



# Macroencapsulation of sodium chloride as phase change materials for thermal energy storage

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## ABSTRACT

Mechanical, structural and thermal characterizations of macroencapsulated sodium chloride pellets obtained using sol-gel method were performed. The application of sol-gel technique requires creating previously a layer to prevent solid salt dissolution. Sodium chloride (NaCl) was considered as phase change material for high-temperature thermal storage units working at 800 °C, which could be of interest for application in next generation concentrating solar power (CSP) plants using supercritical CO<sub>2</sub> power cycles. NaCl pelletization was carried out using six organic binders and poly(methylmethacrylate) (PMMA) was deposited, as sacrificial layer, between the salt pellet surface and the sol-gel coating. Pellets between 2 and 4 mm long, have been encapsulated by deposition of dense and porous TiO<sub>2</sub> and SiO<sub>2</sub> coatings. Thermophysical properties of macroencapsulated pellets were measured by TGA/DSC experiments and customized thermal resistance cycling tests. Material structure was characterized by Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray spectroscopy (EDX) unit. It has been demonstrated that macroencapsulation by sol-gel represents a compatible process with the molten salt transfer fluid. NaCl pellets with hemicellulose (HC) encapsulated with dense TiO<sub>2</sub> coatings presented the best performance in terms of thermal behavior, though still improvements on encapsulation layer is necessary in order to increase the its durability over the cycles.

## 1. Introduction

Nowadays, high temperature solar applications are becoming more attractive and more beneficial for energy saving and CO<sub>2</sub> emissions abatement (International Energy Agency, 2012, 2014). Concentrating solar power (CSP) plants use concentrating solar radiation as energy resource to produce electricity by means of a thermodynamic cycle. Thermal energy storage (TES) is an essential system for CSP plants since it allows dispatchable generation. TES system makes possible to store the thermal energy when the solar resource is abundant and retrieve it during the times of poor solar radiation, such as during a cloudy day or at night.

TES systems in commercial CSP plants are based at present on sensible heat storage, which penalizes the exergy efficiency when steam/water is the heat transfer fluid due to the water phase change (Dincer and Rosen, 2011). For that reason, the development of high temperature thermal storage using latent heat is an area of increasing interest. Latent heat energy storage makes use of phase change materials (PCM), has higher storage energy density than sensible heat storage and the ability to store/release thermal energy at almost constant temperature (Elmouzghi et al., 2014). Suitable PCMs for thermal

storage have high latent heat and melting points at certain temperatures of interest (Liu et al., 2012).

Other desirable properties for choosing PCMs were enumerated by Abhat (Abhat, 1983) and Lane (Lane, 1983) and take into account thermodynamic, kinetic, chemical and economic aspects, such as melting and freezing points in the desired temperature range, high specific heat, latent heat of fusion and density, low density variation between solid and liquid phases, high thermal conductivity, high heat transfer rates, congruent melting, insignificant supercooling, chemical stability, non-corrosive, non-poisonous, non-flammable, abundant supply and low cost. Zalba et al. (Zalba et al., 2003) reported potential PCMs, of which melting temperature is lower than 900 °C, classified into inorganic substances, inorganic eutectics, non-eutectic mixtures of inorganic substances, organic substances and organic eutectics. Alva et al. (Alva et al., 2017) recently reviewed TES materials including composite PCMs (containing high-thermal conductivity particles) and micro-encapsulated PCMs (MEPCMs) within the previous classification. Composite PCMs using carbon nanostructures have been reviewed by Amaral et al. (Amaral et al., 2017).

Inorganic salts are one of the materials suitable for high temperature thermal storage due to their low cost and high availability

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(Elmoughi et al., 2014; Muñoz-Sánchez et al., 2015), however their low thermal conductivity leads to low charging and discharging rates (Muñoz-Sánchez et al., 2015). Kenisarin (Kenisarin and Mahkamov, 2007) listed hundreds of inorganic salts for latent heat storage between 120 and 1000 °C, being most of them fluorides, chlorides, bromides, hydroxides, nitrates, carbonates and other salts. Liu et al. (Liu et al., 2012) classified the pure inorganic salts and salts composites according to their potential use as PCM above 300 °C. Authors describe some of their thermophysical properties such as melting temperature, latent heat of fusion, density, specific heat and thermal conductivity.

PCM encapsulation allows for increasing the contact surface area between the PCM and the heat transfer fluid, so that heat transfer is enhanced and the charging/discharging times are decreased (Elmoughi et al., 2014), providing decreased subcooling and controlling the volume change of the storage material when the phase transition occurs (Milián et al., 2017). Additionally encapsulated materials are easily handled. An important aspect deserving maximum attention is related to the chemical compatibility between the PCM and capsule material and between the capsule material and the heat transfer fluid. According to Milián et al. (Milián et al., 2017), encapsulated inorganic PCMs are classified into core-shell PCMs (PCMs particles covered by another material) and shape stabilized PCMs (composites of PCMs with other materials that retain molten PCMs by capillarity). Most common encapsulation methods for core-shell PCMs include inverse Pickering emulsion, electroplating, solvent evaporation-precipitation method and mechanical packaging. For shape-stabilized PCMs, sol-gel process, infiltration and impregnation encapsulations methods have been reported. In their review paper, Milián et al. identified sol-gel encapsulation as the only physical method for inorganic encapsulated PCMs.

Sol-gel encapsulation requires creating an intermediate sacrificial polymeric layer between the salt and the sol-gel shell that prevents solid salt dissolution during the sol-gel application. Additionally the volume available once the polymeric layer is removed will be contribute to accommodate the PCM thermal expansion when melting and heating occur. Mathur et al. (Mathur et al., 2014) present an optimized and competitive procedure of PCMs encapsulation using a sacrificial polymer and employ on KNO<sub>3</sub> prills. The polymer is located between the core made of salt and the external shell coating and it decomposes at temperature lower than the PCM melting point. Polymers with the best characteristics for encapsulating PCM are degradable flexible plastics, e.g. poly(methylmethacrylate) (PMMA) or poly(ethyl methacrylate) (PEMA), which can be easily removed by thermal treatment.

The macroencapsulation process of PCM for thermal energy storage has been studied by few authors. Muñoz-Sánchez et al. (Muñoz-Sánchez et al., 2015) have reported a theoretical description of the encapsulating PCMs development for their use in a thermocline thermal storage system for CSP. Several PCM have been selected along with inert materials to contain them and encapsulation procedures have been also technically evaluated for every option. Authors conclude that best encapsulation techniques are using preformed shells for metallic PCM and creating external coatings for the salt. Jacob et al. (Jacob and Bruno, 2015) presented successfully encapsulated PCMs with different shell materials (metallic, plastic and inorganic) to enhance the thermal conductivity of the PCM for high temperature energy storage in conjunction with CSP plants. Between the shell materials identified, steel (carbon and stainless), nickel (and nickel alloy), sodium silicate, silicon dioxide, calcium carbonate and titanium dioxide have been identified as deserving further investigation for containing PCMs in high temperature applications such as CSP. A promising technology to store thermal energy in high temperature applications have been developed particularly for inorganic sodium salts, using cylindrical PCMs of sodium nitrate (NaNO<sub>3</sub>) encapsulated by stainless steel, which is applicable to Rankine and other power generation cycles (Zhao et al., 2012). Authors confirmed that capsule size, thermo-physical properties of phase change and encapsulation materials, the properties of the heat

transfer fluid, the nature of flow and the configuration of cylindrical rod in the channel affect the heat transfer process of storage/retrieval of thermal energy. The thermal behavior of NaNO<sub>3</sub> salts and eutectic NaCl–MgCl<sub>2</sub> also encapsulated with cylindrical steel shells, were analyzed using a specialized calorimeter designed for particular size and temperature requirements (Zheng et al., 2013). Bauer et al. (Bauer et al., 2009) examined the thermal stability and thermophysical properties of NaNO<sub>3</sub> and its compatibility with graphite foil. The results showed that NaNO<sub>3</sub> is thermally stable at 350 °C and a small amount of nitrite is formed, but molten NaNO<sub>3</sub> slowly oxidizes graphite foil at 310 °C. Alam et al. (Alam et al., 2015) developed an innovative technique of spherical PCMs encapsulation of NaNO<sub>3</sub> (working temperature range between 120 and 350 °C) ranged from 12.5 to 25.5 mm. The encapsulation does not require a sacrificial layer to accommodate the volumetric expansion of the PCMs on melting. The PCM was encapsulated by a coating of a non-reactive polymer (PTFE), having a thickness of 0.5–0.7 mm, followed by deposition of a metal layer by a novel non-vacuum metal deposition technique.

This work analyses the use of sol-gel method to produce macroencapsulation of high-temperature PCMs made of molten salts. It is considered that this method could lead to develop competitive high-temperature latent heat thermal storage solution for solar thermal applications. NaCl was selected as phase change material since its melting point (800 °C) and then it allows working at higher temperature than current commercial molten salts (i.e. NaNO<sub>3</sub>) using new thermodynamic cycles. Additionally, it has a low cost and is an abundant material. Pelletization of the salt was carried out using six organic binders. The optimized pelletization of sodium chloride is presented in detail in the experimental section. A PMMA coating was deposited, as sacrificial layer, between the salt pellet surface and the sol-gel coating. The shell used to encapsulate the salt was prepared by sol-gel method, depositing dense or porous titania (TiO<sub>2</sub>) or silica (SiO<sub>2</sub>) sol-gel coatings. Sol-gel coatings were prepared from titanium isopropoxide or tetraethyl orthosilicate as precursors and acetyl acetone as complexant agent. Thermophysical properties of macroencapsulated materials were measured by TGA/DSC experiments and designed thermal resistance cycling test. Also, structures of materials were characterized by scanning electron microscopy (EDX-SEM).

## 2. Experimental description

### 2.1. Pelletization of sodium chloride salt

Fig. 1 illustrates the macroencapsulation method followed in this work. A mixture composed of sodium chloride (NaCl) and an organic binder was prepared to produce mechanically-resistant pellets and with porosity enough to accommodate changes in volume by thermal expansions. NaCl powders were milled by using an Agatha mortar and the largest particle size was set at 500 µm after sieving. Then, NaCl powders were mixed with an organic binder (OB) in a mass ratio of NaCl/OB = 10:1. Six different organic binders were selected: methylcellulose (MC), hemicellulose (HC) and polyethylene glycol (PEG) from Sigma; polyvinyl pyrrolidone (PVP) and oxalic acid (OA) supplied by Acros Organics; and carboxymethylcellulose (CMC) from VWR BDH Prolabo. Finally, water was incorporated as solvent to the mixture in a molar ratio of NaCl/H<sub>2</sub>O = 10:1. After getting a uniform mixing, the mixture was kept under stabilization during ten minutes before starting the shaping process. A reference NaCl mixture was also prepared following the same procedure but without addition of organic binder.

Pellets manufacturing was made using a stainless-steel pelletizer composed by two independent parts, first one contained a matrix of vertically oriented cylinders 6.0 mm height and 3.0 mm in diameter whilst the second one had the same matrix with cylindrical boreholes (3.1 mm in diameter). Both pieces were assembled by connecting the cylinders and the holes. Pellets length was fixed controlling the relative distance between the pieces. Boreholes were completely filled by

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