Applied Energy 154 (2015) 616–621

Contents lists available at ScienceDirect

Applied Energy

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

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

Andrea Gutierrez [a], Svetlana Ushak [a,b,*], Hector Galleguillos [a,b], Angel Fernandez [a,b], Luisa F. Cabeza [c], Mario Grágeda [a,b]

[a] Department of Chemical Engineering and Mineral Processing, Center for Advanced Study of Lithium and Industrial Minerals (CELiMIN), Universidad de Antofagasta, Campus Coloso, Av. Universidad de Antofagasta, 02800 Antofagasta, Chile
[b] Solar Energy Research Center (SERC-Chile), Av Tupper 2007, Piso 4, Santiago, Chile
[c] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain

HIGHLIGHTS

- Bischofite as phase change material for TES is studied.
- Thermophysical properties of bischofite mixtures with PEG were determined.
- The aim was to improve the cycling stability of bischofite.
- The heating and cooling during 30 cycles were measured.
- The most stable sample was bischofite + 5% PEG 2 000.

ARTICLE INFO

Article history:
Received 1 December 2014
Received in revised form 5 May 2015
Accepted 13 May 2015

Keywords:
Bischofite
Phase change material (PCM)
Latent heat
Thermal energy storage (TES)
Polyethylene glycol (PEG)
Cycling stability

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.

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) [3], 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: In Europe it is marketed for de-icing of roads, and in Chile, using its high hydroscopicity – to abate dust and to improve mining roads in

* Corresponding author at: Department of Chemical Engineering and Mineral Processing, Center for Advanced Study of Lithium and Industrial Minerals (CELiMIN), Universidad de Antofagasta, Campus Coloso, Av. Universidad de Antofagasta, 02800 Antofagasta, Chile.
E-mail address: svetlana.ushak@uantof.cl (S. Ushak).

http://dx.doi.org/10.1016/j.apenergy.2015.05.040
0306-2619/

the north. On the other hand, the main component of this waste is $MgCl_2{\cdot}6H_2O$ with some impurities [4,5].

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 [6–15]. 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 inorganic PCM [16]. 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} = 98.9 °C, a heat of fusion of 120.2 kJ/kg, and an energy storage density of *esd* = 170 MJ/m^3. The principal drawback for bischofite to be used as PCM as indicated in [16] is its subcooling of 37 K, which is not only high but also not constant in the cooling process of the different cycles (Fig. 1).

Poly(ethylene glycol) (PEG) has been used as organic PCM by itself [17], to prepare polymer blends [18–20], to stabilize composite with active carbon (AC) and graphene compounds [21–25], and to make blends with clay [26,27], but in this research PEG was proposed to be used 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 its heat of fusion significantly. Moreover, this material is considered "green" because of its biodegradability and non-toxicity [28].

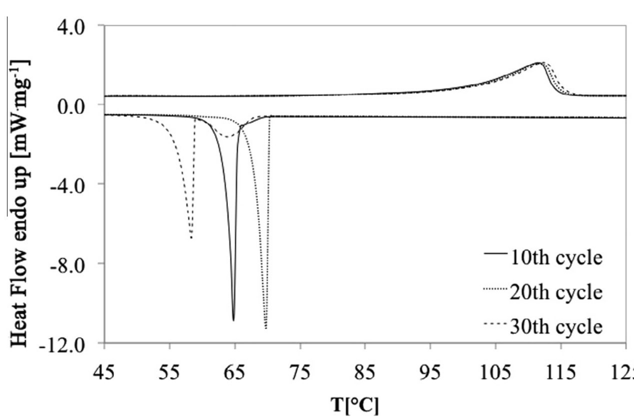

Fig. 1. 10th, 20th and 30th DSC heating and cooling curves of bischofite [16].

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%)

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

Sample	T_F (°C)	ΔH_F (J g^{-1})
Bischofite	98.9	120.2
Bischofite + 5% PEG 600	79.3	61.1
Bischofite + 5% PEG 2 000	98.8	108.8
Bischofite + 5% PEG 10 000	96.5	86.4

A PCM needs to be stable after a number of repeated melting/freezing cycles known as cycling stability [29,30]. This stability includes 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. Thermal stability ensures that the PCM is stable at a constant established working temperature. It can be studied in an oven or with TGA [31].

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. This paper also 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 of about 95% $MgCl_2{\cdot}6H_2O$ and almost 5% of impurities as NaCl, KCl, $Li_2SO_4{\cdot}H_2O$ and $KCl{\cdot}MgCl_2{\cdot}6H_2O$. PEG from MERCK of different molecular weight such as PEG 600 (liquid at room temperature), PEG 2 000 and PEG 10 000 were used as thickener additive to improve thermal stability, the last two PEGs are solid at room temperature which have molecular weight relatively low and high, respectively. 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 different molecular weight PEGs (Table 1). Previously other percentages were tried, but lower quantities of PEGs 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.

2.2. Methods

Thermal stability analysis was determined with TGA/DSC METTLER TOLEDO, in a temperature range of 25–130 °C with a heat rate of 5 °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 NETZSCH with N_2 atmosphere (volumetric flow 20 mL min^{-1}) was used. Melting temperature and heat of fusion were measure in a range between 25 °C and 120 °C. Crucibles of aluminium with 40 μL volume capacity were

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

Compound	Melting temperature (°C)	Heat of fusion (J g^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Density (kg m^{-3})	Ref.
PEG 600	17–22	127.0	0.19$^{(liquid\ 38°C)}$	1126$^{(liquid\ 25°C)}$ 1232$^{(solid,\ 3°C)}$	[3]
PEG 2 000	51.7–57.8	108.6	–	–	[32]
PEG 10 000	66.6	188.7	–	–	[17]