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Glass encapsulated phase change materials for high temperature thermal energy storage

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A B S T R A C T

A new encapsulation method for high temperature phase change materials (PCM) is developed. Nitrate salts and metals are used as the PCM core with melting temperatures in the 300-400 °C range. Borosilicate is used as encapsulating material based on its high thermal resistance, non-reactivity and optical properties. Its transparency combined with the transparency of some PCM in the molten state allows the analysis of the melting process through visual observation. The volume expansion of the PCM is managed through a void space inside the capsules. The capsule design, fabrication, and testing is described in detail. The PCM melting and solidification process is identified using a combination of visual and infrared images. The experimental observations are complemented by a finite difference method to solve the energy equations simulating the transient melting/freezing process inside a spherical PCM. The model analyzes the effect of the convective heat transfer coefficient on the PCM capsule melting and freezing starting times and the duration of the PCM melting process. Boundary conditions are set to match those in the experimental rig developed. Results show that the main system parameters can be qualitatively assessed and adequately determined to describe the experimental observations.

1. Introduction

Encapsulated phase change materials (PCM) are an interesting high energy density solution to store thermal energy near isothermal conditions. They are generally used in a packed bed latent heat storage system, consisting of a storage medium divided into small encapsulated particles which increase the specific surface area exchanging heat with the heat transfer fluid (HTF, e.g. air, steam). This technology is expected to yield to a much more compact storage system compared to its sensible heat storage counterpart. Nevertheless, efficient and cost-effective PCM encapsulation has to be achieved for latent heat packed beds to be reliable and economically attractive. While low temperature phase change materials can be enclosed in a thin, sealed polymeric film maintaining the shape and containing the PCM during the phase change process [1], high temperature encapsulation has been less developed.

New developments in solar thermal power plants call for new, more efficient energy storage solutions in the high temperature (200-800 °C) range. Research related to encapsulating PCM such as inorganic salts (chlorides, nitrates, carbonates), metals or metal alloys has risen accordingly. There is one study of high temperature macro-encapsulation of PCM from the 1990s [2] followed by many investigations carried out in the past five years [3–8]. From the engineering perspective, encapsulation of PCM for solar thermal plants has been challenging because of the high temperatures required: common encapsulating materials such as polymers degrade at such temperatures and other alternatives, such as metals, interact chemically with the core materials. Challenges in high temperature encapsulation are thus mainly related to finding suitable, thermally stable, and compatible materials to exchange heat between heat transfer fluids and PCMs working under high temperature and pressure operating conditions.

Another important concern in high temperature encapsulations is preventing the shell rupture when the PCM core melts and expands in volume during the phase transition. Researchers have tried different approaches to manage volume expansion of high temperature PCM: an organic sacrificial layer that is burned off during the manufacturing procedure [3], agglomerating flexible metal particles between the PCM and the shell [3], a combination of thermally stable polymers (Teflon™) that are not eliminated and an external metal layer [4], metallic deformable shells such as nickel/

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nickel-based [4,5] and stainless steel [6], or even encapsulating the PCM in the liquid state so that when the PCM solidifies and contracts, the required empty space appears between the PCM and the shell [2]. In general, flexible metallic shells have shown issues related to reduced storage capacity after thermal cycling [7,8], mostly due to alloying, corrosion, and chemical reactions between the PCM and shell. Therefore, novel encapsulation materials such as non-reactive metals, ceramic capsules or non-reactive coatings must be developed to solve this problem. Table 1 summarizes the shell materials used in the literature to encapsulate different types of high temperature PCM: nitrates, chlorides and metals.

In the search for a compatible, impermeable medium to both the HTF (steam) and potentially corrosive core materials (inorganic salts), borosilicate was selected as shell material. Several authors have used borosilicate tubes for hydrogen encapsulation, which can withstand 400 bar with an appropriate geometry [14,15]. Borosilicate is also able to withstand high temperatures (500 °C for short-term usage (<10 h); 450 °C for long-term usage (>10 h)) [16]; its high thermal shock resistance is well known (borosilicate, also known as Pyrex™, is a common cookware glass) making it an interesting shell candidate together with its thermal stability/non-reactivity. One of the added benefits of using a glass shell is its transparency, allowing the visualization of the phase change process within the capsule. Up to this date, the visual observation of the melting process has been only carried out with organic low temperature PCM (mainly paraffin wax *n*-octadecane) [17–20]. Therefore, a transparent high thermal resistance glass sphere could allow a similar analysis for high temperature PCM to complement the recently increasing number of numerical studies.

Encapsulating high temperature PCM using borosilicate shells has the following advantages:

- inert shell material: chemically stable with both the PCM (salts, metal alloys) and the HTF (high temperature/high pressure steam).
- high thermal stability and corrosion resistance
- provides structural integrity and easy handling
- available, inexpensive raw material and can be easily coated
- common manufacturing processes exist, could be scaled-up for mass production
- optical properties: its transparency allows a visual analysis of the melting process

However, a few disadvantages have also been identified regarding borosilicate as a shell material:

- risk of mechanical failure (fragile)
- management of the PCM volume expansion in the melting process
- low thermal conductivity

The purpose of this study was to investigate if these main weaknesses can be overcome: the core PCM volume expansion will be handled by filling the capsules only partially, measuring melting/freezing times will determine if the low thermal conductivity for a given shell thickness is a problem, and initial cycling tests will help assess the capsules' mechanical integrity.

Thus, this study presents a unique contribution by developing a new functional macro-encapsulation based on borosilicate shells for high temperature PCM (inorganic salts or metals) with melting temperatures in the 300-400 °C range to be used as latent heat storage in direct steam generation (DSG) solar thermal plants, tackling the problem from the initial design to a proof of concept stage performed by testing single capsules in an experimental rig. We take advantage of the optical properties of the shell material to visually determine the solidification and melting times. The information obtained with a visual camera is complemented with the thermal data from an infrared camera, quantifying the phase transition in the capsule with a non-invasive technique (i.e. instead of inserting thermocouples). An experimental rig is designed to test capsules up to 450 °C, high enough to melt some inorganic salt mixtures and metals while varying the external flow conditions. The results are compared with an analytical model which is used to help understand the process, assist in the design of the capsules, and understand the influence of the different parameters involved.

2. Experimental methods

2.1. Materials (PCM, shell)

The physical properties used in this analysis are presented in Table 2. The borosilicate properties have been extracted from Ref. [16] at 300 °C. A Mettler-Toledo DSC2 Differential Scanning Calorimeter is used to measure the latent heat, the specific heat, and the melting temperatures of the PCM (commercial grade $NaNO_3$ and Pb), while the thermal conductivity and density are literature values from Ref. [21] for Pb and from Ref. [22] for $NaNO_3$.

2.2. Filling ratios, geometry, and energy stored per capsule

The targeted capsule diameter design is 20 mm diameter with 1 mm thickness. This size is a compromise between achieving a maximum allowable size and system design requirements (as smaller capsules have better heat transfer behavior but produce a larger pressure drop in a packed bed), while also taking into consideration the availability of raw materials and ease of manufacturing. It is in the same range as contemporary theoretical modeling studies by Ramos-Archibold et al. [23,24]. Spherical geometry is chosen over cylindrical as it minimizes the shell material for a given PCM volume.

One of the main challenges regarding PCM encapsulation is the management of the PCM volume expansion during the melting process without breaking the capsule from internal stress. Different solutions have been proposed to overcome this difficulty, such as

Table 1
Shell materials used to encapsulate high temperature PCM. (*Present work).

Nitrates	Chlorides	Metals
- Stainless steel [2] - Metal and Clay [3] - Polymer (PTFE) with Nickel coating [4] - Polymer (PTFE-FEP) with Nickel coating [4] - Polymer (FEP) with Nickel coating [4] - Carbon steel 1018 [8] - Stainless steel AISI 321 [9] - Borosilicate glass*	- Stainless steel [2] - Stainless steel 304L [7,8] - Carbon steel 1018 [8] - Carbon steel 1018 with an intermediate layer of high temperature paints or Na_2SiO_3 [10]	- Stainless steel [2] - Nickel with an intermediate Layer of carbon or Ruthenium [5] Stainless steel 304L [7,8] - Nickel [11] - α-Al_2O_3 [12] - Nickel with an intermediate layer of Chromium [13] - Borosilicate glass*