engineering applications.

2. Experimental part

2.1Materials

The astrakanite sample was synthesized from a mix of 18.18 % of Na_2SO_4, 16 % $MgSO_4$ and 66% distilled water. The compounds used were reagent grade from Merck. The mix was prepared at room temperature and heated to 50 ºC to evaporate the water and precipitate 218 g of astrakanite.

The kainite sample used is a waste-salt from the evaporation stage of a salt production process.

2.2 Morphological Characterization

The chemical analysis of the sample composition and its impurities were determined using, a scanning electron microscope, SEM, (Jeol, model JSM6360 LV) coupled to an energy dispersion spectrometer, EDX, (Inca Oxford). The measurements were made at low vacuum, using an electron beam of 20kV, work distance of 10 mm, spot size of 60mm and backscattered electron signal.

2.3 Thermal properties

The astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) and kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) samples, were dried at 40 ºC for 12 h before using.

To evaluate the thermal stability of the salts, the equipments used were: TGA-DSC 1 METTLER TOLEDO and NETZSCH DSC 204 F1, with nitrogen atmosphere (Volumetric flow of 25 $ml \cdot min^{-1}$) and heating rate of 5K/min. Sealed containers made from Aluminum, of 40μL of capacity, were used to contain the samples (10±0.1 mg).

To determine the heat capacity was used a NETZSCH DSC 204 F1 with nitrogen atmosphere (volumetric flow of 20 mL·min^{-1}) at the temperature range from 0 °C to 100 ºC for astrakanite, kainite and anhydrous phase of astrakanite. Sealed containers made from Aluminum, of 40µL of capacity, were used to contain the samples (10±0.1 mg). The RATIO METHOD was used to calculate the Cp values as a function of temperature**.**

3. Results and discussions

3.1 Morphological Characterization

The morphological study for Astrakanite and kainite made using SEM-EDX is presented in Fig.1.

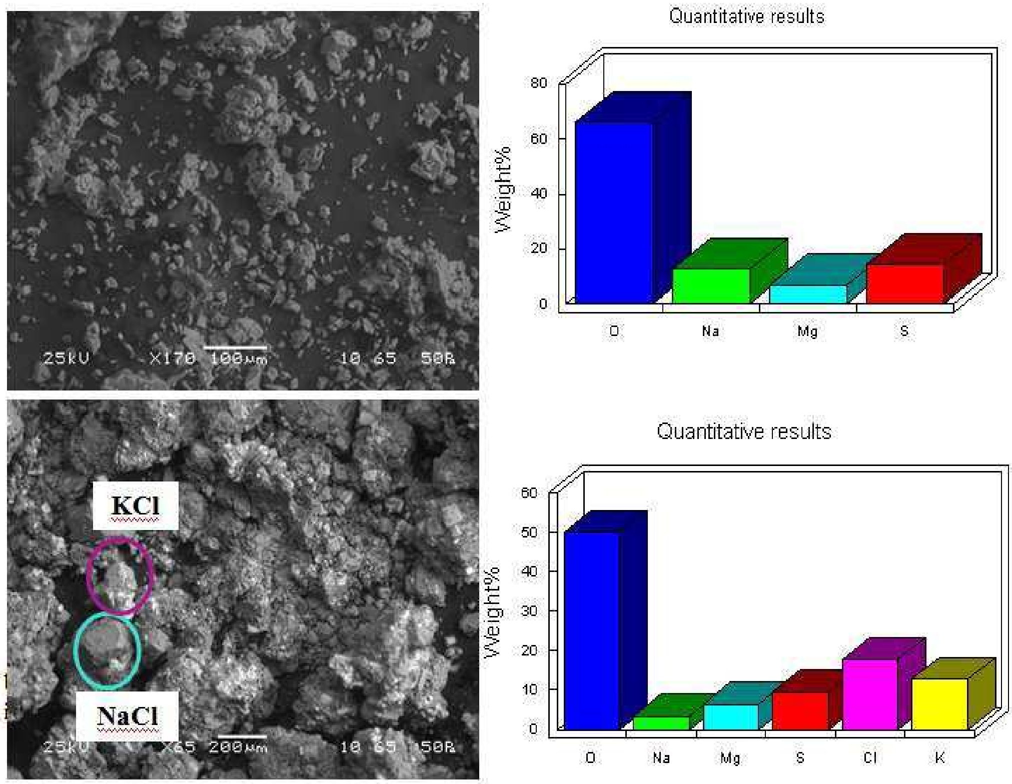

Fig.1. SEM-EDX results for phase identification of a) astrakanite and b) kainite with mayor impurities (only one crystal of each major impurity was indicated)

It can be observed in Fig. 1a, that astrakanite has crystals separated, with rhombohedra shape, and it was not detected the presence of impurities. The discard salt, harvested from evaporation ponds, kainite, presents agglomeration. The SEM-EDX analysis of this sample (see Fig.1b) allow to identify the main component of the agglomerated compound, $KCl\cdot MgSO_4\cdot 3H_2O$, and the main impurities, KCl and NaCl.

3.2. Thermal properties

The **Fig. 2** shows the TGA and DSC curves for astrakanite and kainite.

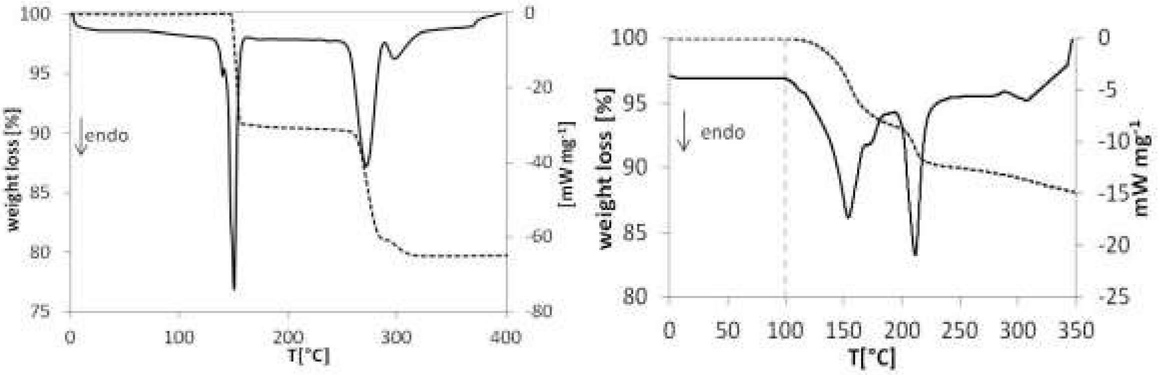

Fig. 2. TG and DCS curves for a) astrakanite and b) kainite.

In the Fig. 2a can be observed that astrakanite sample is stable at the temperature range from 0ºC to 139 ºC. At this last temperature starts a weight loss of the sample, in two stages, until reaching 320 ºC, where an anhydrous phase of astrakanite is formed. The total weight loss is 21 % at 140 ºC to 320 ºC, corresponding to four water molecules released. For the kainite sample (see Fig. 2 b) is observed that weight loss starts at 120 ºC, this lost is 12 %, until the final analysis temperature, 320ºC, is reached. For kainite it was not observed the formation of a stable anhydrous phase.

TG and DSC studies were performed to evaluate the use of the anhydrous phase of astrakanite as a solid TES media at high temperatures. The TG results showed no weight loss between 320 ºC to 750 ºC. DSC results (see Fig. 3) revealed that the anhydrous phase of astrakanite presents a reversible melting – solidification behavior in the range from 570 °C to 680 °C.

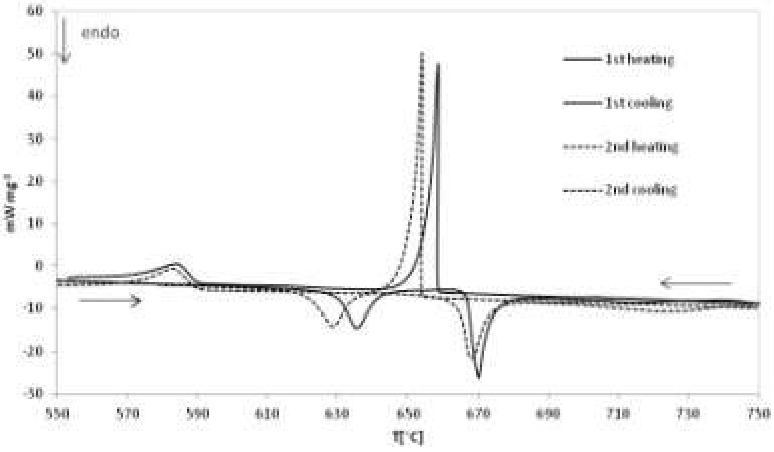

Fig. 3. DSC cyclic study of high- temperature phase of astrakanite sample.

The results obtained of heat capacity for the astrakanite, kainite and anhydrous phase of astrakanite are shown in Fig.4. The average heat capacity for astrakanite is 1.131 J $g^{-1}K^{-1}$ and for kainite 0.985 J $g^{-1}K^{-1}$, at a temperature range from 0 °C to 100 °C, and for the anhydrous phase of astrakanite at high-temperature, is 1.525 J $g^{-1}K^{-1}$.

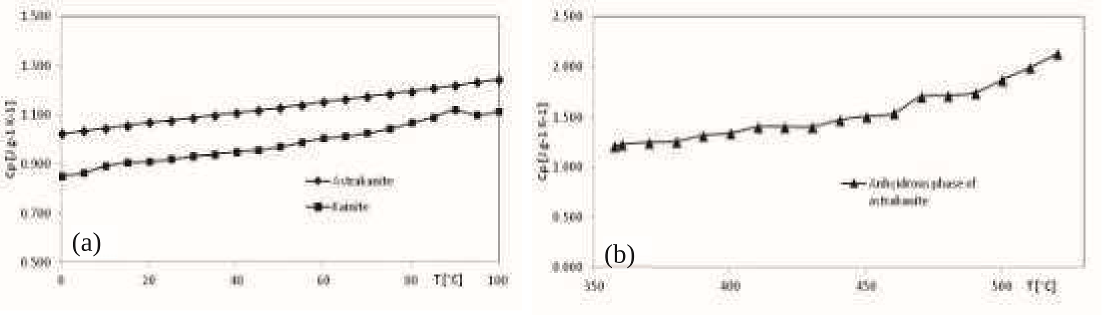

Fig. 4. Heat capacity for a) astrakanite and kainite for the temperature range 0°C to 100°C; b) anhydrous phase of astrakanite

Using the heat capacity values determined and the average density values reported in literature for hydrated salts [4], the thermal properties and cost for the studied salts were compared to typical sensible heat storage materials [5]. The salt cost was estimated based on the cost of the by-products from the Atacama salt lake mining commercialized. The value used was 250 USD/t.

As shown in Fig. 5, astrakanite and kainite are located near the central zone (see Fig. 5a). This section contains ceramics materials [5], which have greater heat capacity than metals and alloys. For the cost comparison of the salts, in Fig. 5b can be seen the studied salts are near halite location, indicating that they have greater heat capacity and lower production cost than typical materials.

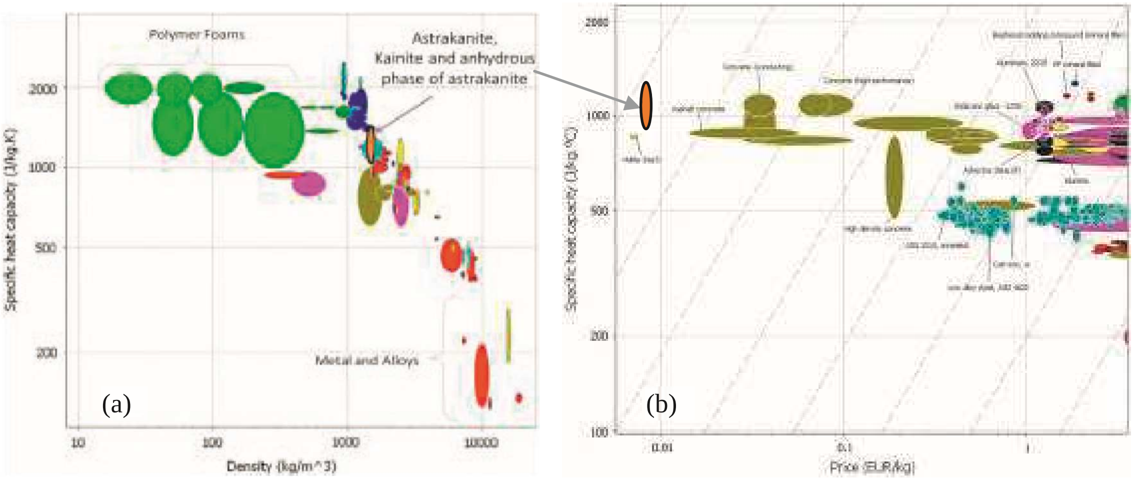

Fig. 5. Comparison of a) thermophysical properties and b) cost of the studied salts with different engineering materials [5].

Further studies will be made to determine the thermal conductivity, thermal expansion, density and energy density storage for the anhydrous phase of astrakanite

Conclusions

It was determined that astrakanite and kainite, waste process-salts from the non-metallic mining industry in northern Chile, are suitable to be used as heat storage materials at low temperatures, from 0ºC to 120 ºC. It was found as well that the anhydrous phase of astrakanite can be used as a solid TES material at a high temperature range, 350ºC to 530 ºC.

Acknowledgements

The authors acknowledge to FONDECYT (grant N° 1120422), ANT 1201 and FONDAP SERC-Chile (grant N ° N º 15110019) for the financial support. A.G. would like to thank to MECESUP ANT1106 for her doctoral fellowship.

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ANNEX V

PAPER PUBLISHED IN MS&T 2014 PROCEEDINGS, PITTSBURGH, USA.

Materials Science and Technology (MS&T) 2014
October 12-16, 2014, Pittsburgh, Pennsylvania, USA

HEAT-TREATED MATERIAL FOR SENSIBLE HEAT STORAGE FROM WASTE OF NON-METALLIC INDUSTRY

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Keywords: Thermal Energy Storage, Sensible heat, Solar Energy, Carnallite

Abstract

TES has taken more importance in the last decades because of the increasing demand of clean energies, to avoid pollution and global warming. Towards this aim, many materials for energy storage have been developed, but many of them are still much expensive and produce lesser energy than conventional fuels. In this research the potential use of waste-process salt, coming from the non-metallic mining industry in northern Chile, as heat storage material was studied. The cost of this salt is low, and it corresponds to the transport cost to the application place mainly. The stability and thermophysical properties of hydrated double salt, carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), were determined by TG and DSC techniques. That information was useful to establish the range of application for this waste-salt. The results proved that a product with fewer molecules of water of this salt is suitable for using as a material for sensible energy storage at high temperature within the range from 250°C to 400°C. .

1. Introduction

Energy consumption has increased in the last decades as well as a constant rise in prices for energy supply; this also means and increase in CO_2 emission, which create an enormous need for implementing more energy supply systems, based on renewable energy sources. But for theses systems can be applied effectively, energy storage is a key element, also to improve the utilization in different economical aspects. Thermal energy storage (TES) plays a significant role in improvement of energy efficiency. Nowadays there are three methods know to store heat or cold, these are sensible heat, latent heat and chemical processes. For a material to be applied to store sensible heat some specific parameters are required for its design [1,2] thermal capacity, conductivity, diffusivity and thermal stability along the thermal cycles. Other important aspects are the high availability, safety, non-combustibility, nontoxicity, long lifetime, low capital costs [3,4,5,6]. The most common materials tested and used for sensible storage at high temperature have been concrete [7] and castable ceramics [8] due to these materials are cheap and they have high thermal capacity. Also, amorphous materials from hazardous wastes [9] or by-products from metallic and mineral industry are proposed by other authors [10] as high temperature storage materials. Furthermore, focus the attention to large scale systems, concentrated solar plant (CSP), industrial TES are based on the sensible heat approach only, taking account the huge quantities of materials of energy storage that are required for these systems, economics are an important driven force; therefore it's a very important issue to evaluate low cost materials through the valorisation of by-products from industrial minerals for solid or liquid sensible heat storage. I order to achieve it; the main objective of this paper is to evaluate waste material from mineral industry in the northern Chile to apply as sensible heat storage at high temperature.

2. Materials and Methods

In the northern of Chile, non-metallic industry as metallic mining is enormous; some of the main products of industrial minerals are nitrate, sulfate, carbonate and chlorides salts. The obtaining process leaves tones of waste and by-products salts, most of them have no industrial applications nowadays. Carnallite, is a by-product salt that precipitates from the evaporation ponds (see Figure 1) and its industrial price is estimated around 210 US$/Ton, in Chile is just used as a raw material to obtain KCl.

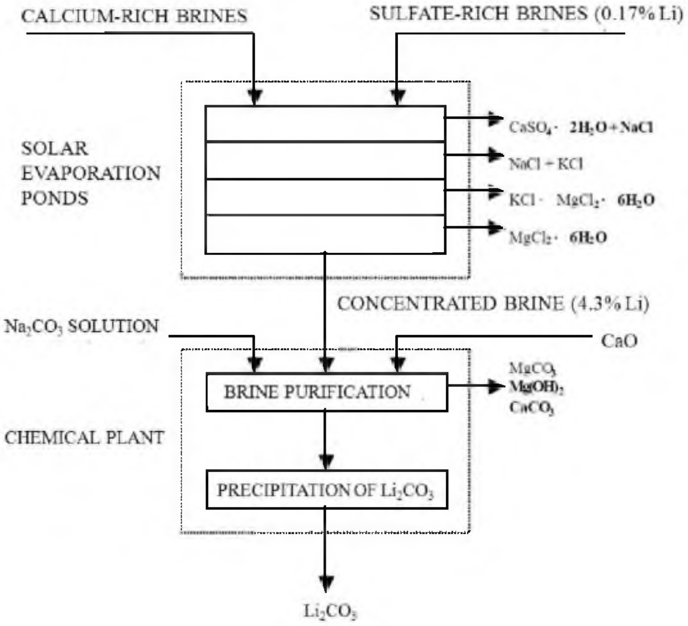

Figure 1. Li_2CO_3 production process from brines. (adapted from [11])

For this research was used carnallite sinthesyzed from KCl (99.5%) and $MgCl_2 \cdot 6H_2O$ (99.9%) both of them were purchased from Merck and used as received. To evaluate thermal stability as a function of temperature, thermogravimetrical method was used. The analyses were performed using alumina crucibles at 1°C/min dynamic mode between 50°C to 1000 °C. The equipment used was a SDT Q600 under N_2 flow of 30 ml/min. Also specific heat was determined within the temperature ranges from 25°C to 85°C and from 250°C to 400°C with the method known as ratio method with a DSC NETZSCH DSC 204 F. In all experiments, sealed standard aluminum pans with lid (40 μL) were used.

3. Results and discussions

3.1 Thermal stability

Thermal stability as a function of temperature was determined for potassium carnallite. In Figure 2 can be seen that within the temperature range from 50°C to 160°C there are mass loss in 2 steps, these percentages (32.58%) represent the loss of 5 molecules of H_2O. Within the range of temperature from 160°C to 400°C there was loss of mass but it wasn't considerable; at 425.75 °C it can be observed a thermal phenomenon, due to there is no change of mass, this phenomenon probably correspond to a phase change; around 650 °C there is a significant loss of mass of about 47% which ends around at 820 °C, temperature where the mass of sample remains constant, with a total mass lost of 88%, considering since measurement started, which means that the sample it decomposes.

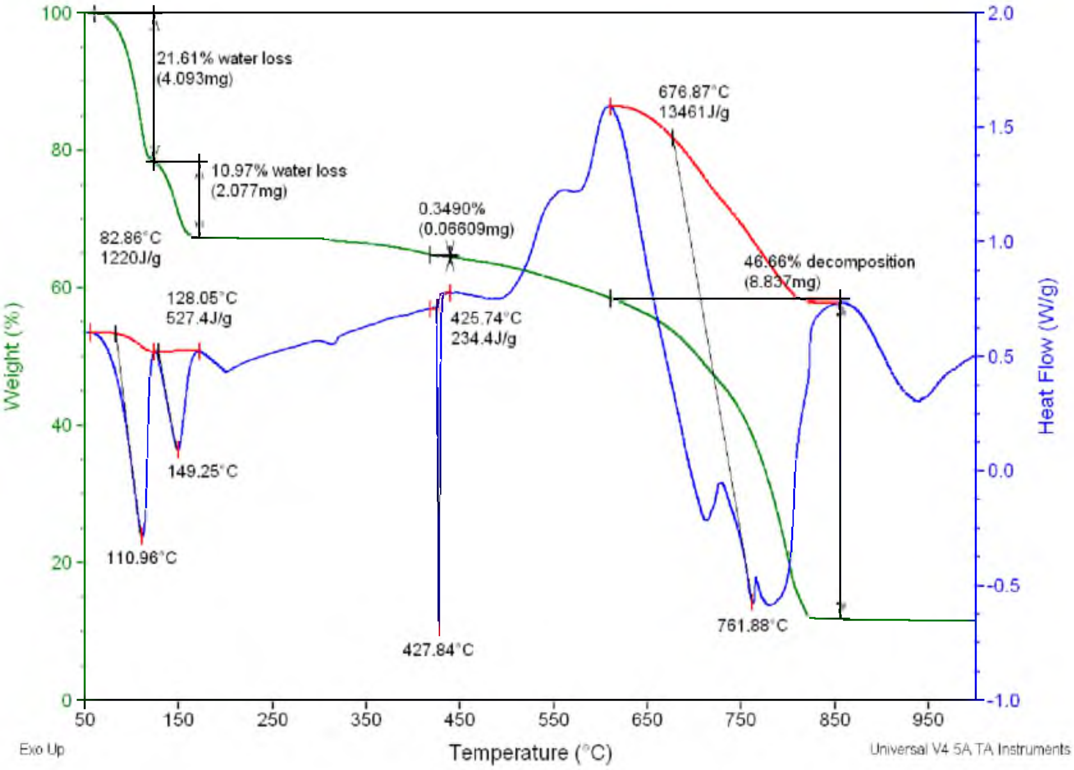

Figure 2 TGA-DSC curves of Postassium Carnallite

3.2 Specific heat

The specific heat for the product after heat treatment was determinate (See Figure 3), the values obtained are similar to the Cp values of other hydrated salts [12] for the range of temperature from 25°C to 85°C and below these values for the range of temperature from 250°C to 400°C. These Cp increases as a function of temperature, for the range from 25°C to 85°C the resulting expression is:

$$C_P(J/(g\,^{\circ}C)) = 2.3235-0.0134\cdot 6\,T(^{\circ}C)+1\cdot 10^{-4}\,T^2(^{\circ}C) \qquad (1)$$

And for the salt after the loss of mol H_2O within the range of temperature from 250°C to 400°C, the resulting expression for the increase is:

$$C_P(J/(g\,^{\circ}C)) = 1.5019-.0063T(^{\circ}C)+1\cdot 10^{-5}\,T^2(^{\circ}C) \qquad (2)$$

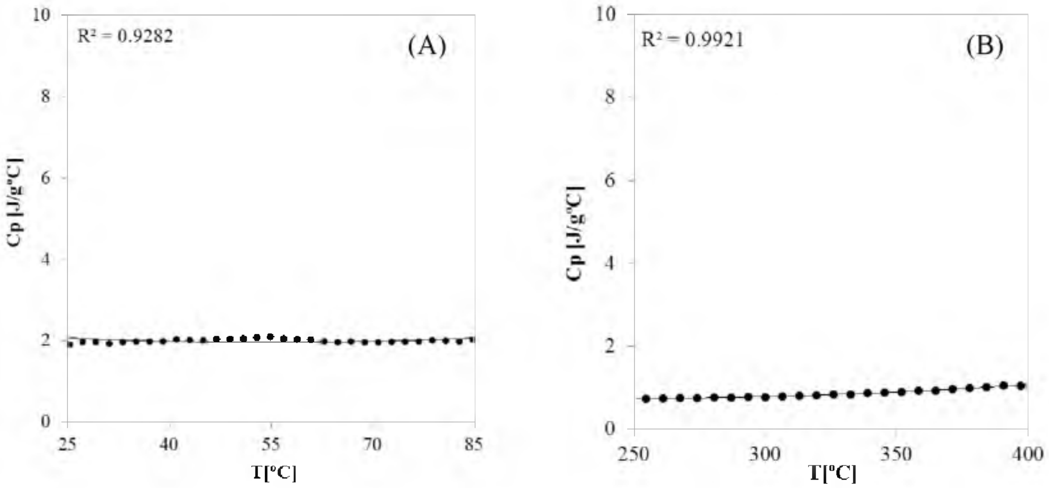

Figure 3 Temperature dependence of heat capacity for product of carnallite with fewer molecules of water (A) from 6 mol H_2O, at 25°C until less than 4 mol H_2O, at 130°C and (B) less than 2 mol H_2O.

4. Conclusions

Thermal stability for carnallite was determinate for the range of temperature from 25°C to 1000°C, the mass remains constant probably as a monohydrate salt $KCl\cdot MgCl_2\cdot H_2O$ within the range of temperature from 200°C to 400°C. The average specific heat for two different ranges of temperature are 1.9987 J/g°C and 0.8609 J/g°C for the range of temperature from 25°C to 85°C and from 250°C to 400°C respectively. According with the results obtained in this research, products of carnallite with fewer molecules of water have potential to be applied as sensible heat storage material, within the range of temperature from 250°C to 400°C. Deeper studies are underway to characterize thermophysical properties of this material to support these potential applications, results will be reported in due course.

Acknowledgements

The authors would like to acknowledge the collaboration of the company SALMAG. The authors acknowledge to FONDECYT (grant N° 1120422), CONICYT/FONDAP SERC-Chile N° 15110019, and the Education Ministry of Chile Grant PMI ANT 1201 for the financial support. Andrea Gutierrez would like to acknowledge for her doctoral scholarships to the Education Ministry of Chile (ANT 1106) and CONICYT/PAI N° 7813110010.

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