Thermo-mechanical analysis of copper-encapsulated NaNO₃–KNO₃

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Abstract

The present paper presents a numerical study to investigate and assess the heat transfer behavior of a copper and salt composite. A mixture of nitrates, KNO₃–NaNO₃, within a deformable spherical shell coating of copper will be used as an encapsulated phase change material, E-PCM. In the context of a thermo-mechanical analysis of this E-PCM, a simulation is proposed to determine its storage capacity and properties. The melting, or solidification of the encapsulated PCM particles do not provoke cracking of the deformable shell.

Keywords: Copper-encapsulation; Nitrate salts; Simulation; Phase change material; Thermal energy storage; Comsol Multiphysics

1. Introduction

Thermal energy storage (TES) has received an increasing interest over the past years in different applications such as waste heat recovery, thermal solar capture, zero-heat houses, aerospace applications, and for thermal protection purposes. In the thermal solar applications or for heat recovery from hot industrial flue gases, it is very interesting as high temperature thermal energy storage (HTTES) provides continuity and enhances the potential of a solar system allowing this technology to get a faster development and acceptance due to its increase of efficiency and usability (Zhang et al., 2013a; Pità et al., 2013; Cáceres et al., 2013; Fernandez et al., 2012). For thermal protection applications, there is a strong interest in understanding and predicting the conditions where it is possible to cool damaged electrical equipments and/or electronics and telecommunication devices, and even severely damaged nuclear reactor cores (Lipinski, 1984). Thermal management utilizing solid–liquid PCMs is one of the most interesting passive thermal storage techniques, due to their inherent advantage of simplicity and reliability. TES techniques can be classified as sensible heat storage and latent heat storage. The latter is particularly attractive, since it provides a high energy storage density and can store the energy as the latent heat of fusion at a constant temperature. The latent heat absorption phenomenon, associated with melting of a suitable PCM, could be efficiently used to delay or modify the temperature rise of the surface subjected to a high heat flux (Zhang et al., 2013b).

Despite PCMs being widely promoted for HTTES systems due to their capability of storing significant amounts of energy within a small PCM volume and at a moderate temperature variation, most PCMs suffer the problem of low thermal conductivity which extends the charging and discharging periods. In order to improve the thermal conductivity of PCMs, extensive investigations have studied the addition of different high thermal conductivity materials, such as either mixing graphite within nitrate salts under isotropic pressure (Lopez et al., 2010), or using metal foams (Zhao et al., 2010; Neville and Rabiei, 2007; Elgafy and Lafdi, 2005; Ismail...
and Trullenque, 1993; Ho and Chu, 1996; Lopez, 2007). Past and current researches have demonstrated that porous foams (graphite, copper, aluminum or metal alloys) embedded within PCMs are a feasible storage material for low temperature applications, whereas applications at high temperatures are less documented. The objectives of the present paper will be focused on HTTSES, as is supposed to be used in thermal solar capture system (Zhang et al., 2013a; Pitié et al., 2013; Cáceres et al., 2013; Chen et al., 2010), where the discontinuity of solar energy can be overcome by an integrated system with PCMs.

Many models have been presented in order to determine the heat transfer behavior in porous media (Bear, 1988; Pinder and Gray, 2008; Cushman, 1997), but due to the specific conditions of this problem, such studies require a different treatment of the transport equations involved in the system. A mathematical method, known as the volume averaging method, was developed by Whitaker (1999), and has subsequently been used in the modeling process of diffusion equations in porous media (Valdés-Parada and Alvarez-Ramirez, 2011), turning the intrinsic micro-analysis of this problem into an averaged approach on a macro scale. These models are generally solved by numerical methods: due to the complexity of the differential partial equations, analytical solutions are seldom possible and simulations are more efficient on computing resources. Some of these numerical approaches were previously presented in literature (Zabaras and Deep, 2004; Smith, 2005; Garcia, 2007). Porous media models, applying the volume averaging method, have been very useful to describe and simulate the fluids behavior in these geometries. These models have been used in thermal control applications that extend from temperature managing on nuclear reactor cores to thermal protections of electronic equipment and specific devices as mentioned before (Ismail and Trullenque, 1993; Ho and Chu, 1996; Cao and Faghri, 1990; Bain et al., 1971). Since thermal control applications have been developed from these models, they are of growing importance (Oddou et al., 2011; Chapotard and Tondeur, 1983). One of the most important model applications considers heat storage. The theoretical treatment of a variety of models has been assessed by Quintard and Whitaker (1996, 1998a,b) and by Ahmadia and Quintard (1998): these treatments deal with heterogeneous porous media using the volume averaging method in the transport equations of momentum, mass and energy. In this context, heat storage models are trying to improve the efficiency of a PCM assessment, by simulations with specific boundary conditions. The current research is based on the model of the closed solid sphere developed by Lopez et al. (2010) and later extended by Pitié et al. (2011). These authors present a model of confined melting in composite materials made of graphite-nitrates and ceramic-nitrates respectively. In order to model heat storage at high temperature, and therefore the melting of the salt, these authors have proposed phase change models accounting for the pressure effects of the molten salt within the thermo-mechanical analysis.

In the context of HTTSES, a copper and nitrates composite is proposed in the present paper, considering the high thermal conductivity of copper and better mechanical strength in comparison with previously studied graphite composites. The present paper therefore proposes a first attempt to understanding salt melting within a copper spherical coating, by providing an appropriate thermo-mechanical treatment.

Consider a 25 mm O.D. sphere of solid salt (\(R_m = 12.5 \text{ mm}\)) with a 40\% KNO\(_3\) + 60\% NaNO\(_3\) composition and a concentric coating sphere of 28 mm O.D. (\(R = 14 \text{ mm}\)), made of copper (Fig. 1). The wall of the sphere allows heat transfer inside the material. The thermodynamic behavior of material properties and therefore thermo-mechanical coupling will be studied, especially toward heat capacity, average temperature and internal energy as affected by a constant temperature during a definite time. The melting front proceeds according to the variable radius \(r_f\).

The inner radius \(r_f\) represents the decreasing radius as the PCM melts, and hence delineates the solid part of the salt. The present paper uses the hypotheses of Lopez to validate the code (Ho and Chu, 1996). These main hypotheses concerning both phases include:

For the salt in its liquid phase:

1. The density \(\rho_s\), specific heat \(C_p_s\) and thermal conductivity \(k_s\) are constant, independent of pressure and temperature.
2. The liquid pressure within the shell is uniform.
3. For the salt in its solid state:
4. It can be considered as homogeneous, with constant values of density \(\rho_s\), specific heat \(C_p_s\), and thermal conductivity \(k_s\).
5. It is non-deformable.
6. The shell wall (copper) is considered to be:
7. Homogeneous, isotropic and exhibiting a linear elastic behavior.
8. Present at a known and uniform temperature.
9. At the interfaces, the following conditions are proposed:
10. It is equal to the temperature of the inner phase at the melting front.
11. An equality of temperature and pressure at the copper/salt interface.

Spherical symmetry, as defined in hypotheses (2) and (6), allows us to reduce the three-dimensional problem of heat transfer to a single-dimension.

The manufacturing of spherical capsules to contain a phase change mix has till now not been possible, since the capsules applied by vapor deposition or electrolysis have proven to be leaking molten PCM during the thermal cycles of charging and
discharging due to the porosity of the coating capsule (Pitie et al., 2013). The approach of different geometries, e.g., a tubular capsule with height to diameter ratio close to unity, can however be approached by an equivalent sphere (Zhang et al., 2014). Tubes of higher height to diameter ratio, will need to be simulated in cylindrical coordinates.

It is moreover assumed that corrosion between copper and salts is negligible. This assumption is not trivial since chemical reactions occur between metals and salts (in different degrees depending on the metal), and high temperatures and pressures affecting the materials could alter the material’s properties. Although pure copper has one of the highest galvanic numbers or nobility of the active metals, in extreme conditions of e.g. temperature and pressure imposed in the model, it could be subject to salt corrosion. Previous studies (Gravier et al., 2012; Zhong, 2002; Li and Zinkle, 2012) have however determined that corrosion is not a major issue within the operating temperature and salt concentration ranges, thus confirming that the corrosion phenomena can be neglected in the present thermo-mechanical study. The thermal instability of the nitrate PCM should also be considered, with nitrate salts slowly decomposing to nitrites, according to:

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- + 0.5 \text{O}_2 \quad \text{(as function of the partial pressure of O}_2 \quad \text{and the temperature)} \]

with subsequent reactions:

\[ \text{NO}_2^- \rightarrow \text{O}_2 + 1.5 \text{O}_2 + \text{N}_2 \]

and

\[ \text{CO}_2 + \text{O}_2 \rightarrow \text{CO}_3^{2-} \]

It is hence important to provide some O₂ on top of the nitrate PCM, and to limit the presence of CO₂, since these secondary reactions might change the composition of the nitrate mix, alter its physical properties, and could lead to an excess pressure in the capsule.

3. Mathematical model

The numerical model is based on solving the heat diffusion equation to both copper coating and to the phase change material inside the coated shell. Since it is assumed that there is no velocity field in the molten PCM phase, convective heat transfer in the salt is neglected.

Because of the symmetry, the system was formulated in one-dimensional polar coordinates. The outer side of the enclosure was assumed to be subject to free convection at external temperature, while the inner surface is assumed to be perfectly insulated. The heating power is presented by introducing a uniform heat generation inside the heated material.

3.1. Pressure effects in the thermodynamic balance

At salt fusion, pressures and temperatures influence the thermodynamic balance of the phases. Volumes and entropies must be expressed as functions of pressure and temperature in order to analyze the phase balance of salts in the coating. As proposed by Lopez (2007) and Pitie et al. (2011), the Gibbs–Duhem equation is used to relate the variables defining the thermodynamic state of a phase (i = l (liquid); s = s (solid))

\[ u_i = -s_i T + P \left( \frac{1}{\rho_i} \right) \]  

\[ \frac{\partial u_i}{\partial T} = -s_i \]  

\[ \frac{\partial u_i}{\partial P} = \frac{1}{\rho_i} \]  

where \( u_i \) represents the internal energy or chemical potential, \( T \) is the temperature, \( P \) the pressure, \( s_i \) represents the entropy of phase \( i \) and \( 1/\rho_i \) represents the volume of a unitary mass in terms of phase \( i \) density.

A second order Taylor expansion of \( u_i \) around \( u_{i0} = u_i(T_0, P_0) \) representing the initial internal energy can be written as:

\[ u_i = u_{i0} + \frac{\partial u_i}{\partial T}(T - T_0) + \frac{\partial u_i}{\partial P}(P - P_0) + \frac{1}{2} \frac{\partial^2 u_i}{\partial T^2}(T - T_0)^2 \]

\[ + \frac{1}{2} \frac{\partial^2 u_i}{\partial P^2}(P - P_0)^2 + \frac{\partial^2 u_i}{\partial T \partial P}(P - P_0)(T - T_0) \]  

(4)

Eqs. (2) and (3) can be written in terms of their thermodynamic definitions:

\[ \frac{\partial^2 u_i}{\partial T^2} = -\frac{\partial s_i}{\partial T} = -C_{Pi} \]

\[ \frac{\partial^2 u_i}{\partial P^2} = -\frac{\partial(1/\rho_i)}{\partial P} = -\beta_i \]

\[ \frac{\partial^2 u_i}{\partial T \partial P} = -\frac{\partial(1/\rho_i)}{\partial T} = \frac{\alpha_i}{\rho_i} \]

where \( C_{Pi} \), \( \alpha_i \) and \( \beta_i \) represent, respectively, the specific heat, the thermal dilatation coefficient and the isothermal compressibility.

Eq. (4) can be expressed as:

\[ u_i = u_{i0} - s_{i0}(T - T_0) + \frac{1}{\rho_i} (P - P_0) - \frac{1}{2} C_{Pi0} (T - T_0)^2 \]

\[ - \frac{1}{2} \beta_i (P - P_0)^2 + \frac{\alpha_i}{\rho_i} (P - P_0)(T - T_0) \]  

(6)

where \( T_0 \) and \( P_0 \) represent the initial temperature and pressure, respectively.

In the thermodynamic balance, \( u_i = u_{i0} \), the temperature variation of both phases (solid and liquid) may be expressed as

\[ 0 = -(s_{i0} - s_{i0})(T - T_0) + \left( \frac{1}{\rho_{i0}} \right) (P - P_0) \]

\[ - \frac{1}{2} \left( \frac{C_{P_{i0}}}{T_{i0}} - \frac{C_{P_{i0}}}{T_{i0}} \right) (T - T_0)^2 + \frac{1}{2} \left( \frac{\rho_{i0}}{\rho_{i0}} - \frac{\beta_{i0}}{\rho_{i0}} \right) (P - P_0)^2 \]

\[ + \left( \frac{\alpha_{i0}}{\rho_{i0}} - \frac{\alpha_{i0}}{\rho_{i0}} \right) (P - P_0)(T - T_0) \]  

(7)

Then factorizing by \((T - T_0)\), the solution is given as:

\[ T_f(P) = T_{i0}(P) + \frac{-b + \sqrt{b^2 - 4ac}}{2a} \]  

(8)
where
\[
a = -\frac{1}{2} \left( \frac{C_p}{T_0} - \frac{C_p}{T_0} \right)
\]
\[
b = -\left( s_{i0} - s_{a0} \right) + \left( \frac{\alpha_{a0}}{\rho_{i0}} - \frac{\alpha_{a0}}{\rho_{a0}} \right) (P - P_0)
\]
\[
c = \left( \frac{\alpha_{i0}}{\rho_{i0}} - \frac{\alpha_{a0}}{\rho_{a0}} \right) (P - P_0)^2
\]

In a thermodynamic balance, the fusion enthalpy may be expressed as,
\[
\Delta h(T_f, P) = \Delta s(T_f, P) T
\]
(10)

The fusion entropy variation, using Eqs. (2) and (6), is:
\[
\frac{\partial s_i}{\partial T} = -s_i = -s_{i0} - \frac{C_p}{T_0} (T - T_0) + \frac{\alpha_{i0}}{\rho_{i0}} (P - P_0)
\]
(11)

Then
\[
\Delta s(T_f, P) = s_{i0} + \frac{C_p}{T_0} (T - T_0) - \frac{\alpha_{i0}}{\rho_{i0}} (P - P_0).
\]

so
\[
\Delta s(T_f, P) = (s_{i0} - s_{a0}) + \left( \frac{C_p}{T_0} \right) (T - T_0)
\]
\[
- \left( \frac{\alpha_{i0}}{\rho_{i0}} - \frac{\alpha_{a0}}{\rho_{a0}} \right) (P - P_0)
\]
(12)

The entropy variation, and hence the enthalpy variation, decreases with pressure if \( \alpha_{a0}/\rho_{a0} > \alpha_{i0}/\rho_{i0} \).

The same procedure can be applied to the volume variation. Using Eqs. (3) and (6), expression (13) is obtained:
\[
\frac{1}{\rho_i} = \frac{1}{\rho_{i0}} (1 + \alpha_i (T - T_{i0}) - \beta_i (P - P_0))
\]
(13)

3.2. Heat transfer equation in proposed geometry

Based on the assumptions above, the energy equation governing the heat transfer process in the copper-coated material takes the following form:
\[
(\rho C_p)_c \frac{\partial T_c}{\partial t} = \nabla \cdot (k_c \nabla T_c)
\]
(14)

where \( (\rho C_p)_c \) represents the copper heat capacity formed by its density and specific heat respectively and \( k_c \) is the copper heat conductivity.

\( T_c = T_c(\vec{x}, t) \), \( \vec{x} = (x, y, z) \) represents the temperature of copper in position \( \vec{x} \).

As the geometrical problem is that of a circumstance, by a simple change of variable, Eq. (14) can be expressed in polar coordinates as
\[
(\rho C_p)_c \frac{\partial T_c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( k_c r^2 \frac{\partial T_c}{\partial r} \right)
\]
(15)

where \( T_c = T_c(r, t) \), with \( r_m < r < R \).

And the boundary condition is
\[
k_c \frac{\partial T_c}{\partial r} = 0, \quad r = R
\]
(16)

Using the hypotheses mentioned above, the energy transport equation to the salts coated by copper, can be developed as follows:
\[
(\rho C_p)_s \frac{\partial T_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( k_s r^2 \frac{\partial T_s}{\partial r} \right) \quad 0 < r < r_f
\]
(17)

\[
(\rho C_p)_s \frac{\partial T_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( k_s r^2 \frac{\partial T_s}{\partial r} \right) \quad r_f < r < r_m
\]
(18)

where \( T_1 \) and \( T_r \) represent temperatures of liquid and solid phases respectively.

With hypotheses (7) and (8), the limit continuity conditions can be expressed as:
\[
T_f = T_l(r, t) = T_s(r, t) \quad r = r_f
\]
(19)

\[
k_l \frac{\partial T_l(r, t)}{\partial r} - k_l \frac{\partial T_c(r, t)}{\partial r} = -\rho_l \Delta h_f \frac{\partial r_f}{\partial t}
\]
(20)

Eqs. (15)–(18) allow expressing the equivalent form as (Crank, 1998):
\[
(\rho C_p)_{eq} \frac{\partial T_{salt}(r, t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( k_{eq} \frac{\partial T_{salt}(r, t)}{\partial r} \right)
\]
\[
-\rho_{s} \Delta h_f \frac{\partial T_f(r, t)}{\partial t} > 0 \quad 0 < r < r_m
\]
(21)

\( f_s = f_s(r, t) \) represents the fraction of solid salt. This fraction is modeled by the approximation of the Heaviside function at \( T_{salt} = T_f \)
\[
f_s(\vec{x}, t) = \frac{1}{2} \left( 1 + \tanh \left( \frac{T_f - T_{salt}}{\Delta T} \right) \right)
\]
(22)

where \( \Delta T \) is the temperature range where the function is smoothing in order to avoid numerical problems with differentiation.

\((\rho C_p)_{eq} \) and \( k_{eq} \) represent the equivalent heat capacity of the salt and the equivalent heat conductivity of the salt, respectively:
\[
(\rho C_p)_{eq} = (\rho C_p)_s (1 - f_s) + (\rho C_p)_s f_s
\]
\[
k_{eq} = k_s (1 - f_s) + k_s f_s
\]
(23)

(24)

The boundary conditions may be expressed as:
\[
k_{eq} \frac{\partial T_{salt}(r, t)}{\partial r} = 0, \quad r = 0
\]
(25)

\[T_{salt}(r, t) = T_m(t), \quad r = r_m(t)
\]
(26)

where \( T_m(t) \) is the temperature at the salt–copper interface.

3.3. Mechanical analysis of the geometry

In order to study the composite material behavior at high temperatures and pressures, a mechanical analysis of resistance and elasticity has to be performed and included into the mathematical model. As mentioned before it is assumed that the composite material has a linear elastic behavior, which means that it obeys Hooke’s law.
It is assumed negligible inertia, so Stokes equation is used as:

\[ -\nabla \cdot \sigma = 0 \]  
(27)

For a linear isotropic metal, a temperature increase, \( \Delta T \), produces a uniform expansion but no shear and the expansion is proportional to a material constant \( \alpha \) (coefficient of thermal expansion, being \( 16.6 \times 10^{-6} \) for copper). The additional strain due to heating is thus:

\[ \varepsilon_T = \alpha \Delta T \]

For a Polar coordinates parameterization, where \( \varepsilon_r = \alpha u/\partial r \) and \( u \) is the displacement vector in the radial direction.

Since the investigated geometry is a perfect circle with the temperature being a condition imposed all around the geometry, the problem becomes a one-dimensional problem in terms of the radius. Due to the perfect symmetry, angular displacement is neglected in the heat transfer equation, being function of the radius only.

The constitutive equations for a linear elastic isotropic solid can hence be expressed as (Roylance, 2000):

\[ \sigma = [C] \varepsilon \]
(28)

where \( \sigma \) is the strain tensor, \([C]\) is a matrix of elastic constants that must be determined from experiments and \( \varepsilon \) represents the strain tensor of the material.

In a mechanical system under structural loads with varying temperatures, the total stress will be the combination of structural and thermal stresses. For 1D analysis in the radial direction, and for an elastic material, we can write:

\[ \sigma_{rr} = E(\varepsilon_{rr} - \varepsilon_T) \]
(29)

where \( \sigma_{rr} \) is radial stress, \( E \) is an elastic constant, \( \varepsilon_{rr} \) is radial strain due to the boundary interaction salt/copper and \( \varepsilon_T \) is a thermal strain.

For a linear isotropic material, a temperature increase, \( \Delta T \), produces a uniform expansion but no shear and the expansion is proportional to a material constant \( \alpha \) (coefficient of thermal expansion, being \( 16.6 \times 10^{-6} \) for copper). The additional strain due to heating is thus:

\[ \varepsilon_T = \alpha \Delta T \]

For a Polar coordinates parameterization and \( \varepsilon_{rr} = \alpha u/\partial r \), where \( u \) is the displacement vector in the radial direction and \( \alpha \) is a coefficient of thermal expansion of the material.

This system uses the temperature at a given point as calculated from the heat transfer equation, and feeds Eq. (29) which finally determines material stress.

Eq. (30) expresses the boundary continuity between copper and salt:

\[ \sigma_{rr} = P \]
(30)

where \( P \) is the pressure produced by the melting salt, assuming that its volume expansion will be constrained by the copper wall. \( P \) is determined by the Lopez (2007) approach.

Note that in this first attempted modeling, the mechanical stress equation does not re-feed a value to the heat transfer equation, meaning that the salt mixture is not submitted to the copper pressure, whilst the copper structure does support the salt’s pressure. This is a major difference between this model and the ones presented by Lopez (2007) and Pitie et al. (2011), where the thermo-mechanical coupling is stronger by considering the copper’s deformation into the heat transfer equation.

### 4. Results and discussion

#### 4.1. Background information

To validate the Lopez model, the thermodynamic properties of the KNO3–60%NaNO3 salt are listed in Table 1. The initial temperature of PCM is 293.15 K.

For the shell, the study will focus on geometrical and mechanical properties of copper.

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- \( E_{copper} = 117 \) GPa and \( \alpha_{copper} \) representing the copper shell Young’s module, and coefficient of thermal expansion respectively.
- Transition temperature of copper is 1357.77 K.

Comsol Multiphysics was used to assess the behavior through the procedure of “Thermal Stress that contains Heat Transfer and Solid Mechanics phenomena”, necessary to obtain values to validate the model. It uses an extra-fine mesh of 6046 elements in order to provide results with a minimum error range. Two sets of results will be presented hereafter.

#### 4.2. Heating at imposed and constant surrounding temperature

In order to test the new composite material for thermal storage, the above model equations were used in a first simulation where a constant temperature of 550 K all around the geometry was accepted (e.g. by a circulating Heat Transfer Fluid around the E-PCM), whilst the initial E-PCM temperature was 293 K. Material properties are assumed initially constant.

#### 4.2.1. Simulation results are illustrated hereafter

In order to study the evolution of the material properties, a first simulation was run until a complete melting was obtained throughout the PCM (melting point = 496 K). Fig. 2 illustrates the temperature of the material with time in seconds, being 3 s (C.1), 10 s (C.2), 50 s (C.3), 300 s (C.4), 600 s (C.5), 900 s (C.6), 1000 s (C.7), and 1031 s (C.8) respectively. Clearly, complete melting is achieved between 1000 and 1031 s.

The figure illustrates the progressive heating of the E-PCM. The heat distribution within the geometry becomes homogeneous with increasing time. The high thermal conductivity of copper allows a fast and efficient heat transfer toward the center of the geometry, faster than obtained with SiC or graphite (Ho and Chu, 1996; Ahmadia and Quintard, 1998).

The calculation of the inner pressure of the copper shell is illustrated in Fig. 3. When complete melting is achieved, the
pressure reaches its maximum of 850 MPa (0.85 GPa), hence far below the Young’s modulus value of 117 GPa (Quintard and Whitaker, 1998b), being the transition from elastic to plastic behavior of copper: the inner pressure created is hence certainly insufficient to crack the shell. At the tested temperature, the copper is far below its melting point. The value of the pressure in the copper shell at 30% molten PCM is about 35% lower than the results of Pitie (Ahmadia and Quintard, 1998), obtained for nitrate salts in a rigid graphite shell. For graphite coated nitrates, Lopez et al. (2010) predict the complete melting of the salts after 2000 s of heating and at a temperature of 247 °C (520.15 K), with an internal pressure of 3 GPa. The extended time (2000 s) is due to the lower thermal conductivity of the graphite shell when compared its copper equivalent.

In its completely molten state, the PCM will have absorbed its sensible and latent heat being ~518 kJ/kg in total. Whilst considering that this complete melting is achieved in a reasonable charging period (~1000 s) without any danger of cracking the copper shell, it is clear that the copper-nitrate composite is a valid combination for use in advanced thermal energy storage.

4.3. Cooling at imposed and constant surrounding temperature

For the cooling process, and subsequent to the heating process till 550 K with complete melting of the nitrate salt, an external temperature of 400 K was imposed around the geometry. Full melting was achieved after 1031 s. These temperatures are in the range of typically most thermo-solar plants that use salts in their heat storage process. The simulation, illustrated in Fig. 4, shows that at 2780 s, the copper reaches 400 K, which means that in a period of 1749 s, the copper was cooled from 550 K to 400 K.

The different curves represent different times of simulation, being 1550 s (C.1), 1600 s (C.2), 1700 s (C.3), 1800 s (C.4), 1900 s (C.5), 2063 s (C.6), 2500 s (C.7), 2700 s (C.8) respectively. As the material is being cooled, the heat distribution in the geometry becomes again homogeneous throughout time. Despite the high copper thermal conductivity, the low thermal conductivity of the solidifying PCM reduces the cooling rate.

In the fundamental assumptions, it was stated that natural convection in the melt is not considered, and the cooling progress is hence calculated on the basis of sole conduction. Recent experiments (Zhang et al., 2014) have demonstrated that the cooling rate is enhanced by the occurring natural convection in the melt. The natural convection contribution to the overall heat transfer coefficient could not be calculated and the authors (Zhang et al., 2014) proposed to deal with the problem by increasing the thermal conductivity of the melt by 20–40%.

The complete charging/discharging cycle, expressed as pressure versus time, is illustrated in Fig. 5.

In the cooling process, the pressure decreases with time (and hence with inherent temperature). Decreasing pressures are moreover a guarantee that the shell will not crack.

Fig. 6 shows the evolution of the pressure in the charging and discharging processes.

Finally, Fig. 7 illustrates the evolution of total heat, sensible heat and latent heat versus time.
The total weight of the material is 0.01805 kg. The latent heat of phase change exceeds the sensible heat when melting/solidification occurs. The peak at 1031 s, corresponds to the time required for complete melting of the PCM.

5. Conclusions

The thermo-mechanical model of a PCM coated in a spherical copper shell was examined for the charging and discharging cycles.

Charging was predicted to take ~1000 s from 293 till 550 K. A discharging period of ~1600 s is needed to cool the E-PCM to 400 K. The cooling rate of the melt is possibly enhanced by the occurring natural convection.

The volume expansion upon melting and associated pressure increase is beyond the acceptable mechanical properties of the copper shell and shell cracking is not expected to occur.

The novel copper/salts composite was proven to be an attractive material for heat storage. A future study will assess the material properties in more extreme conditions, by e.g., including the effect of rising pressures on salt’s properties (assumed constant in the present first approach).

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