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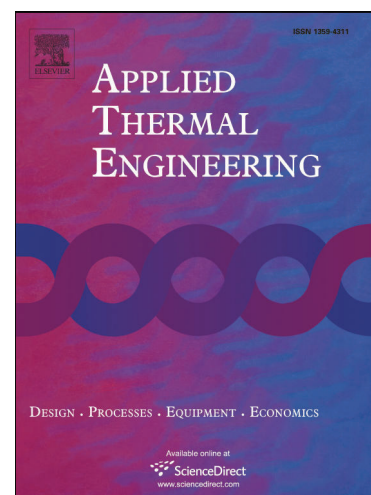
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Thermal performance of a PCM firefighting suit considering transient periods of fire exposure, post – fire exposure and resting phases

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Abstract

Firefighting scenarios may be characterized by various transient periods (i.e. phases), which consist of diverse environmental conditions. Firefighters usually encounter fire exposure, post fire exposure and resting phases. Development of new and improved protective clothing must be able to provide protection throughout all these phases, as burnouts may still occur after fire exposure due to accumulation of heat in the garment. The incorporation of phase change materials (PCMs) in firefighting garments has been shown to minimize the potential of heat hazards only during fire exposure. Thus to get more knowledge on their thermal performance, in this work, the effect of PCM incorporation in post fire and resting phases were also numerically studied. The numerical code was validated for all phases. Five potential PCM candidates were considered. Exposure phases were characterized by high- medium and low- heat flux intensities (84, 12 and 5 kW/m²) with variable exposure times whilst post –exposure and resting phases were characterized by different wind speeds (i.e. ambient convective coefficients). Optimal PCM masses, times to second and third – degree burns as well as PCM suit cooling times were calculated to reflect thermal protective performance in each respective phase. The data generated allows for PCM short-listing from a set of potential PCM candidates along with its geometrical parameters, considering a wide range of characteristics of the various phases that consist a typical firefighting scenario.

Keywords: Firefighting garment; Phase change material; Numerical simulation; post-fire burnout; second degree burns; third degree burns

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1. Introduction

Firefighters face thermal stressful situations that may cause severe burns or even death. To avoid such situations, the suit has an important role to fulfill [1]. Hence, improvements in firefighting garments are always required. A possibility of improvement relies on the increase of the garment thermal performance by the inclusion of phase change materials (PCM) [2–6]. Some works show guidelines to estimate PCM properties, mass and its position in the firefighters suit [5–9]., Despite the extensive research on the application of PCMs for the fire exposure phase, the scenarios considered are limited to specific fire heat fluxes and exposure times, therefore reducing the applicability of such data. Additionally, the analyses were done neglecting the effect of the energy accumulated in the suit on the firefighter's skin, when the firefighter escapes from direct exposure to fire or takes a break. This may lead to misleading conclusions about the choice of the PCM. For those reasons, a detailed investigation of the heat transport in a suit with PCM for transient ambient conditions (i.e. exposure to flame, post-fire and rest) is justified.

In order to obtain optimal performances, the inclusion of PCMs in firefighting garments requires knowledge about the PCM choice and its mass. The mass to be incorporated depends on many factors. In this study, a PCM mass choice criteria for firefighting garments is suggested, taking into account a wide range of possible exposure scenarios that the firefighter can face. PCM mass choice is also a problem in other PCM applications such as in the automobile sector and clothing industry [10–12]. Several authors report the masses used, however, justification of their choice is, usually, not reported. Others perform parametric studies to observe the influence of the mass on the PCM cooling effect, but the analysis is usually for only one PCM and does not take into account an optimal performance criteria. Oró et al. [13] incorporated 4 kg of a PCM (RT-27) into the inner roof of a car to control its inner temperature during hot summer days. The authors reported a cooling effect that lasted for about 80 min and recognized the necessity of a mathematical model in order to predict optimal PCM masses in function of the process variables such as external ambient conditions and parking time. Hamdan et al. [14] suggested and validated an integrated PCM- fabric bio-heat model which was used to study the effects of melting temperature and mass of the incorporated PCM. Chou et al. [15] studied the effect of using different PCMs with different melting temperatures (i.e. Ice, PCM(5) and PCM(20)) on the cooling of a firefighter during a treadmill exercise. The subjects faced a

warm environment during the treadmill (30 °C, 50 % RH) and the masses used for Ice, PCM(5) and PCM (20) were 1.05, 1.69 and 1.34 kg, respectively. The PCMs provided cooling effect throughout the exercise, however it is unclear whether the PCM masses put were the optimum.

Occurrence of 2nd and 3rd degree burns is likely during firefighting exposures. In 2nd degree burns, the firefighter suffers damage both to the epidermis and dermis regions, and natural healing is still possible [16]. Whilst for 3rd degree burns, there is destruction of blood vessels, hindering the possibility of natural healing [16]. As adequate PCMs promote the storage of incoming heat at lower temperatures during fire exposure phase, it is to expect that this stored heat will have a great influence on the post-fire exposure phase, where third degree burnouts are likely to happen [6]. Hence, it is rather of interest not only to analyze how the inclusion of adequate PCMs relates to the time to second degree burnout (exposure phase), but also to see how much longer the firefighter has until a third degree burnout occurs (post-exposure phase).

Information about the post fire stage regarding the design of PCMs FPC is scarce in the literature. Properties associated to the ambient encountered by firefighters in the post exposure phase may change the thermal behavior of the firefighting garment. Torvi et al. [17] proposed and validated a heat transfer model for a firefighting garment, and conducted a parametric study involving different ambient convective heat fluxes, supposing a high – intensity heat exposure. They concluded that the ambient convective heat flux had a marginal effect on the temperatures obtained after the fire exposure. Song et al. [18] considered different garment configurations and experimentally analyzed how stored thermal energy influences the occurrence of burns, for different heat exposure scenarios. They concluded that thicker fabrics promote stored energy burns (i.e. burns after fire exposure). The authors mention that, in some cases, the release of stored energy towards the skin can make up to 50 % of the total skin damage required for a burnout. The same authors in a similar study [19] proposed correlations relating the fabric thickness with the time to burnout. The authors considered low radiant heat exposures. Su et al. [20] proposed and validated a heat transfer model for a three layer firefighting garment assembly. The authors analyzed the effect of stored energy on thermal performance. According to this study, ambient temperature marginally influences thermal performance.

In the recovery phase, the firefighter usually doffs the firefighting garment and rests. During this time, the firefighting garment cools down, releasing the remaining accumulated energy from the fire exposure. The existence of PCMs in the firefighting garment prolongs the cooling time, as it needs to re-solidify [3]. The choice of a PCM with adequate properties to minimize the garment cooling time is also important so the firefighter can don the PCM garment again.

In resume, in this work, both PCM optimal choice and mass were calculated taking not only into account the exposure phase, but also the post – exposure and recovery phases as well. A list of

five potential PCM candidates was considered. PCM minimum masses were calculated for high – medium – and low- intensity heat flux exposures, for various exposure durations. The difference between second and third degree burn times was afterwards calculated for the post-exposure period in function of the previous exposure intensity and duration. This difference in burnout times was labeled alarm time, i.e. the time that the firefighter has until suffering irreversible burns. Second and third degree burnouts have had special attention devoted in previous works also regarding thermal performance in PCM FPC [20–23]. Different post – exposure scenarios characterized by different ambient convective coefficients were considered. Lastly, it was assumed that the firefighter doffs the PCM firefighting suit at the end of the exposure phase and the cooling time was obtained for the different PCMs.

2. Materials and Methods

2.1. Problem description

In order to analyze the effect of PCMs in enhancing the garment thermal protection [5,24], a typical firefighting protective clothing (FFPC)-skin system was used (Figure 1). The simulation domain consists in a series of layers of garment (i.e. outer shell, PCM and inner layer; at blue in Figure 1) and of skin (i.e. epidermis, dermis and subcutaneous; at orange in Figure 1). The performance of the PCM FFPC clothing is studied for a dynamic scenario of fire exposure, post-fire exposure and resting phase. In the fire exposure period, the external surface of the garment (boundary 1 in Figure 1a) is initially subject to a sudden heat flux for a given exposure time (i.e. mimicking exposure to flame) that ensures almost a reversible burn (i.e. a second-degree burn). After, the garment is no longer in direct exposure to the flame and the heat exchange between the garment and the environment can occur by convection and radiation (Figure 1b and c). During this time, we were interested to study how long the firefighter can handle without getting a third degree burn or how long the firefighter should wait until the garment is completely cooled down. This may happen in two ways: i) firefighter is wearing the PCM FFPC and the simulation domain is the system FFPC-skin (post - fire phase, Figure 1b) or ii) the PCM FPC is taken out and the simulation domain consist only in the garment with both the boundaries exposed to the environment conditions (resting phase, Figure 1c). Three heat fluxes were chosen to reflect the different fire scenarios that firefighters can encounter: 84, 12 and 5 kW/m² [5]. For the post-fire exposure and resting phase, the garment performance was assessed for windy and no wind conditions (e.g. inside fire truck).

The PCMs studied are shown in

Table 1[25]. These PCMs were chosen essentially based on their melting temperatures. Rubitherm PX 82, however, has been previously incorporated in firefighting garments [3]. The melting temperature has to be low enough not only because the PCM should melt for the different exposure scenarios [6], but also because the skin burn should, if at all, happen after the PCM is fully melted (i.e. maximum PCM efficiency). The PCM mass also influences the PCM efficiency, as a higher PCM mass takes a longer time to melt.. The data outlined in [6 - Figure 17], gives rough estimates of melting temperatures and PCM mass ranges which could potentially originate maximum PCM efficiency and protection to the firefighter, for each of the exposure scenarios. It was based on these data that the PCMs listed in

Table 1 were chosen. In the simulation, a variation in the PCM mass was considered by changing the PCM thickness while ensuring constant density.

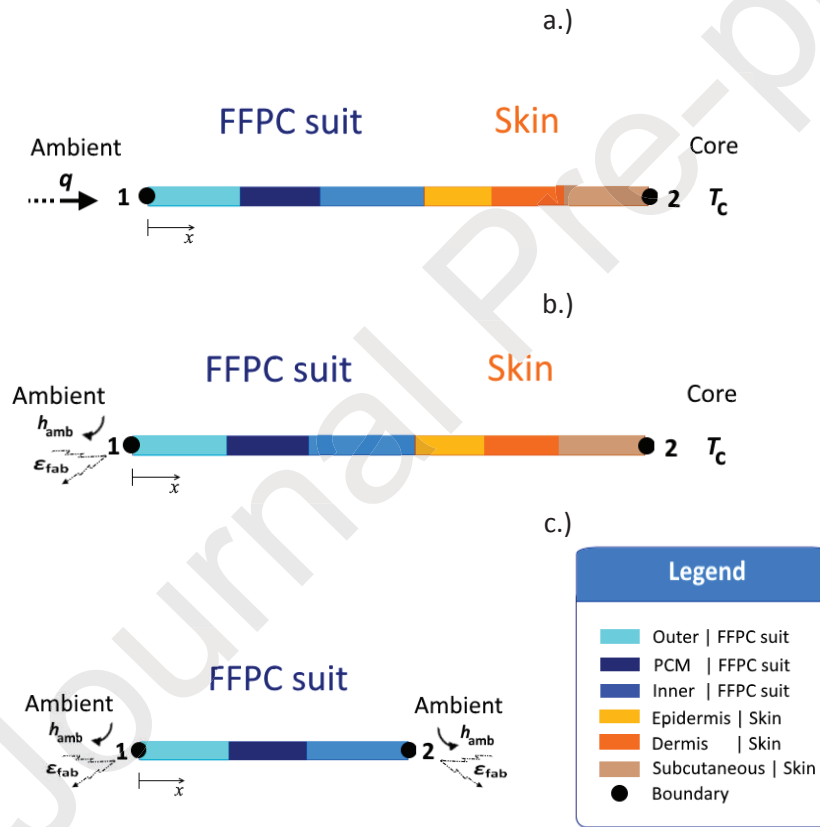


Figure 1 - Geometry and boundaries of (FFPC)- skin system: a.) for heat exposure; b.) for post - fire period when PCM FFPC is not removed; c.) for resting period when garment is removed

Table 1 - PCMs and their thermophysical properties used in this study (retrieved from [25]); T_m , ΔH_m , Cp_s , Cp_l , k_s , k_l , and ρ_s stand for melting temperature, latent heat of fusion, solid specific heat, liquid specific heat, solid thermal conductivity, liquid thermal conductivity and density of the solid phase, respectively.

| | T_m (°C) | ΔH_m (kJ/kg) | Cp_s (kJ/kg/K) | Cp_l (kJ/kg/K) | k_s (W/m/K) | k_l (W/m/K) | ρ_s (kg/m ³) |
|---|---------------|-------------------------|---------------------|---------------------|------------------|------------------|----------------------------------|
| Stearic acid | 54 | 157 | 1.76 | 2.27 | 0.29 | 0.17 | 940 |
| CH₃COOH · 3H₂O | 58 | 266 | 1.68 | 2.37 | 0.43 | 0.34 | 1450 |
| Barium hydroxide octahydrate | 78 | 280 | 1.34 | 2.44 | 1.26 | 0.66 | 2180 |
| Rubitherm PX82 | 82 | 105 | 1.6 | 1.6 | 0.1 | 0.1 | 690 |
| Magnesium nitrate hexahydrate | 89 | 140 | 2.5 | 3.1 | 0.65 | 0.5 | 1640 |

2.2. Boundary conditions

Firefighters encounter several types of heat exposure scenarios, from mild exposures in which the firefighter doesn't need special clothing, to flash fire scenarios where the firefighter must have special protective clothing [26]. McCarthy and co-workers [27] used exposures of 2.5, 10, and 20 kW/m² for 15 min, 5 min, and 30 s, respectively, as boundary conditions for the external garment layer. Other researchers [24] used exposures of 83.2 kW/m² and 1.2 kW/m² for periods of 5 min and 3 s respectively, to simulate low and high intensity firefighting. In this work, three heat exposure intensities were considered. They include low - and medium-intensity exposures (5 and 12 kW/m²) corresponding to pre-flashover conditions, and a high intensity exposure (84 kW/m²) representing flash fire conditions [5]. In this study, the exposure times were not fixed. This option was done in order to obtain more generic results regarding the exposure scenario the firefighters are subjected to.

After the heat exposure scenario, the firefighter is likely to be exposed to a windy environment as well as to a reduced ambient temperature. Torvi et al. [17] characterized the post fire environmental scenario as having a constant ambient temperature (27 °C), and convective heat fluxes in the range of 2-10 W/m²K. Ghazy et al. [28] considered an equivalent temperature, but used a correlation for natural convection to estimate the ambient convective heat flux. Su et al. [20] considered ambient temperatures in the range of 0 – 50 °C and a correlation to estimate the ambient convective heat flux. Li et al. [29] used different wind speeds to characterize the thermal protection, implying different convective heat fluxes. Butler et al. [30] provides a list of typical ambient temperatures and wind speeds found in firefighting scenarios, as they are data taken from live fires. From the works above, it was possible to define an ambient temperature and the ranges in which the convective fluxes should be taken. The ambient temperature was assumed constant and equal to 25 °C. The convective heat coefficients considered were varied

from 0 W/m²K to 90 W/m²K. That is, it varied from when no or only natural convection was present (e.g. inside fire truck), to cases where strong winds were up to 25 m/s (e.g. exposed to forest fires or to blower fans).

Thus, the following boundary conditions were considered:

$$-k \frac{\partial T}{\partial x} \Big|_{x=0} = q \quad \text{for } 0 < t \leq t_{\text{exp}} \quad \text{eq. 1}$$

$$-k \frac{\partial T}{\partial x} \Big|_{x=0} = -h_{\text{amb}}(T_{\text{fab}} - T_{\text{amb}}) - \varepsilon_{\text{fab}} \sigma (T_{\text{fab}}^4 - T_{\text{amb}}^4) \quad \text{for } t > t_{\text{exp}} \quad \text{eq. 2}$$

where t_{exp} is the heat flux exposure time and h_{amb} , T_{fab} , T_{amb} and ε_{fab} represent the ambient convective heat flux, the fabric surface temperature, the ambient temperature, and the fabric emissivity respectively (i.e. $\varepsilon_{\text{fab}} = 0.9$ [31]).

2.3. Mathematical model and assumptions

The firefighting garment is essentially composed of an outer layer, a PCM layer and a thermal inner layer (Figure 1). The general dimensions of the various layers in the FFPC-skin system are shown in Table 2. The outer shell and thermal inner layers of the garment were considered to be a Kevlar®/PBI fire resistant fabric and an Aralite ® fabric, respectively [15, 16]. The firefighting garment ensemble may also contain a moisture barrier [9], but, following related works in the literature [5, 14], it was not considered in this work as the effect of PCM is larger than that of moisture barrier [24].

Conductive heat transport in the outer and inner domains was modeled using the Fourier equation [6]. Their thermophysical properties were assumed temperature dependent (Table 2).

Table 2 - Thermophysical properties of the outer and inner layer of the garment and skin layers [32,33]; ρ , C_p , k , and L stand for, respectively, density, specific heat, thermal conductivity, and layer thickness. k_{air} and k_{fibre} stand for the air and clothing fiber thermal conductivity, respectively.

| | ρ (kg/m ³) | C_p (J/kg/K) | k (W/m/K) | L (mm) |
|---------------------|--------------------------------|---|---|-------------|
| Outer | 323 | $1300 + 1.6 \cdot (T [\text{K}] - 300)$ | $0.8 \cdot k_{\text{air}} + 0.2 \cdot k_{\text{fibre}}$ | 0.6 |
| Inner | 74.2 | $10.4 \cdot T [^\circ\text{C}] + 1225$ | $0.0003 \cdot T [^\circ\text{C}] + 0.0304$ | 3.59 |
| Epidermis | 1200 | 3600 | 0.24 | 0.08 |
| Dermis | 1200 | 3300 | 0.45 | 2 |
| Subcutaneous | 1000 | 2500 | 0.18 | 10 |

The apparent heat capacity method was used to simulate the phase change (eq. 3) in the PCM layer. The apparent heat capacity method derives from a weak formulation of the phase change problem, namely the enthalpy formulation. Essentially, the position of the interface is implicitly taken into account by an apparent heat capacity (C_{app}), which not only considers the sensible, but also the latent heat associated with the phase change [34]. This makes it possible to avoid problems associated with interface tracking methods [35]. The following conservative one-dimensional energy equation is then applied in the PCM domain:

$$\rho C_{\text{app}} \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \cdot \left(k \frac{\partial T}{\partial x} \right) \quad \text{eq. 3}$$

where ρ , T , t and k , represent, respectively, density, temperature, time and thermal conductivity. The index app stands for apparent. The PCM thermophysical properties in equation 3 were considered solely phase dependent ([15,16,26];

Table 1).

The apparent specific heat curve was assumed to have the following form [5,9,24,36]:

$$C_{\text{app}} = \frac{dH}{dT} = \frac{d}{dT} \left[0.5 \times \lambda \times \text{erf} \left(\frac{T - T_m}{T_0} \right) + C_{\text{PCM}}(T - T_m) \right] = \lambda \times \frac{\exp \left(-\frac{T - T_m}{T_0} \right)^2}{T_0 \sqrt{\pi}} + C_{\text{PCM}} \quad \text{eq. 4}$$

where H , T_m , λ , and C_{PCM} are, respectively, the total enthalpy, the melting temperature, the latent heat, the specific heat and T_0 is a variable associated to the mushy region. Identical mushy

regions were assumed for all PCMs. Both melting and re-solidification processes (i.e. charge and discharge processes) were assumed to be described by the same apparent heat capacity relationship with temperature.

For the skin layers, the one-dimensional heat transfer was simulated according to eq. , where the second term on the right-hand side represents the heat removed through blood circulation (only applied for dermis and subcutaneous layers [5,9,24]):

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \cdot \left(k \frac{\partial T}{\partial x} \right) - G \rho_b C_b (T - T_c) \quad \text{eq. 5}$$

where the indexes b and c stand for blood and core, respectively. Blood perfusion rates (G) were assumed constant in dermis and subcutaneous layers (i.e. $1.25 \times 10^{-3} \text{ s}^{-1}$ [5,9,36]) and the blood density (ρ_b) was set at 1060 kg/m^3 for all skin layers.

A skin burn model was used to estimate the time for a second and third degree burns to occur. This was done following the initial work of Henriques [37], which tries to quantify the thermal damage to the skin through the so-called burn integral, obtained from the evolution of skin temperature over time. A second-degree burn at the epidermis/dermis interface was acknowledged when the Henriques' burn integral implied Ω values equal to unity (with parameters from [38]). Identical procedure was done for the third degree burns, but at the dermis/subcutaneous interface. The difference between both was considered the alarm time.

At the initial time, the core body temperature was assumed constant at 37°C [5, 11, 14, 24], and the clothing layers were assumed to be at 34°C . The initial temperature of the different skin layers was assumed to vary linearly between 34°C (epidermis – garment inner layer interface) and 37°C (core; [5, 25]).

A finite element approach was used to solve the governing equations with a first order discretization scheme. Time-steps of 0.1 s and 1 s for the exposure and post- exposure phases, and a maximum number of mesh elements of 800 were found adequate to ensure grid-independent results.

2.4. Model validation

In our previous work [6], the model predictions of temperature histories were validated against experimental and numerical results found in the literature [14,24], obtained during fire exposure phase. In this work, the accuracy of the model to predict the cooling phase was evaluated by comparison of temperature predictions obtained from Ghazy ([31] ;Figure 2). Ghazy [31] performed a numerical study on a typical firefighting garment assembly considering exposure and post-exposure phases. Temperature histories along the FFPC suit and skin layers over time were obtained (Figure 2).

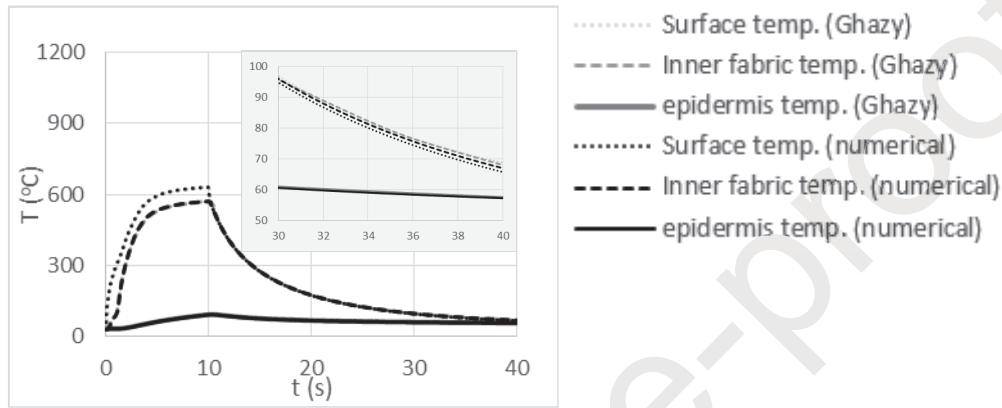


Figure 2 - Temperature history comparison between numerical results and those obtained from Ghazy [31] for different position in the firefighting garment - skin system.

Differences in the temperature profiles obtained are negligible; differences of less than one degree are observed in the epidermis surface. Hence, these consistent results indicate that the transient model predictions are accurate, and so, can be used to study the garment cooling phase.

3. Results and Discussion

The mass that is incorporated in an FFPC needs to be minimized, as weight is a critical factor for the firefighter. Firstly, for the exposure phase, optimal/minimal (just to prevent a 2nd degree burn) PCM masses (m_{PCM}) for the different exposure heat flux intensities and durations (i.e. t_{exp}) were obtained for each PCM (Section 3.1). For the post-exposure phase, the alarm time (t_{alarm}) was calculated for the intended exposure heat flux intensities and durations (t_{exp}), also taken on account the effect of the ambient conditions (i.e. variable h_{amb}). Lastly, it was assumed that the firefighter doffs the PCM FFPC during the resting phase (i.e. right after the exposure) and the PCM FFPC cooling time ($t_{cooling}$) for the intended exposure times (t_{exp}) was obtained for the different PCMs (Section 3.3).

The masses shown below refer to an area coverage of 0.35 m², which corresponds approximately to the front upper body area of the firefighter [6].

3.1. PCM mass calculation during fire exposure

The optimal/minimum PCM mass (m_{PCM}) essentially depends on the PCM properties, as well as on the intended exposure intensity and duration (t_{exp}).

Figure 3 shows the minimum PCM masses needed for the firefighter to survive the fire exposure without burns (i.e. without 2nd degree burn), for the three exposure heat flux intensities.

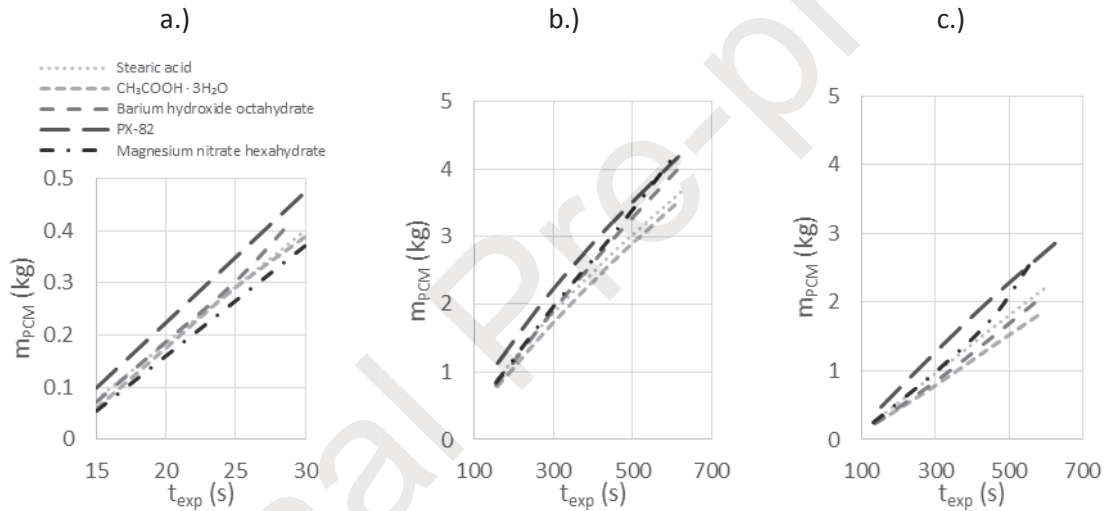


Figure 3 - Minimal PCM masses (m_{PCM}) obtained for different exposure times (t_{exp}) and indicated PCMs for a.) high - b.) medium- and c.) low - intensity heat exposures

For the FFPC suit without the PCM layer (not included in the figures), maximum exposure times (i.e. without 2nd degree burn) of 12 s, 34 s, and 55 s were obtained for the high – medium- and low- intensity heat intensities. If these values are compared with those of Figure 3, it can be concluded that there is a very significant increase of time to reach a 2nd degree burn when a PCM is used, particularly for the medium and low – intensity exposures

According to Figure 3, the required PCM mass (m_{PCM}) increases linearly with the intended exposure time (t_{exp}) for almost all exposure intensities. For example, for the low – intensity exposure (Figure 3c), $\text{CH}_3\text{COOH}\cdot 3\text{H}_2\text{O}$ increases linearly from a mass requirement of ~0.2 to ~1.9 kg in order to increase exposure sustenance from 141 to 563 s, respectively. This tendency is in accordance with findings from previous works [6].

The best PCM choice is naturally the one that requires the lowest minimum mass (m_{PCM}), however, this choice depends on the intended exposure time (t_{exp}). For example, for the medium – intensity heat exposure scenario (Figure 3b), whilst magnesium nitrate hexahydrate might be the PCM with the lowest mass requirement for short exposure times (i.e. < 150 s), the contrary is true for long exposure times (i.e. > 150 s). Furthermore, an oversight in the PCM choice can lead to a significantly increase in the firefighter load, particularly for higher exposure times (e.g. a maximum deviation of ~ 0.6 kg is obtained for 600 s; Figure 3b).

Figure 3a, high- intensity heat exposure, shows that the PCM with the lowest mass requirement is Magnesium nitrate hexahydrate, for all t_{exp} considered (Figure 3a). Even though, Magnesium nitrate hexahydrate is the PCM with the lowest latent heat and the highest melting temperature, it has a significantly higher specific heat than the others (

Table 1). In a high- intensity heat exposure, a significant amount of energy is stored in the PCM as sensible heat in the liquid phase. PX-82 is the PCM with the highest mass requirement because it has the lowest specific heat (1.6 kJ/kg/K). So, it can be concluded that the latent heat present does not influence the exposure times greatly for high – intensity short duration exposures. This puts into question whether or not the inclusion of a PCM is justified for high intensity short duration exposures such as these.

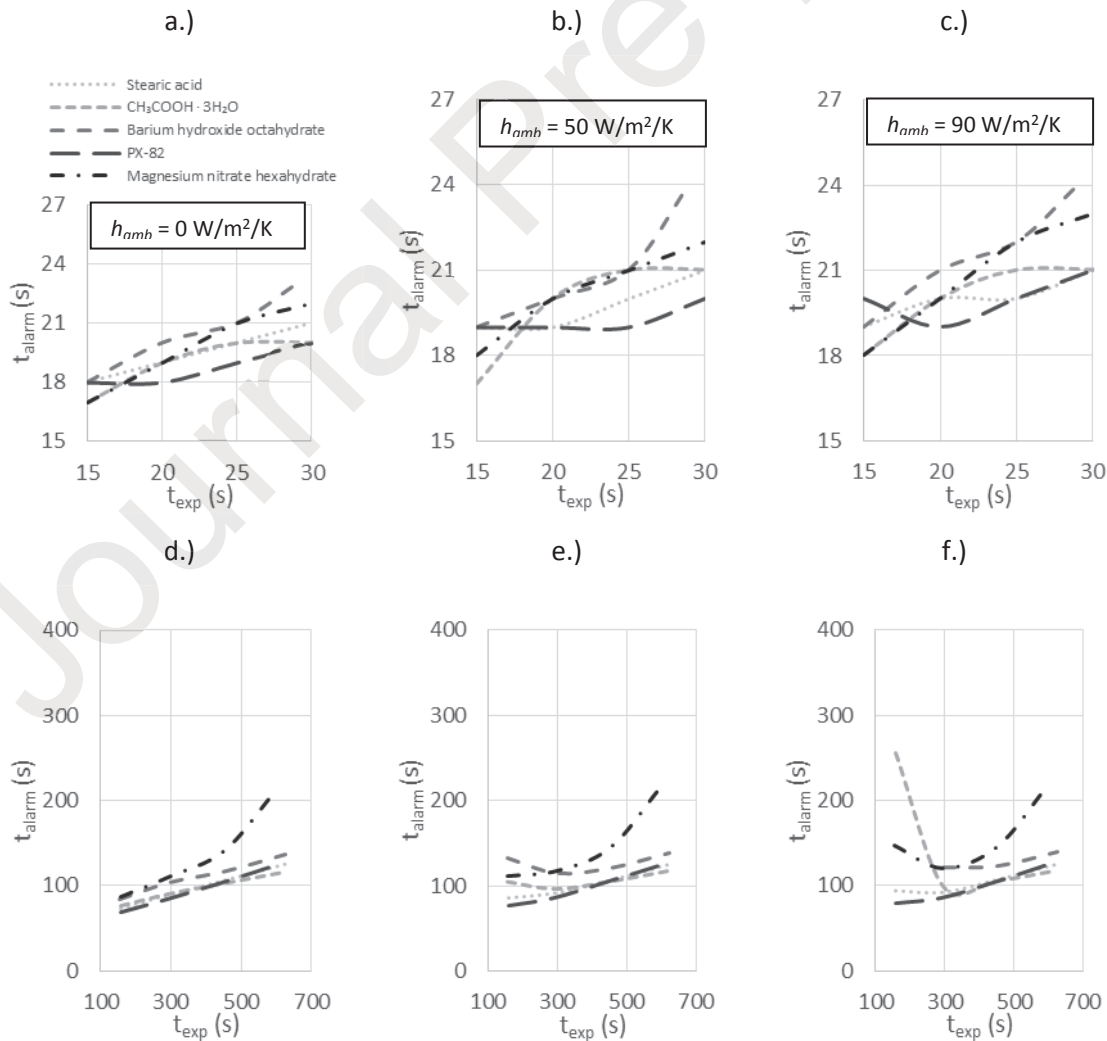
For the medium – intensity heat exposure scenario (Figure 3b), as less heat is accumulated in the sensible and more in the latent form, PCM latent heat and melting temperature become more important on the minimal mass obtained. For a given mass, PCMs with higher latent heats and lower melting temperatures have the capacity to store greater amounts of energy at lower temperatures. So, the mass requirements for a given t_{exp} will be lower. $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ originates the lowest mass requirement. For $t_{exp} = 600$ s, mass requirement for the PCM with highest melting temperature and lowest latent heat (i.e. Magnesium nitrate hexahydrate) is 4.1 kg whilst for $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ is 3.5 kg. Barium hydroxide octahydrate has a slightly higher latent heat, but a much higher melting temperature, hence the mass requirement, especially for higher t_{exp} (Figure 3b), is greater. For the low – intensity exposure, similar trends are registered (Figure 3c). Contrary to the medium intensity exposure, Barium hydroxide octahydrate originates a lower mass requirement than stearic acid. That is, the difference in melting temperatures between the two PCMs does not influence the mass requirements as much as the difference in latent heat, in this exposure intensity.

Hence, for the high- medium- and low-intensity heat exposures, Magnesium nitrate hexahydrate and $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ are the PCMs with the lowest mass requirements respectively. To note that for the high – intensity exposure, the inclusion of a PCM might not be justified as most of the incoming heat is accumulated in the sensible form.

3.2. Alarm time during post-fire exposure

One of the benefits of incorporating a PCM in a firefighting suit is the accumulation of incoming heat energy at lower temperatures. Such, allows to extend the presence of the firefighter in the fire scenario before a second-degree burn occurs as shown in Section 3.1. Despite this, the accumulated energy in the PCM is eventually released towards the environment and the firefighters' skin during the post-fire exposure. This exposes the firefighter to a third degree burnout risk which must be addressed.

Using the minimal masses calculated above (i.e. m_{PCM}), the alarm time (t_{alarm}), defined as the difference between times to second and third degree burnout, has been obtained as an indicator for the adequacy of a PCM choice for the post – fire exposure phase. Figure 4 shows that a PCM choice based on this criterion is heavily dependent on the exposure time considered (t_{exp}) as well as on the ambient conditions and exposure scenarios.



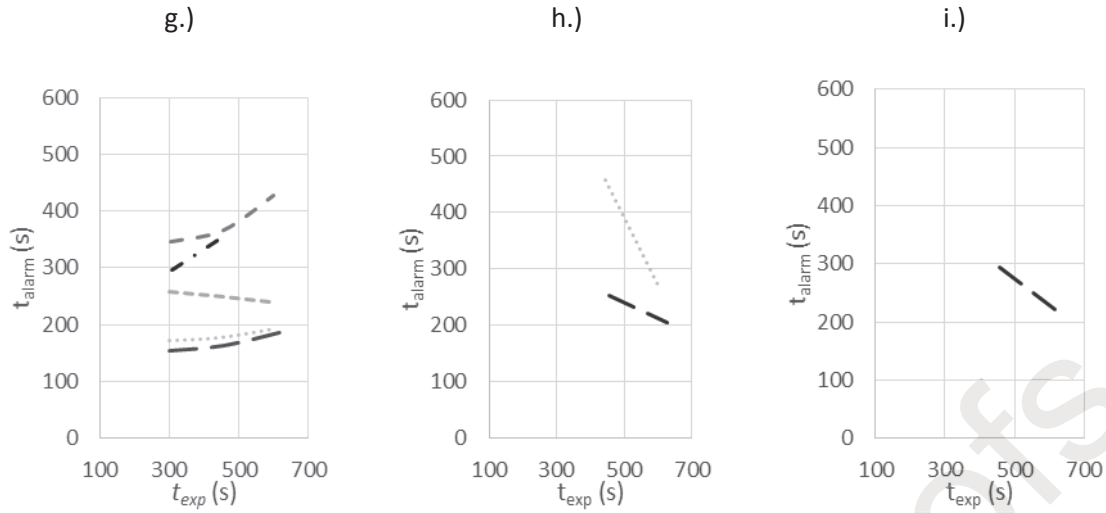


Figure 4 - Alarm times (t_{alarm}) obtained for different exposure times (t_{exp}) and indicated PCMs for the a-c.) high – d-f.) medium – g-i.) low intensity heat exposure, for the indicated h_{amb}

Firstly, let us compare the alarm times of Figure 4 obtained for high-intensity heat exposure (a-c) with a reference FFPC that does not contain a PCM layer. With the reference FFPC the obtained alarm times are 19 s, 20, and 21 s for $h_{amb} = 0, 50$ and $90 \text{ W/m}^2/\text{K}$, respectively. These values are not far off when compared to the ones with PCM inclusion (i.e. Figure 4a-c). But, for the medium and low – intensity exposures however, it turns out that if a PCM layer is not included, the alarm time does not exist (i.e. no third degree burn is reached); the accumulated heat is smaller and it is mostly removed to the environment. However, it should be highlighted that the inclusion of a PCM allows for greater exposure times (it is possible to double the time; Figure 3). With this in mind, consider the post fire scenarios after, again, a high – intensity exposure (Figure 4a-c). For $h_{amb} = 0 \text{ W/m}^2/\text{K}$, the alarm times obtained for all exposure durations are in the range of 18-24 s, for all PCMs. The way t_{alarm} varies with t_{exp} is different for each PCM. For example, for PX-82, t_{alarm} stays constant for $15 \text{ s} < t_{exp} < 20 \text{ s}$ and then rises almost linearly to a t_{alarm} of 20 s (Figure 4a). On the other hand, if barium hydroxide octahydrate is the incorporated PCM, t_{alarm} increases to a maximum of 20 s and then stabilizes. These variations can be explained essentially by the nature of the Henriques burn criteria [37]. The Henriques burn criteria depends on the temperature histories obtained at the skin for a given incorporated PCM with enough mass to sustain a given t_{exp} . For different t_{exp} , different temperature histories are obtained. If these are very different from each other, this will enhance the influence of the exponential nature of the Henriques integral on the time to burn obtained and hence on the alarm time. This is also true for other h_{amb} . Little variation on the t_{alarm} exists when h_{amb} is increased to $50 \text{ W/m}^2/\text{K}$ and $90 \text{ W/m}^2/\text{K}$. However; there are slight variations in the nature of the tendencies of t_{alarm} with t_{exp} , for each respective PCM.

For the medium – intensity exposure, the tendencies registered are different (Figure 4d-f). Consider the case for $h_{amb} = 0 \text{ W/m}^2/\text{K}$ (Figure 4d). For all PCMs, there is a general increase of t_{alarm} with t_{exp} . This is due to the increase of the thermal resistance provided by the incorporated PCM. For Magnesium nitrate hexahydrate however, an exponential rise occurs for $t_{exp} > 450 \text{ s}$. This is because solid PCM might be present in the PCM after the exposure [6]. This also occurs for the remaining h_{amb} . For $h_{amb} = 50 \text{ W/m}^2/\text{K}$, apart from there being a general difference in the t_{alarm} obtained for all PCMs and t_{exp} , differences in the tendencies exist for low t_{exp} . For example, for Barium hydroxide octahydrate, t_{alarm} decreases with t_{exp} for $150 \text{ s} < t_{exp} < 350 \text{ s}$. It reaches a minimum for a t_{exp} of 350 s. Notice however that such minimum is still greater than the t_{alarm} obtained for $h_{amb} = 0 \text{ W/m}^2/\text{K}$, for the same t_{exp} . If a lower t_{exp} is considered, less heat is stored in the PCM FFPC and hence it cools down faster due to heat rejection towards the ambient originating less heat flowing towards the skin and causing skin damage over time. When t_{exp} is big enough so that the rejected heat towards the environment does not affect the heat flowing to the skin, a minimum t_{alarm} is reached. Similar phenomena are observed for $h_{amb} = 90 \text{ W/m}^2/\text{K}$. The absence of t_{alarm} values for a given t_{exp} simply means that a third degree burn for that PCM and t_{exp} is not reached. This happens because the rejected heat towards the environment is considerable (e.g. Barium hydroxide octahydrate, $t_{exp} < 300 \text{ s}$, Figure 4f).

Figure 4g-i show the t_{alarm} obtained for the different t_{exp} and PCMs for the low – intensity exposure. As can be seen, for $h_{amb} = 0 \text{ W/m}^2/\text{K}$, no t_{alarm} is obtained for $t_{exp} < 300 \text{ s}$, for any of the PCMs. The incoming energy from the exposure is much lower due to the lower intensity when compared to the medium- exposure intensity. For $h_{amb} = 50 \text{ W/m}^2/\text{K}$ and $90 \text{ W/m}^2/\text{K}$, the occurrence of a third degree burn for any PCM and t_{alarm} becomes almost non – existent except for a few cases. Hence, the cases of greatest benefit of adding a PCM are those where no alarm times are registered for the medium and low – intensity heat exposures (e.g. Figure 4g; $100 < t_{exp} < 300 \text{ s}$; for all PCMs). Otherwise the inclusion of a PCM layer on one hand will indeed allow for greater exposure times (Figure 3), but on the other, will also originate the occurrence of third degree burns causing the firefighter to have a limited time to remove the firefighting garment (i.e. t_{alarm}). However as shown above, this limited time is considerable, especially for medium- and low- intensity heat exposures.

3.3. Cooling time during resting phase

Another important aspect that influences PCM choice is the time the FFPC PCM takes to cool down. Different PCMs will originate different cooling times. PCMs with higher melting temperatures and lower latent heats will cool faster. In this section, it is assumed that the

firefighter takes off the PCM FFPC when the exposure ends (i.e. at t_{exp}). With this in mind, cooling times were calculated for the various PCMs for the different scenarios (Figure 5).

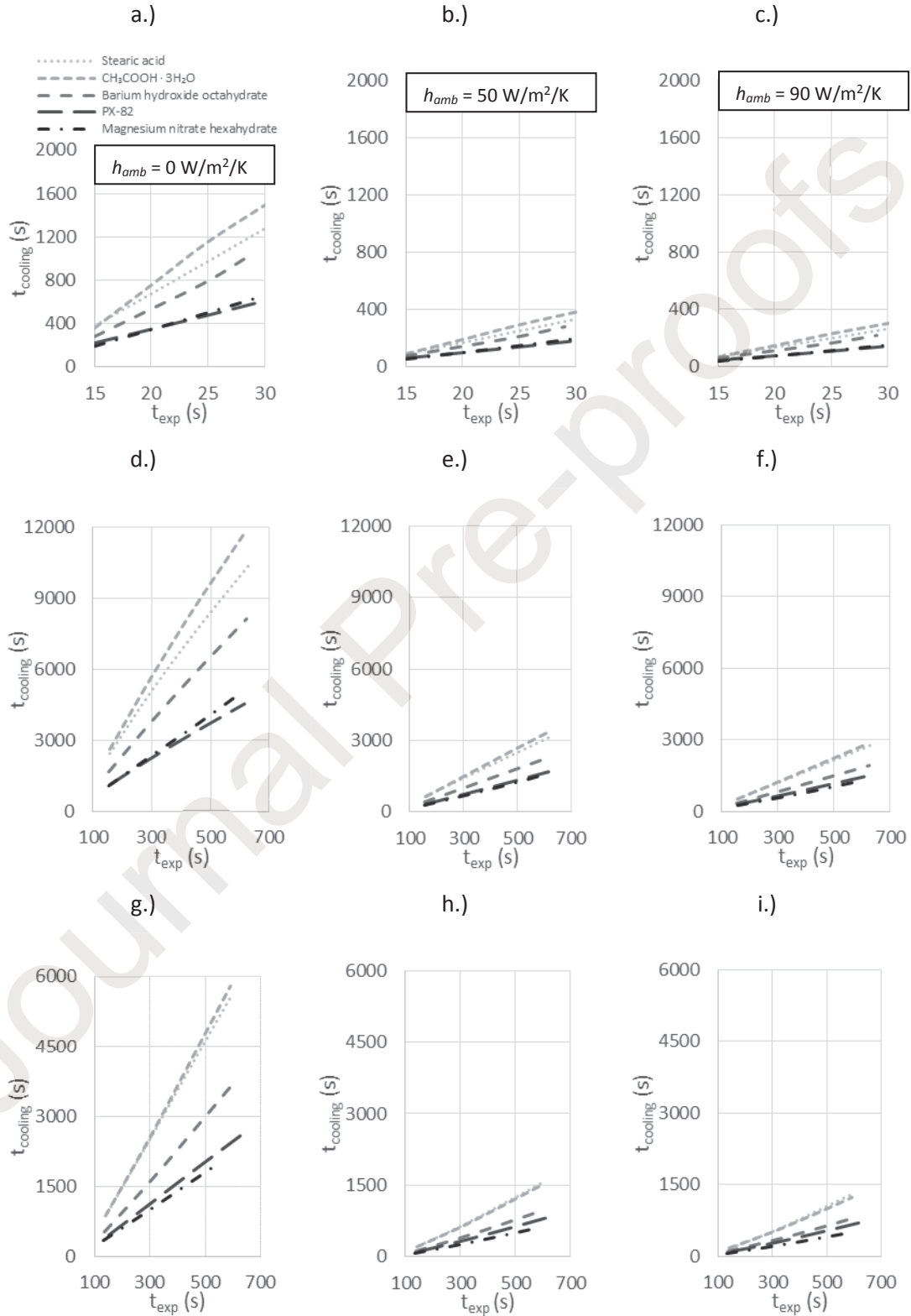


Figure 5 - Cooling times ($t_{cooling}$) obtained for different exposure times (t_{exp}) and indicated PCMs for the a-c.) high – d-f.) medium – g-i.) low intensity heat exposure, for the indicated h_{amb}

For the exposure time (t_{exp}) and wind conditions (i.e. h_{amb}) ranges considered in this study (Figure 5), an FFPC without PCM would take between 32 – 175 s, 22 – 145 s, and 17 – 122 s for the high – medium and low – intensity heat exposures. Notice that, by rough inspection these values are significantly smaller than the ones obtained when a PCM layer is considered (Figure 5).

PCM FFPC tend to take long times to cool down especially when no wind is present ($h_{amb} = 0$ W/m²/K). Even if the firefighter takes out the protective clothing in a chilled environment, the firefighter will have to wait a considerable time in order for it to cool down. For example, for the medium – intensity heat exposure scenario and no wind conditions (Figure 5d), for $t_{exp} = 300$ s, cooling times ($t_{cooling}$) vary between 2192 and 5606 s for all PCMs. The reason for such substantial cooling times is due to the presence of latent heat in the PCM. However, when the protective clothing is left in a windy environment, cooling times can drop significantly. For example, at moderate wind conditions ($h_{amb} = 50$ W/m²/K), the cooling times referred above drop to 675 – 1464 s (Figure 5e). Windy conditions may be due to natural or forced convection. For example, blower fans may be available in the fire trucks nearby for cooling down purposes. However, there comes a time when a significant increase in wind speed does not really contribute to a faster cooling time. As an example, consider the case when very high windy conditions are present (i.e. $h_{amb} = 90$ W/m²/K). The cooling times referred above only further drop to 554 s-1204 s (Figure 5f).

Hence, it becomes clear that submitting the protective clothing to high speed cooling winds may drastically decrease the cooling time, up to a certain point. Another thing to point out is the significant difference in the cooling times obtained, for the different PCMs. To note from the example above, that this difference is almost 4 – fold when $h_{amb} = 0$ W/m²/K and drops to about 2-fold when $h_{amb} = 90$ W/m²/K. This shows that PCM choice has less influence in the cooling time for higher h_{amb} (higher wind speeds), and this is understandable because the heat is rapidly dissipated towards the environment, rendering the transient heat transfer phenomena in the PCM negligible. But, even though, for increasing h_{amb} , the cooling times of the different PCMs tend to diverge for higher t_{exp} . For example, for the medium – intensity heat exposure when no air movement is present (i.e. $h_{amb} = 0$ W/m²/K), for $t_{exp} = 150$ s, PCM cooling times range from 1087 – 2643 s whilst for $t_{exp} = 600$ s, they range from 4574 – 11828 s. This tendency is simply explained by the increase in PCM mass present in the FFPC, allowing for a greater heat storage in it, and hence a bigger influence of its properties on the cooling time.

Speaking about the PCM properties, for all exposure scenarios and ambient environments considered, Magnesium nitrate hexahydrate tends to originate the lowest cooling time with a

few exceptions (Figure 5). In fact, the PCMs are ordered in the Figure by decreasing cooling times, for all exposure scenarios and exposure times. For example, for the low – intensity heat exposure scenario, when no air movement is considered (Figure 5g), $\text{CH}_3\text{COOH}\cdot 3\text{H}_2\text{O}$, Stearic acid, Barium hydroxide octahydrate and PX-82, originate cooling times, in the t_{exp} range of about 150-600 s, between 935 – 5638 s, 875-5794 s, 521-3702 s, 463-2572 s respectively, whilst Magnesium nitrate hexahydrate originates a cooling time between 329-2023 s. . This order is inversely related with the melting temperatures of the respective PCMs. That is, Magnesium nitrate hexahydrate having the highest melting temperature (T_m) of 89 °C, originates the lowest $t_{cooling}$, followed by PX -82 with a T_m of 82 °C and Barium hydroxide octahydrate, Stearic acid, and $\text{CH}_3\text{COOH}\cdot 3\text{H}_2\text{O}$ each having a T_m of 78 °C, 58 °C and 54 °C respectively. Hence, the melting temperature strongly affects the $t_{cooling}$. This was expected, since higher melting temperatures allow for a greater temperature gradient between the PCM and environment. The melting temperature becomes specially significant when the latent energy in the PCM FPC is substantial and also for high values of PCM masses (and consequently high t_{exp}). This further explains the huge discrepancy of obtained cooling times for high t_{exp} , for the different PCMs.

Thus, for most exposure intensity and durations, Magnesium nitrate hexahydrate would be the PCM which originates the lowest cooling time, and hence would satisfy the best criterion. Other PCMs can be chosen depending on the time the firefighter has to recover during the resting period.

4. Conclusions

Numerical simulations were conducted to study the effect of PCM choice and optimal mass on the thermal behavior of a PCM firefighting suit, considering a dynamic scenario of fire exposure, post-fire exposure and resting phase. In a first section, a list of PCMs with potential application was selected. The choice was based on their melting capabilities during the fire exposure. Next, optimal PCM masses were calculated for different exposure times and heat intensities. It was shown, that there is a relationship between the intended exposure time and required PCM mass. To allow for a more comprehensive design of the PCM FFPC the post-fire scenario was also analyzed. Alarm times were calculated for the various PCMs and exposure scenarios, which gave an idea of the escape time the firefighter has. Lastly, PCM FFPC cooling times were analyzed for fires that require more than one attack. The following specific conclusions were obtained:

- For a high – intensity and short duration exposure, the inclusion of a PCM might not be justified as most heat is accumulated in the sensible form. The addition of a material with a high specific heat could provide enough protection without the need for it to change phase.
- For a medium and low-intensity long duration exposures, $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ is the PCM with lowest mass requirements due to its high latent heat and low melting temperature. For exposures in the range of $\sim 150 - 600$ s, $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ masses of ~ 1 kg – 3.5 kg and $\sim 0.5 - 2$ kg should be sufficient to provide full protection during the exposure, for medium- and low– intensity exposures respectively. If a different PCM is considered, the required mass should in principle not be very far off the ranges of PCM masses shown in this work, as long as full melting is verified during the exposure and before a second – degree burn is reached. Hence, they can for example be used as initial mass estimates for a potential PCM that has not been considered in this work.
- Regarding the post – fire exposure, for low exposure times, $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ tends to originate the highest alarm times. Whilst for high exposure times, Magnesium nitrate hexahydrate tends to originate the highest. This is true for almost all exposure intensities and ambient convective coefficients (few exceptions occur for the high – intensity exposure).
- For medium and low-intensity exposures, a change in wind conditions (i.e. h_{amb}) can have a major influence in the alarm time obtained, especially for PCMs with low melting temperature and high latent heat such as $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ and Barium hydroxide octahydrate.
- The cooling of a PCM FFPC is strongly correlated to the melting temperature of the PCM in consideration. A PCM such as Magnesium nitrate hexahydrate originates low cooling times whilst $\text{CH}_3\text{COOH} \cdot 3\text{H}_2\text{O}$ is exactly the opposite. Big differences between the cooling times are obtained for low h_{amb} . For high h_{amb} , such differences become negligible. The thermal performance of PCM FFPCs is critically dependent on the PCM choice and ambient conditions.

The data shown above can help a PCM FFPC designer in the initial stages of research and development. Tangible guidelines and estimates of key parameters are provided associated to the PCM choice, and the PCM FFPC performance.

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HIGHLIGHTS:

- Optimal PCM mass choice criterion in function of exposure scenario
- Severe burns promoted after fire exposure by PCM inclusion
- PCM FPC cooling times significantly dependent on PCM choice

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: