



Confined melting in deformable porous media: A first attempt to explain the graphite/salt composites behaviour

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ABSTRACT

This paper deals with phase change in composite materials made of graphite and a phase-change material (PCM). The composites are manufactured by compressing a solid mixture of salt and graphite particles. In previous works, the interest of such materials for thermal energy storage at high temperature has been highlighted. They are characterized by quite high energy storage capacity as well as high thermal conductivity. However, first melting/crystallization of these composites could lead to significant salt leakage and shows some *a priori* unexpected features like melting over a range of temperature instead of at constant temperature and significant loss of heat storage capacity. A poro-thermo-elastic analysis is carried out in this paper for understanding salt melting within the graphite matrices and for proposing reliable ways for composite materials improvement. An intentionally simple think-model, based on mass and energy conservation equations, pressure-dependent liquid–crystal equilibriums, linear elasticity laws and Poiseuille-like flow, is proposed. In spite of the simplicity, the model turns out to be apt to explain main macroscopic features of materials melting as observed in calorimetric tests. The influence on melting dynamics of parameters like the heating rate, the pore-wall rigidity and thickness, the salt volume expansion and the pore connectivity is investigated and several ways for composite materials improvements are discussed.

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1. Introduction

High temperature thermal energy storage (HTTES) is recognised today as an important issue for energy saving and efficient energy utilisation in the industrial process heat sector (cf. [1,2]) as well as a key element to achieve successful market introduction of power generation based on new conversion techniques and renewable energy resources (cf. [3,4]). In spite of the interest, no or very few examples of commercial HTTES systems are realised. Main reason is the still too high investment cost of the existing technology. For applications using transfer fluids undergoing a process at constant temperature, like wet steam during condensation or evaporation, latent heat storage based on salts have been identified as a promising option for economic heat storage solutions. However, the low thermal conductivity of salts ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ [5]) is a limiting factor for applications requiring high power level.

At low temperature, different ways for enhancement of the thermal conductivity of phase-change materials (mainly paraffin waxes) have been proposed and tested in the past. Using metal fillers such as aluminum or copper additives [6–8], metallic foams [9] or fins [10–12] is the oldest one. It was found that the time for charging (discharging) the storage system is significantly reduced.

However, metal fillers add significant weight and cost to the storage systems. In addition, corrosion could appear when using salts. Paraffin waxes supported within the porous structure of silica catalyst [13] or activated carbon [14] are interesting alternative ways to metal fillers because of their low density. Some other authors have proposed conductivity enhancement techniques based on carbon fibers [15,16] and graphite foams saturated with PCM [17–21]. Main advantages of graphite are high thermal conductivity, low density and chemical resistance, which make it compatible with most storage media.

In the framework of the European project DISTOR [22], the feasibility of conductivity enhancement techniques based on graphite has been demonstrated with $\text{KNO}_3/\text{NaNO}_3$ (50 mol%, eutectic) for applications at 225 °C. Different types of graphite and three different elaboration routes have been considered: (a) *dispersion* of the graphite flakes in the molten salt under mixing; (b) *uniaxial* compression at room temperature of an initial mixing of expanded natural graphite and salt powder; and (c) *isostatic* compression (same pressure applied in all directions) at room temperature of an initial mixing of ground expanded natural graphite and salt. Thermal properties of graphite/salt materials have been studied in deep in Refs. [23,24]. One notes that compression (axial or isostatic) is a much more efficient way for heat transfer enhancement than dispersion. For instance, thermal conductivity of compressed materials with 20 wt% of graphite ($21 \text{ W m}^{-1} \text{ K}^{-1}$) is four times

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