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Characterization of wastes based on inorganic double salt hydrates as potential thermal energy storage materials

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ABSTRACT

Thermal energy storage (TES) is seen today as a key technology to reduce the existing gap between energy demand and energy supply in many energy systems. There are, currently, three well known methods to store thermal energy and they are: sensible heat storage (SHS), latent heat storage (LHT) and thermochemical heat storage. Every method has its own thermophysical requirements for the mediums of storage, such as thermal stability, high enthalpy of phase change or reaction, high heat capacity and suitable temperature of the thermal phenomenon for a respective application, among others. In this regard, the composition of materials usually needs to be modified in order to improve their performance or to reach a determined requirement. As a consequence, the costs of potential TES materials to be applied in renewable energy systems are too high to compete with traditional systems using fossil fuels. On the other hand, several wastes and by-products from the non-metallic mining, such as salt hydrates and double salts, are available without any application but accumulating in the mining sites. This is the case for astrakanite ($Na_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$) and lithium carnallite ($LiCl{\cdot}MgCl_2{\cdot}7H_2O$) with no current application, and potassium carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) used as a supplementary raw material to obtain KCl. Since the costs of these materials are close to zero, they were characterized as TES materials taking into account the properties required for the three methods of storage. Results showed that astrakanite and potassium carnallite have potential to be applied as thermochemical material at low-medium temperature (< 300 °C). Also, a dehydrated product obtained from astrakanite showed potential to be applied as phase change material (PCM) at high temperature, from 550 °C to 750 °C. Nevertheless, lithium carnallite did not show potential to be applied as TES material due to it low thermal stability, presenting partial decomposition below 200 °C.

1. Introduction

Thermal energy storage (TES) is seen today as a key technology to reduce the existing gap between energy demand and energy supply in many energy systems [1,2].

There are three well known methods to store energy and they are detailed below:

1.1. Sensible heat storage (SHS)

The first and most studied method up to date is the SHS. This is the amount of energy involved to increase or decrease the temperature of a substance without experiencing a phase change [3]. It is calculated with following Eq. (1):

$$Q_{sensible} = \int_{T_1}^{T_2} C_p{\cdot}dT \tag{1}$$

As can be seen in Eq. (1) $Q_{sensible}$ strongly depends on the c_p of the material. The themophysical requirements of materials for SHS are divided and listed in two main groups:

1.1.1. Physical and technical requirements

- High density
- Temperature range fitted to the application
- High cyclic stability

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Nomenclature

TES	Thermal Energy Storage
SHS	Sensible Heat Storage
LHS	Latent Heat Storage
PCM	Phase Change Material
TCM	Thermochemical Material
SEM	Scanning Electron Microscope
EDX	Energy dispersive X-ray spectrometer
TG	Thermogravimetry
MS	Mass Spectrometer
DSC	Differential Scanning Calorimetry
HT	High Temperature
XRD	X-Ray Diffraction
HR	Heating rate, K/min
$Q_{sensible}$	Sensible Heat, J/g
Q_{latent}	Latent Heat, J/g
c_p	Heat Capacity, J/g K
T	Temperature, °C
T_{onset}	Onset temperature, °C
$\Delta_F H$	Enthalpy of Fusion, J/g
$\Delta_S H$	Enthalpy of Solidification, J/g
$\Delta_D H$	Enthalpy of Dehydration, J/g
$\Delta_H H$	Enthalpy of Hydration, J/g
wt%	Percentage of weight loss %

– Large scale production methods
– Non-corrosive
– Low system complexity
– Low vapor pressure in the temperature range

1.1.2. Thermal requirements

– High energy density
– High thermal conductivity
– Low thermal diffusivity
– Good specific heat capacity
– Thermal expansion coefficient

These requirements are defined most of the time based on the application conditions. Once this is established, it starts the searching of materials that address the majority of the requirements. While all the mentioned properties are important, Fernández et al. [4] determined that the thermal requirements are the most significant, reporting as well the merit index of such material to be used to store sensible heat. In addition, the energy density is one of the most significant property. For the SHS materials, the theoretical energy density can be calculated multiplying the c_p by the density of the material.

1.2. Latent heat storage (LHS)

The second method of storage is LHS which is used when a higher energy density, compared to SHS, is required in a given application [3]. The solid to liquid phase change is chosen most of the time in order to avoid technical issues. The energy stored for this method is calculated as follows:

$$Q_{latent} = \int_{T_1}^{T_{pc}} C_{p,s}\cdot dT + \Delta H_{pc} + \int_{T_{pc}}^{T_2} C_{p,l}\cdot dT \quad (2)$$

In this case, the materials used are known as phase change materials (PCM) [5], and the constant temperature of the phase change is taken as an advantage in their application. The requirements of the materials for LHS are divided in the same two groups as before [6]:

1.2.1. Physical and technical requirements

– Low density variation and small volume change
– High energy density
– Small or no subcooling
– No phase segregation
– Low vapor temperature
– Chemical and physical stability
– Compatible with other materials

1.2.2. Thermal requirements

– Suitable phase change temperature fitted to application
– Large enthalpy of phase change ($\Delta_F H$ and $\Delta_S H$) and specific heat (c_p)
– High thermal conductivity (except for passive cooling)
– Reproducible phase change
– Thermal stability
– Cycling stability

In this case, Barreneche et al. [7] determined the merit index to select the best candidate to be used as PCM, where the database reported considers the main thermal properties required for it. That is, the phase change enthalpy, ΔH_{pc} and the energy density of potential materials.

1.3. Thermochemical energy storage

The last method to store energy is thermochemical energy storage, where the energy stored is produced by a reversible chemical reaction or during a sorption process. Usually, solid-gas reactions are considered, due to the technical advantages of separating a gas from a solid to store the materials (products of reaction), and later combination in order to start the inverse reaction. The materials used to store thermochemical energy are known as thermochemical materials (TCM). The requirements of the materials for thermochemical energy storage are divided in the two groups as well [8]:

1.3.1. Physical and technical requirements

– Low density and small volume change
– High energy density
– No phase segregation
– Chemical and physical stability
– Compatible with other materials - Non-corrosive

1.3.2. Thermal requirements

– Reversible reaction
– Control of the kinetic model
– Control of the structure changes
– Water stability within crystal structure (For salt hydrate and hydroxide systems)
– Proper particle size
– Control of the impurities
– Solubility of the TCM in the working conditions (P, T)
– Suitable working temperature range fitted to the application
– Large energy involved in the reaction ($\Delta_D H$ and $\Delta_H H$ for Salt hydrate and hydroxide systems)
– High thermal conductivity
– Thermal stability