

Latent heat thermal energy storage units in HVAC systems for energy management

Pere Moreno Argilés

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PhD Thesis

Latent heat thermal energy storage units in HVAC systems for energy management

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Lleida, 28 de Abril de 2014

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Resum

La demanda d'energia no és constant durant el dia, aquesta fluctua de manera important entre les anomenades hores pic i hores vall. Aquesta fluctuació provoca un desajust entre la generació i la demanda d'energia que s'intenta pal·liar amb incentius al consumidor com, per exemple, abaratint el preu de l'electricitat durant les hores valls. L'emmagatzematge d'energia tèrmica (TES, per les seves sigles en anglès) es presenta com una alternativa real per mitigar aquest desajust energètic, ajudant en la gestió de la demanda a nivell global. Aquests sistemes permeten aplanar la corba de demanda energètica utilitzant, per exemple, els equips de climatització durant hores vall per emmagatzemar energia tèrmica i subministrar-la durant les hores pic sense la necessitat d'utilitzar els equips de climatització. Això provoca una millor gestió de la producció d'energia i la possibilitat d'augmentar la utilització d'energies renovables, amb la consegüent reducció d'emissions de gasos d'efecte hivernacle a l'atmosfera.

La utilització de tancs d'aigua per l'emmagatzematge de energia per mitjà de calor sensible és un sistema àmpliament utilitzat en sistemes de calefacció, instal·lacions solar, etc. D'altra banda, la utilització de materials de canvi de fase (PCM) en sistemes d'emmagatzematge tèrmic ha tingut una menor implementació degut al fet de tractar-se d'una tecnologia que encara necessita ser més desenvolupada, i també en gran part a la inversió econòmica que requereix.

L'objectiu d'aquesta tesi doctoral és estudiar l'aplicació d'un sistema d'emmagatzematge d'energia tèrmica, utilitzant materials de canvi de fase, amb una bomba de calor convencional. El treball realitzat és part d'un projecte europeu del 7^è Programa Marc (FP7 – 262285 - HESTOR) el qual tenia com a objectiu la construcció i posterior experimentació d'un prototip basat en aquest tipus de sistema, aplicat tant per a calefacció com per aire condicionat. A més, en la tesi també s'inclou una descripció de sistemes similar estudiats anteriorment per altres autors, es presenta un model matemàtic que descriu la descàrrega d'un tanc amb PCM i es presenta un estudi de corrosió de diferents metalls quan estan en contacte amb PCM.



Resumen

La demanda de energía no es constante durante el día, fluctúa de una manera importante entre las llamadas horas pico y horas valle. Esta fluctuación provoca un desajuste entre la generación y la demanda energética que se intenta paliar con incentivos al consumidor como, por ejemplo, abaratando el precio de la electricidad durante las horas valle. El almacenamiento de energía térmica (TES, por sus siglas en inglés) se presenta como una alternativa real para paliar este desajuste energético, ayudando en la gestión de la demanda a nivel global. Estos sistemas permiten aplanar la curva de demanda energética utilizando, por ejemplo, los equipos de climatización durante horas valle para almacenar energía térmica y subministrarla durante las horas pico sin necesidad de utilizar los equipos de climatización. Esto provoca una mejor gestión de la producción de energía y la posibilidad de aumentar la utilización de energías renovables, con su consiguiente reducción de las emisiones de gases de efecto invernadero a la atmosfera.

La utilización de depósitos de agua para la acumulación de energía por medio de calor sensible es un sistema ampliamente usado en sistemas de calefacción, instalaciones solares, etc. Sin embargo, el uso de materiales de cambio de fase (PCM) en sistemas de almacenamiento térmico ha tenido una menor implementación debido al hecho de tratarse de una tecnología que necesita un mayor desarrollo, y también en gran parte, a la inversión económica que requiere.

El objetivo de esta tesis doctoral es estudiar la aplicación de un sistema de almacenamiento de energía térmica, usando materiales de cambio de fase, en un equipo de bomba de calor convencional. El trabajo realizado forma parte de un proyecto europeo del 7º Programa Marco (FP7 – 262285 – HESTOR) el cual tenía como objetivo la construcción y posterior experimentación de un prototipo basado en este tipo de sistema, aplicado tanto para calefacción como para aire acondicionado. Además, en la tesis también se incluye una descripción de sistemas similares estudiados anteriormente por otros autores, se presenta un modelo matemático que describe la descarga de un tanque de PCM y se presenta un estudio de corrosión de diferentes metales cuando están en contacto con PCM.



Summary

Energy demand is not constant through the day since it fluctuates between the peak and off-peak periods. This fluctuation causes a mismatch between energy generation and demand which can be mitigated by consumer's incentives, such as lowering the price of electricity during off-peak time. Thermal energy storage (TES) is presented as a real alternative to mitigate the energy mismatch and having influence on the demand management at a global level. These systems are able to flatten the customer's load profile, using for instance the HVAC systems during off-peak period to accumulate thermal energy and supply it over peak time without using the HVAC device. As a result, better energy production management can be achieved, which implies that the utilisation of renewable energies is increased, with the consequent GHG emissions reduction.

The use of water storage tank to accumulate thermal energy by means of sensible heat is a widely used system in heating systems, solar installations, etc. However, the use of phase change materials (PCM) in thermal energy storage has not been implemented so much, partly, because this technology needs more development and also due to the high economic investment required.

The aim of this PhD thesis is to study the application of a TES system, based on phase change materials, working together with a standard heat pump. The work done is part of a 7th Framework Programme project (Grant Agreement Number FP7 – 262285 - HESTOR) which objective was the construction and the experimental evaluation of a prototype device based on this technology able to provide both space heating and cooling. Moreover, the thesis also includes a state-of-the-art review on similar systems found in the literature, the development of a mathematical model which describes the discharge process of a PCM tank and the corrosion study of metals when they are in contact with different PCM.

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NOMENCLATURE

Nomenclature

COP Coefficient of performance

DSM Demand side management

HVAC Heating ventilation and air Conditioning

HTF Heat Transfer Fluid

LHTES Latent heat thermal energy storage

PCM Phase change materials

SPF Seasonal performance factor

TES Thermal energy storage

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Introduction

1 Introduction

1.1 Space heating and cooling equipment consumption

The building sector is associated with around 39% of the final energy consumption in Europe. However, the energy savings potential of this sector is substantial and can bring significant benefits at individual, sectorial, national and international levels [1].

Nowadays, space heating and cooling are estimated to account more than a third of global energy consumption in residential and commercial sectors (Figure 1). These enduses represent significant opportunities to reduce energy consumption, improve energy security and reduce CO_2 emissions due to the fact that space heating provision is dominated by fossil fuels while cooling demand is growing rapidly in countries with high carbon-intensive electricity systems [2].

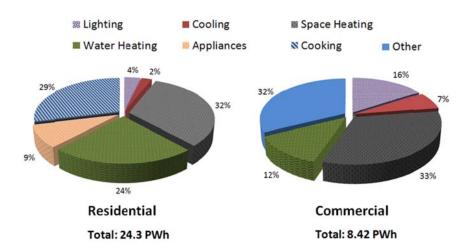


Figure 1. World building final energy consumption by end-use in 2010 [3].

In that regard, the European Union faces serious energy challenges. It has committed itself to the '20-20-20' initiative: reducing greenhouse gas emissions by 20 %, increasing the share of renewables in energy consumption to 20 % (compared to 11.6 % in 2009), and improving energy efficiency by 20 %, all by 2020. To put this into effect, the EU adopted a comprehensive and clearly targeted energy and climate package [2].

Heat pumps are considered a technology that can contribute to achieve these objectives, since they are able to supply efficiently heat and cold from renewable sources such as



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air, water or soil. Furthermore, according to the EU Directive on Renewable Energy (Directive 2009/28/EC [4]) they are regarded as renewable energy when the Seasonal Performance Factor (SPF) is greater than 2.5.

1.2 Heat pumps

Heat pumps are widely used to supply heat and cold for residential, commercial and industrial uses, such as space heating and cooling, water heating, freezing and refrigerating. Since heat pumps consume less primary energy than conventional heating systems, they are an important technology for reducing CO₂ emissions. However, the overall environmental impact of electric heat pumps depends very much on how the electricity is produced.

The coefficient of performance (COP) is perhaps the most important parameter from the point of view of manufacturers and consumers. It is used to define the efficiency of the heat pump and indicates the ratio of heating or cooling provided to electrical energy consumed. However, the technical performance of a heat pump depends on the heat source and the operating conditions. Ideally, heat source for heat pumps in buildings should have high and stable temperature during the heating season, appropriate thermophysical properties, and should not be corrosive or polluted. However, the use of heat pumps is determined in most cases by the availability of the heat source.

As a primary heat/cold source, heat pumps can use outdoor air, water or soil. The efficiency of heat pumps based on water sources is generally higher because surface water is usually colder than air when space cooling is needed (e.g. summertime) and warmer than air when space heating is needed (e.g. wintertime).

The utilisation of heating and cooling equipment usually matches with the on-peak demand period when, as a rule, the electricity tariff is more expensive. The demand fluctuation causes a mismatch between generation and demand of energy at global level which is tried to be mitigated through consumer's incentive. However, technologies





such as thermal energy storage (TES) are able to modify the demand curve and get better energy management.

1.3 Thermal energy storage (TES)

Increasing societal energy demands, shortage of fossil fuels, and concerns over environmental impact are providing impetus to the development of renewable energy sources such as solar, biomass and wind energies. Because of their intermittent natures, effective utilisation of these and other energy sources is in part dependent on the availability of efficient and effective energy storage systems [5].

Today TES is considered an advanced energy technology. The use of TES systems has been attracting increasing interest in several thermal applications, e.g. active and passive solar heating, water heating, cooling and air conditioning. TES is often the most economical storage technology and appears to be the only solution for correcting the mismatch between the supply and demand of energy. It can contribute significantly to meet society's needs for more efficient, environmentally benign energy use [6].

The main objective of TES systems is to alter energy-use patterns in order to obtain economic savings. According to Dincer [6] this objective can be achieved in several ways:

- The consumption of purchased energy can be reduced by storing waste or surplus thermal energy available at certain times. For example, solar energy can be stored during the day for heating at night.
- The demand of purchased energy can be reduced by storing electrically
 produced thermal energy during off-peak periods to meet the thermal loads that
 occur during high-demand periods. For instance, an electric chiller can be used
 to charge chilled water TES at night for reducing the electrical demand peaks
 usually experienced during the day.
- The acquisition of additional equipment for heating, cooling or air-conditioning applications can be deferred and the equipment sizing in new facilities can be reduced. The equipment can be operated when thermal loads are low to charge





the TES system. Energy can be withdrawn from storage to help meet the maximum thermal loads that exceed equipment capacity.

Furthermore, not only TES systems provide energy savings but also the environmental impact can be reduced. This can be achieved by reducing the energy consumption, the conservation of fossil fuels through efficiency increases and/or the fuel substitution and the reduction in GHG emissions.

Some strategies are available for charging and discharging storage to meet heating and cooling demand during peak hours. Figure 2 presents the full storage (a) and the partial storage strategies for cold storage. In the full storage strategy the entire daily cooling demand is shifted from on-peak to off-peak period. Ideally this strategy provides the highest operating cost savings since the cooling equipment run during off-peak hours (usually at night) and all the cooling loads are met from the TES system during the demand time. The full storage strategy is most attractive when on-peak demand charges are high or when the on-peak period is relatively short. In these scenarios electricity costs are reduced since the cooling/heating equipment is off during on-peak period when the electricity is more costly. However, the main disadvantage of this strategy is the TES system cost comparing to partial storage strategies since bigger tanks are needed to store more thermal energy. In partial storage strategy (b) the cooling equipment is sized to run at its full capacity all the time and part of the peak-period cooling load is met by the TES system. This strategy is particularly attractive for applications where the peak cooling load is much higher than the average load. One of the main advantages of this strategy is that smaller cooling equipment is needed since it does not need to meet the peak demand. The third strategy shown in Figure 2 (c) is a variation of the partial storage and is a demand limiting strategy. Here, the cooling equipment runs at reduced capacity during peak period, and is often controlled to limit the thermal demand of the facility. Demand savings and equipment costs are higher than in partial storage-load levelling but lower than the full storage system.

Partial storage is often the most economic option, and therefore, represents the majority of thermal storage installations. This TES strategy can present lower initial costs than full storage, particularly if the design incorporates smaller equipment.



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Therefore, the type of TES strategy to implement should be evaluated according to load requirements, electricity cost saving achieved by the storage and initial cost of the TES system.

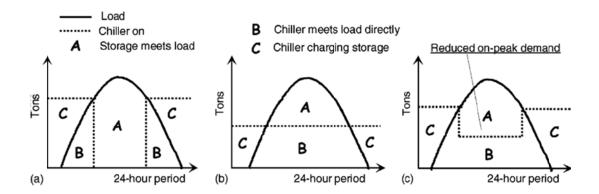


Figure 2. Operating TES strategies for cold storage. (a) full-storage, (b) partial-storage load-levelling and (c) partial-storage demand-limiting [5]

For the design of TES systems high energy storage density and high power capacity for both charging and discharging processes are desired. There are three main methods of TES: sensible, latent and thermochemical energy storage.

1.3.1 Sensible heat storage

Sensible heat storage is the most common way to store thermal energy. Here, the energy is accumulated by raising the temperature of a solid or liquid, as shown in Figure 3. Sensible heat storage systems use the heat capacity and the change of the material temperature during the processes of charging and discharging.

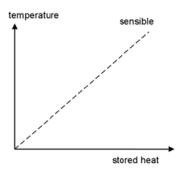


Figure 3. Heat storage as sensible heat leads to a temperature increase when thermal energy is stored.



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The sensible energy stored in any material can be calculated using the following equation:

$$Q_{sensible} = \int_{T_1}^{T_2} m \cdot C_p \cdot dT$$
 Equation 1

where $Q_{sensible}$ is the sensible energy stored, m is the mass of the storage material, C_p is the specific heat of the material, and dT is the temperature change. The temperature change ($\Delta T = T_2 - T_1$) depends on the application and is limited by the heat source and the demand requirements.

1.3.2 Latent energy storage

Latent heat thermal energy storage is particularly attractive since it provides high energy storage density. This way of storage is based on the phase change of a material, i.e. solid/liquid or liquid/gas. However, liquid/gas transformations are not practical due to the large volume changes or high pressures required to store the materials in the gas phase. Heat storage as latent heat for the case of solid-liquid phase change is shown in Figure 4 in comparison to sensible storage. Materials used as latent heat storage are commonly named phase change materials (PCM).

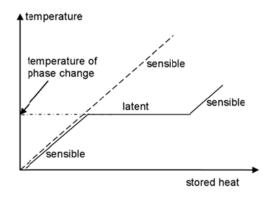


Figure 4. Heat storage as latent heat for the case of solid-liquid phase change.

Taking a temperature interval $\Delta T = T_1 - T_2$ the stored energy in a PCM can be calculated as follows:



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$$Q_{latent} = \int_{T_1}^{T_{pcm}} m \cdot C_{p,s} \cdot dT + m \cdot \Delta H_{pcm} + \int_{T_{pcm}}^{T_2} m \cdot C_{p,l} \cdot dT$$
 Equation 2

where Q_{latent} is the sensible and latent energy stored, m is the mass of the storage material, $C_{p,s}$ and $C_{p,l}$ are the specific heat of the material in solid and liquid state respectively, dT is the temperature change, and ΔH_{pcm} is the heat of fusion at the phase change temperature T_{PCM} .

Compared to conventional sensible heat energy storage, latent storage needs a smaller weight and volume of material for a given amount of energy. Besides, latent heat storage is able to store energy at a nearly constant temperature which corresponds to the phase change temperature of the material. On the other hand, the major disadvantage of using phase change materials for energy storage is their low thermal conductivity, leading to low charging and discharging rates (especially for organic based materials) [7]. Nevertheless, several studies have been focused on the enhancement of the PCM thermal conductivity by including fins in the tubes whether the PCM is used in a heat exchanger system, or by the impregnation of PCM into a metal or graphite matrix [8].

Several authors have reviewed PCM candidates to be used for thermal energy storage [9]-[11]. According to the specific application, the PCM should satisfy some physical requirements such as suitable phase change temperature, large phase change enthalpy, cycling stability, little subcooling and good thermal conductivity. Abhat [12] presented a classification of the substances for thermal energy storage (Figure 5).

Paraffin present low phase change enthalpy and conductivity and higher fire risk hazard than salt hydrates; however, these substances show good thermal and chemical stability and low corrosion rate when they work in contact with metals. On the other hand, salt hydrates have greater phase change enthalpy and are usually cheaper but present some disadvantages such as higher degree of subcooling, corrosion and phase separation.



Introduction

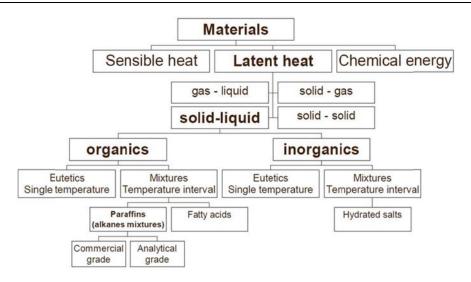


Figure 5. Classification of PCM for thermal energy storage [12].

1.3.3 Thermochemical energy storage

Thermochemical systems rely on the energy absorbed and released in breaking and reforming molecular bonds in a completely reversible chemical reaction [10]. Reactions are represented by:

$$A + HEAT \iff B + C$$

In storage system based in thermochemical reactions heat is required to get chemicals B and C from A. In this process heat is absorbed (charging process) and chemical B and C have to be stored in separate vessels at ambient temperature. On the other hand, discharging process takes place with the reaction between chemicals B and C, releasing the energy previously stored.

1.4 Heat pumps with TES

The utilization of heat pumps with TES systems are presented as a promising technology to shift electrical loads from high-peak to off-peak periods, thus serving as a powerful tool in demand-side management (DSM) [13]. The benefits of this technology are focused on the energy cost savings by using thermal energy stored during low-cost electricity tariff. As a consequence, energy management may be enhanced through



Introduction

electricity network balance and environmental benefits may be achieved with the incorporation of renewable energies in the market.

In this PhD, the research is focused on the use of TES using phase change materials (PCM) in domestic heat pumps for short term storage. The study involves theoretical and experimental analysis of a TES tank in order to evaluate its thermal behaviour. A state-of-the-art review about the use of PCM in domestic heat pump and air-conditioning systems is presented first in order to place the topic.



Objectives

2 Objectives

The main objective of this thesis is to evaluate the thermal behaviour of latent heat TES (LHTES) tanks when they are coupled to a heat pump. This study was carried out following the specific objectives listed next:

- To describe the state-of-the-art review of using LHTES systems in domestic heat pumps. The objective here was to provide the required background and describe the potential applications of these systems according to the studies found in the literature.
- To experimentally test a heat pump coupled to PCM storage system under summer conditions. The TES system was used to shift the cooling load of a testing house-like cubicle and the objective was to analyse the thermal behaviour of the storage system and evaluated the time that the system was able to maintain the indoor temperature of the cubicle under a comfort temperature range.
- To develop a mathematical model of a PCM storage tank used for cooling applications. Some other objectives were achieved here:
 - o This model provided the outlet heat transfer fluid (HTF) temperature evolution and heat transfer rate during discharging process.
 - o The evaluation of different model parameters was discussed regarding the computational time and accuracy of the results.
 - The uncertainty of the input variables was analysed aiming to know how it affected to the results of the simulations.
- Corrosion tests were carried out in order to evaluate the compatibility of different metals and metal alloys in contact with PCM. The compatibility between PCM and the encapsulation material is a key factor to ensure long term stability of the system. The PCM tested were selected taking into account their potential use for heating and cooling applications.

CHAPTER III



PhD thesis structure

3 PhD thesis structure

The PhD thesis is based on four SCI papers, two of them have already been published in SCI journals and the other two have been submitted at the time of the submission of this thesis. Figure 6;Error! No se encuentra el origen de la referencia. shows the flow of the chapters and the journal papers that came from the research.

The first paper, presented in Chapter IV, is used to place the topic of this thesis. A state-of-the-art review about the use of PCM in domestic heat pump and air-conditioning systems for short term storage is presented. Here, studies from the literature are described according to how the PCM storage is used in heat pump systems for space heating and cooling applications. Theoretical and experimental studies are included in this review where different PCM, such as paraffin, salt hydrates and ice, are used.

Chapter V presents the experimental results of a TES-heat pump system which aimed to shift the cooling demand of a small-house used as testing room. This study was carried out as part of an FP7 European project (n°262285). Here, two identical TES tanks were connected to the heat pump, one to the condenser and the other to the evaporator, in order to store heat and cold. The configuration of the system enables the system to supply energy for heating and cooling demand; however, this paper is focused on space cooling. The thermal behaviour analysis of the tanks during charging (cold storage) and discharging (cold supply) processes and the space cooling evaluation is presented in this study. Moreover, a comparison between the tank using either PCM or water as energy storage medium is carried out.

The third paper of the thesis presents a theoretical model of the cold storage tank used in the experimental set-up. The mathematical model is based on the heat capacity method and predicts the discharging process in terms of cooling capacity, cold supplied and HTF and PCM temperature evolution. This paper also contains an uncertainty analysis of the input parameters in order to evaluate which one have more influence on the results.

CHAPTER III



PhD thesis structure

The validation of the mathematical model is essential to demonstrate its ability on predicting the real thermal behaviour of the tank. The first validation results are included in the second part of Chapter VI since they were not part of the paper; however, they are intended to be presented in another paper in the short term.

The last paper, described in Chapter VII, presents a corrosion study of metals and metal alloys in contact with different salt hydrate PCM. This study was carried out simultaneously with the other work presented in the thesis. The compatibility between PCM and metals is an important issue to ensure long term stability of the TES system, as well as to avoid the potential damage to the close environment in case of encapsulation leakage. Although the TES tank evaluated in this thesis, in both theoretical and experimental part, uses PCM encapsulated in plastic packages, the utilization of bulk PCM tanks, working as a shell-and-tubes heat exchanger, was taken into account for further investigation using the experimental set-up. Moreover, new corrosion data is needed to ensure the potential utilisation of substances found in the literature as PCM.

The corrosion test analysed the suitability of using four different metals and metal alloys when working together with salt hydrate PCM. The PCM tested are divided in two main groups: PCM for heating application and PCM for cooling application, depending on their melting temperature.

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CHAPTER III

PhD thesis structure

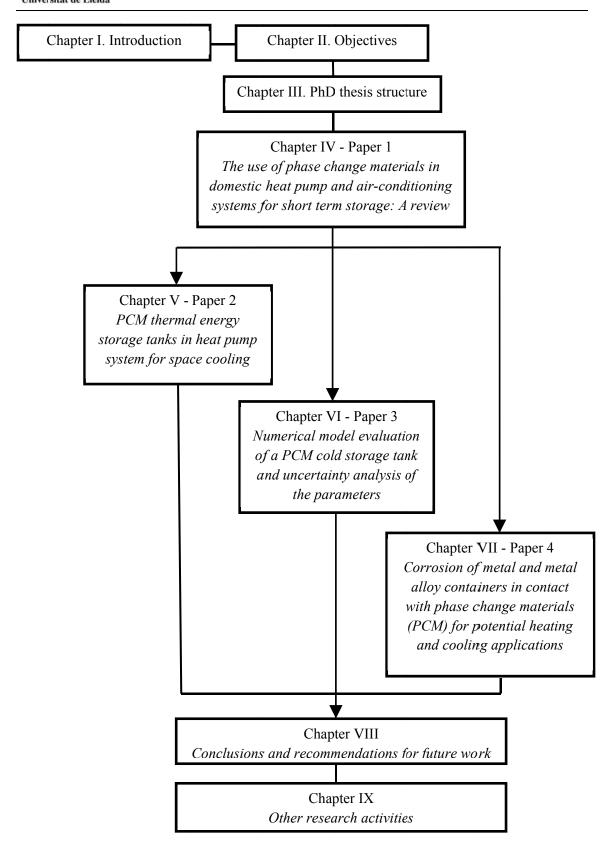


Figure 6. PhD thesis structure



The use of phase change materials in domestic heat pump and airconditioning systems for short term storage: A review

4 The use of phase change materials in domestic heat pump and airconditioning systems for short term storage: A review

4.1 Introduction

A state-of-the-art review on PCM thermal energy storage used in domestic heat pump and air-conditioning devices is presented in Chapter IV. This specific application of TES has been studied by few authors so further study about their performance is needed. Thus, experimental and simulated studies from the literature where the thermal behaviour of the systems is evaluated have been gathered in this review,

Papers found in the literature suggest different storage configuration where the PCM are used in bulk or macro-encapsulated. In the first option the storage system works like a shell and tube heat exchanger where one of the fluids is replaced by PCM. In the latter configuration, the PCM is encapsulated in spherical or flat slabs packages and they are placed inside the TES tanks. The type of PCM used depends on the application since a wide range of PCM with different phase change temperature can be used.

4.2 Contributions to the state-of-the-art

The review presented in this chapter is divided in two main groups: systems for space heating and systems for space cooling application. They are summarised in Table 1.

The first group includes the installation of the storage system in the compression cycle of the heat pump in order to store thermal energy from the exhaust heat produced by the condenser. Also the utilisation of PCM storage systems for defrosting the outdoor coil of the heat pump is included in this first group. Although there are some defrosting solutions, such as reverse-cycle operation, some authors studied the inclusion of storage buffers in order to reduce the defrosting time and energy consumption during this process. Finally, the named hybrid systems are also reviewed here, which include heat pumps coupled to PCM radiant floor and solar collectors working together with heat pump and storage systems.



The use of phase change materials in domestic heat pump and airconditioning systems for short term storage: A review

The space cooling group is focused on the use of PCM storage systems in air-conditioning. Similarly to the previous group the TES system is also evaluated when it is incorporated in the compression cycle. The cold storage rates during charging and discharging processes and the COP of the system are analysed. Also the use of the storage systems to store the exhausted heat from the condenser is presented here. The last subgroup corresponds to hybrid systems for space cooling, which includes air-conditioning coupled to PCM radiant floors and storage systems located into air-conditioning ducts.

The state-of-the-art review is described in the following publication:

 P. Moreno, C. Solé, A. Castell, L. F. Cabeza. The use of phase change materials in domestic heat pump and air-conditioning systems for short term storage: A review. Renewable and Sustainable Energy Reviews 39 (2014) 1-13.

The main conclusions of the state-of-the-art can be summarized in the following points:

- > TES systems connected to heat pump for space heating:
 - As expected, the use of PCM result in tanks size reductions (up to 30 %),
 and hence a reduction in cost and space.
 - Some authors present the TES system as a defrosting solution when ice is accumulated on the evaporator. These studies analyse the reduction on defrosting time and energy consumption during this process. The time can be reduced by 60 % using the storage system.
 - o TES systems working together with a heat pump and other auxiliary systems such as radiant floor or solar collectors are also described in this review. They are mainly focused on the evaluation of the COP for the whole system.
- > TES systems coupled to air-conditioning devices for space cooling:
 - Some studies evaluate the heat transfer rate during charging and discharging processes of the TES systems when they are incorporated to air-conditioning devices.



- o The rejected heat from air-conditioning devices can be also stored by means of PCM storage systems. This solution was investigated by different authors using shell and tube heat exchanger tanks filled with paraffin waxes with a melting temperature of 45 °C.
- O Also PCM incorporated in a radiant floor system and in the air ducts is presented. The authors studied the amount of daily cooling demand stored by the PCM system and the time that the room temperature remained constant by using the energy supplied by the TES system.

Table 1. Studies presented in the state-of-the art review on the use of PCM in domestic heat pump and air-conditioning systems for short term storage.

Applicati	on	Reference	
Space			Hamada and Fukai [14]
	TES within th	e heat pump cycle for load shifting	Agyenim et al. [15]
			Leonhardt and Müller [16]
			Daikin [17]
	PCM energy	storage as defrosting solution	Jiankai et al. [18]
heating			Minglu et al. [19]
		Heat pump-radiant floor with TES	Mazo et al. [20]
	Hybrid systems		Cabrol et al. [21]
		Solar-heat pump with TES	Kaygusuz [22]
			Niu et al. [23]
		Solar- heat pump with ground-source and TES	Han et al. [24]
			Fang et al. [25]
	TES within th	e air-conditioning cycle for load shifting	Fang et al. [26]
Space cooling			Mettawe et al. [27]
	PCM energy storage as heat recovery		Zhang et al. [28]
			Gu et al. [29]
	Hybrid systems	Air-conditioning in radiant floor	Nagano et al. [30]
	Systems	TES in air-conditioning ducts	Yamaha et al. [31]



The use of phase change materials in domestic heat pump and airconditioning systems for short term storage: A review

4.3 Journal paper

Renewable and Sustainable Energy Reviews 39 (2014) 1-13



Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews





The use of phase change materials in domestic heat pump and air-conditioning systems for short term storage: A review



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¥ ₩ ¥ Universitat de Lleida

CHAPTER IV

The use of phase change materials in domestic heat pump and airconditioning systems for short term storage: A review

The paper "The use of phase change materials in domestic heat pump and air-conditioning systems for short term storage" (doi:10.1016/j.rser.2014.07.062) is included from page 18 to page 31.

























5 Experimental analysis of a PCM thermal energy storage tank coupled to a heat pump for space cooling

p. 31-43

Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

6 Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

6.1 Introduction

The modelling of PCM storage units for heating and cooling applications has been widely studied. The PCM can be used in bulk, so the systems works as a shell-and-tubes heat exchanger [14],[34], or encapsulated in spherical capsules [35], or flat slabs [36]. Most of the authors focused their studies in obtaining a model which predicts the thermal behaviour of the units in charging and discharging processes.

This chapter presents a mathematical model of the cold TES tank used in the experimental study presented in the previous chapter. Both the packages and the PCM are commercially available products from PCM Products [33]. Since this system was aimed to work together with cooling equipment the PCM selected had a phase change temperature of 10 °C [5].

In this study not only the TES tank model was evaluated but also the computing time according to the accuracy of the results was also analysed. Moreover, an evaluation of the input parameters uncertainties was also included. In that regard, few studies have been found in the literature about the study of uncertainties. One was found for PCM-air systems [37] and it showed the great importance of such information. Therefore, the evaluation of the effect of uncertainties in PCM-liquid systems was required.

6.2 Contribution to the state-of-the-art

The mathematical model described in this chapter is a two-dimensional model based on the heat capacity method solved by implicit finite difference. The model aims to predict the thermal behaviour of a 103-litres PCM tank during the discharging process, i.e. predicting the outlet HTF temperature and the heat transfer rate.

The nodes distribution of the numerical model is shown in Figure 10. As seen in the schematics, the real flat slabs configuration inside the tanks was simplified since symmetric thermal behaviour with respect to the horizontal plane that crosses their



Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

centre was considered. Two-dimensional heat transfer inside the PCM was considered, so there is a gradient inside the PCM in both parallel and perpendicular directions. On the other hand, one-dimensional model is used for the HTF since the gap between two slabs is small compared to the PCM thickness.

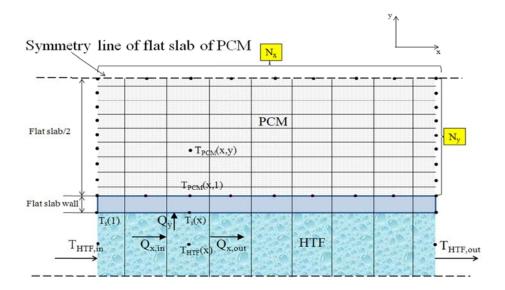


Figure 10. Nodes distribution of the numerical model.

The first part of the study deals with the evaluation of the simulations accuracy, regarding the reference case, and the computational time needed to solve the equations. The number of nodes on each axis (N_x and N_y), the time step, and a simplification on the calculation of c_{PCM} were considered. The latter consisted in using $c_{PCM;old}$, which corresponds to the specific heat calculated in the previous iteration of the implicit finite difference method, instead of using c_{PCM} which is evaluated at the present iteration as a function of the (unknown yet) PCM node temperature. The simulations were run for each combination of parameters in order to find out the best configuration in terms of computational time and accuracy.

The second part of this study analyses the effect that uncertainties in input parameters have in the results. The evaluation was carried out taking different inlet parameters: PCM properties, HTF properties and heat transfer parameters (convection coefficient and thermal conductivity of the plastic encapsulation). A reference value and its uncertainty range (by means of a set percentage of error) were given for each parameter. Table 2 presents the input parameters considered and its uncertainties.



Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

Table 2. Reference parameter values and uncertainties

Variable	ρ_{PCM}	k_{PCM}	\mathcal{C}_{PCM}	$T_{ m melt}$	$ ho_{ m HTF}$	\mathcal{C}_{HTF}	<i>V</i>	$T_{ m HTF;in}$	$h_{ m HTF}$	$k_{ m wall}$
Units	kg/m ³	$W/(m \cdot K)$	J/(kg·K)	°C	kg/m ³	$J/(kg \cdot K)$	m ³ /h	°С	$W/(m^2 \cdot K)$	$W/(m \cdot K)$
Reference	1470	0.43	DSC	11.7	Water	Water at	0.6	Eq.(9)	Given	0.5
value	14/0	0.43	curve	11.7	at $T_{\rm HTF}$	$T_{ m HTF}$	0.0	Eq.())	by EES	0.5
Error	±5%	±5%	±5%	±1	±5%	±5%	±5%	±1	±30%	±5%

Results were compared against the case where reference values of the parameters were used. Simulations were performed varying only parameter and maintaining the rest in the reference value. Therefore, two cases were generated for each parameter, corresponding to the two extreme values of the uncertainty interval. The average heat transfer rate during discharging process was used as output value to evaluate the effect of the uncertainties introduced in the input parameters.

The main contribution to the state-of-the-art can be summarized in the following points:

- ➤ The number of nodes and different time steps were evaluate to get the best configuration in terms of computing time and accuracy. The results showed that using the highest time step and the lowest number of nodes one can obtain important reduction of computing time with reasonable accuracy regarding the reference case.
- The use of the PCM specific heat calculated in the previous iteration ($c_{PCM;old}$), instead of using the specific heat from the present iteration (c_{PCM}), resulted to be a good solution since it provided important computational time reduction, in spite of a slight increase when using the lowest time step.
- ➤ Using constant heat transfer fluid (HTF) properties can also lead to shorten the computing time, though the error produced is more important.
- ➤ The input variable uncertainty analysis indicated that the inlet HTF temperature and the PCM properties are the parameters which influence the most in the results.

This research is described in the following publication:



Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

• G. Zsembinszki, P. Moreno, C. Solé, A. Castell, L. F. Cabeza. Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters. Applied Thermal Engineering 67 (2014) 16-23.

6.3 Validation of the mathematical model

The experimental validation of the mathematical model described previously is presented in this chapter. Numerical results are compared to experimental ones in order to demonstrate the validity of the proposed model to reflect the real behavior of the system. This evaluation is part of a further study which also will include the uncertainty propagation analysis of the input parameters in both experimental and simulated results.

The theoretical model used for the simulations was configured according to the combination of parameters suggested by the results of the paper, i.e. 30 seconds as time step, $N_x = 10$, $N_y = 10$, the use of $c_{PCM;old}$ as approximation of the PCM specific heat, the use of HTF constant properties (density, specific heat, and convection heat transfer coefficient), and PCM constant properties (density and thermal conductivity, given by the manufacturer's specification). The inlet HTF temperature from the experimental data was introduced in the model to run the simulations. The outlet HTF temperature, the heat transfer rate and the energy discharged were the parameters used to evaluate the mathematical model.

The comparison between the experimental and simulated outlet HTF temperature is presented in Figure 11. The temperature profiles show good agreement during all the discharging process, achieving a mean absolute deviation (MAD) of 0.12 °C, calculated by Equation 3.

$$MAD = \frac{1}{n} \sum_{i=1}^{n} \left(T_{HTF;out}^{sim,i} - T_{HTF;out}^{ref,i} \right)$$
 Equation 3

Small differences are observed during the first part of the discharge, where the simulated outlet HTF temperature is slightly higher than the experimental one. Between minute 60 and 90 both curves match perfectly well, while after that the simulated temperature remains slightly below the experimental. However, these differences are

Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

small enough to consider the model validated. This behaviour is more clearly seen in the PCM temperature profile, where the MAD is 0.61 °C.

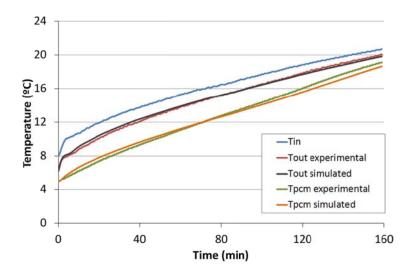


Figure 11. Inlet HTF temperature, experimental and simulated outlet HTF temperature and experimental and simulated PCM temperature

Furthermore, the heat transfer rate and energy supplied calculated by the simulations are compared with the experimental ones in Figure 12. The heat transfer rate follows the behaviour shown by the temperature and, although the slight differences, the average heat transfer rates are 874.42 W for the simulated test and 877.14 W for the experimental one. Moreover, the supplied energies in both cases are almost equal, 2.31 kWh and 2.32 kWh for the simulated and experimental test, respectively.

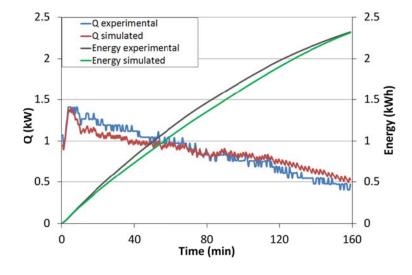


Figure 12. Heat transfer rates and supplied energies of the simulation and the experimental test

Numerical model

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CHAPTER VI

Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

The differences in the heat rate transfer are minimized when an effective PCM thermal conductivity is used. Since the theoretical model does not account for convection inside the PCM flat slab (only conduction is considered), the effect of natural convection in liquid PCM in the experimental system leads to higher heat transfer rates.

The initial PCM thermal conductivity taken for the simulations was 0.43 W/(m·K), based on the manufacturer's specification. In order to determine the effective thermal conductivity of the PCM that would account for natural convection, a parametric study was performed using the numerical model. The mean absolute percentage error (MAPE) of the heat transfer was used as the objective function to minimize (Equation 4):

$$MAPE = \frac{1}{n} \sum_{i=1}^{n} \left(\left| \frac{Q^{\text{sim,i}} \cdot Q^{\text{ref,i}}}{Q^{\text{ref,i}}} \right| \right) \cdot 100 \%$$
 Equation 4

The results presented in Figure 13 indicate that taking 0.83 W/(m·K) as effective thermal conductivity gives the lowest error compared to experimental results.

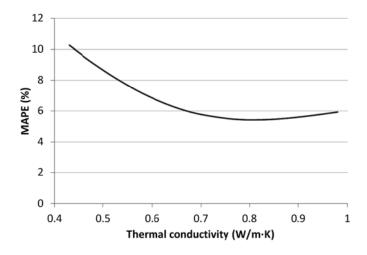


Figure 13. MAPE results according to the PCM thermal conductivity

Further simulations were performed using the effective thermal conductivity. As seen in Figure 14 the model is able to predict better both the outlet HTF temperature and the PCM temperature when using 0.83 W/(m·K). The MAD has been reduced to 0.06 °C for the outlet HTF temperature and 0.14 °C for the PCM temperature, which means that the accuracy of the model has been increased with the use of the effective thermal conductivity.

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Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

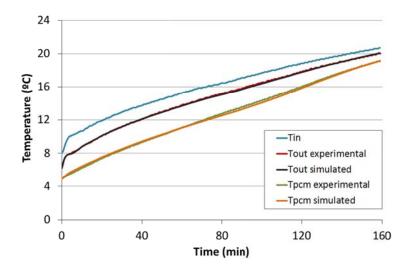


Figure 14. Inlet HTF temperature, experimental and simulated outlet HTF temperature and experimental and simulated PCM temperature using 0.83 W/(m·K) as PCM effective thermal conductivity

The accuracy of the heat transfer rate has been also enhanced, as shown Figure 15. Only between minute 70 and 110 the simulated heat transfer rate is slightly higher than the experimental one. In terms of average heat transfer rate the simulated value is 906.57 W, which is 3.35 % higher than the experimental one. Also the discharged thermal energy is 3.44 % higher in the simulations than the experimental one.

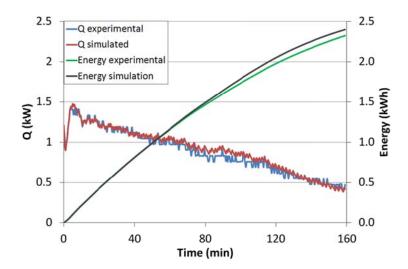


Figure 15. Heat transfer rates and supplied energies of the simulation and the experimental test using 0.83 W/(m·K) as PCM effective thermal conductivity

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CHAPTER VI

Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

In conclusion, the mathematical model is able to predict the thermal behaviour of the PCM storage tank in terms of outlet HTF temperature, PCM temperature, heat transfer rate and discharged energy. However, the results can be improved using 0.83 W/(m·K) as PCM effective thermal conductivity, thus considering all the heat transfer phenomena occurring inside the PCM package during the PCM melting process.



Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

6.4 Journal paper

Applied Thermal Engineering 67 (2014) 16-23



Contents lists available at ScienceDirect

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Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters



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CHAPTER VI

Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters

The paper "Numerical model evaluation of a PCM cold storage tank and uncertainty analysis of the parameters" (doi:10.1016/j.applthermaleng.2014.02.055) is included from page 53 to page 59.















Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

7 Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

7.1 Introduction

One of the main disadvantage of using inorganic substances as PCM is the corrosion produced when they are in contact with metals. When designing TES systems with PCM the evaluation of the compatibility between PCM and metals is an important issue to ensure long term stability of the container, as well as to avoid the potential damage to the close environment in case of encapsulation leakage [38].

Although in the experimental part of this thesis the PCM were encapsulated in plastic packages the use of bulk PCM in the TES tanks was also taken into account for further investigation. When using PCM in bulk, the system works like a common shell-and-tubes heat exchanger where one fluid is replaced by the PCM, so that the HTF flows through the metallic tubes while the PCM surrounds them. The evaluation of these systems has been of great interest to many researchers [39].

The PCM tested in this study were selected according to their potential application in TES systems working together with low temperature heating, such as heat pumps, and air-conditioning. All the PCM evaluated were salt hydrates and their phase change temperatures match with the PCM used in the experimental set-up tested in this thesis.

Some studies about metal corrosion caused by PCM can be found in the literature [41]-[44]. The necessity to obtain more data through evaluating different PCM and metals led to carry out the study presented next.

7.2 Contribution to the state-of-the-art

This chapter presents the corrosion study of different metal and alloy samples in contact with PCM that can be used as TES medium for heating and cooling applications. This research is described in the following publication:



Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

P. Moreno, L. Miró, A. Solé, C. Barreneche, C. Solé, I. Martorell, L. F. Cabeza.
 Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications. Applied Energy 125 (2014) 238-245.

The PCM evaluated in this study were salt hydrates within two different phase change temperature ranges: from 45.5 to 48.5 °C and from 10 to 15 °C, which match with low temperature heating and cooling system. Commercially available PCM and substances from the literature were analysed when they were in contact with the samples. They are listed in Table 3 and their compositions and melting temperatures are indicated in the paper presented in this chapter.

Table 3. PCM evaluated in the corrosion test

PCM for coolin	g application	PCM for heating application			
Nomenclature	PCM	Nomenclature	PCM		
PCM A	S10 from PCM Products	PCM F	S46 from PCM Products		
PCM B	C10 from Climator	PCM G	C48 from Climator		
PCM C	ZnCl ₂ ·3H ₂ O	PCM H	MgSO ₄ ·7H ₂ O		
PCM D	NaOH·1.5H ₂ O	PCM I	$Zn(NO_3)_2 \cdot 4H_2O$		
PCM E	K ₂ HPO ₄ ·6H ₂ O	PCM J	$K_3PO_4\cdot 7H_2O$		
1011112	11/111 04 011/0	PCM K	$Na_2S_2O_3 \cdot 5H_2O$		

Two metals (copper and aluminium) and two metal alloys (stainless steel 316 and carbon steel) were used as samples to test the corrosion caused by the PCM. All these samples had the same size (50 mm length, 10 mm width and a thickness of 0.5 mm) and were immersed inside glass test tubes which contained the PCM in order to combine each sample with the different PCM.

The methodology used in this study is an adaptation of the Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens (ASTM G1-03). Thus, the glass tubes containing both the PCM and the metal sample were maintained at constant temperature to ensure their liquid phase, since it is the worse corrosion case scenario. Thus, the PCM for cooling application were kept at ambient temperature (22)



Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

°C) while the PCM for heating application were maintained at 60 °C inside a furnace. The samples were removed from the test tubes after one week (seven days), four weeks (28 days), and 12 weeks (84 days), in order to evaluate the evolution of the corrosion rate over time. The metal samples were weighted at the beginning of the experimentation and after each time period to evaluate the mass loss. Also visual evaluation was performed seeking for bubbles, precipitates, surface changes, and pitting process.

Finally, the corrosion rate CR (mg/cm²·year) was calculated using Equation 5, where A is the metal sample area (cm²), (t_o-t) is the experimental time (one, four and twelve weeks) and Δm is the mass loss (mg), calculated by Equation 6. Here, m(t_o) is the initial sample mass and m(t) is the mass measured after each time period.

$$CR = \frac{\Delta m}{A \cdot (t_0 - t)}$$
 Equation 5

$$\Delta m = m(t_0) - m(t)$$
 Equation 6

The main contribution of this study to the state-of-the-art can be summarized in the following points:

- ➤ New data about corrosion in metals caused by PCM was presented. The compatibility of the containers with the PCM used in TES systems is a key issue to ensure their operational life.
- > Conclusions about the PCM for cooling applications:
 - The two commercial PCM and NaOH·1.5H₂O presented high corrosion rate when they were in contact with copper samples, so they are not recommended to be used in cooper encapsulation. Figure 16 shows the copper sample in contact with S10, inside the test tube and before cleaning after 12 weeks. It can be seen the blue colour of copper salts (sulphates or chlorides) and the salts deposited over the metal sample.



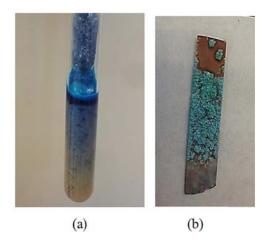


Figure 16. S10 + copper corrosion tests. (a) Sample in test tube after 12 weeks of testing; (b) metal sample with copper salts after 12 weeks of testing and before cleaning.

- According to the results stainless steel was the best option to be used with any of the PCM tested since it showed very low corrosion rate in any case.
- O All the PCM tested with carbon steel presented high level of corrosion. Commercial PCM C10 was the only one which showed higher corrosion after 12 weeks than after 4 weeks, since the corrosion of the other ones decreased with time.
- ZnCl₂·3H₂O and NaOH·1.5H₂O showed aggressive corrosion when tested with aluminium and even ended up with the final degradation of the metal. The commercial PCM C10 was the only recommended with aluminium.
- The tests of the PCM for heating application concluded that:
 - All the PCM tested with copper presented high corrosion rates. The corrosion of the C48 was higher after 12 weeks of experimentation while it decreased with time for the other ones (Figure 17).
 - o Similarly to the PCM for cooling applications, any of the PCM tested were recommended to be used with stainless steel containers.
 - o Only C48 presented corrosion rate low enough to be recommended with carbon steel containers. The others showed high levels of corrosion.
 - The corrosion tests carried out with aluminium determined that only C48 and MgSO₄.7H₂O presented low corrosion rate.

Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

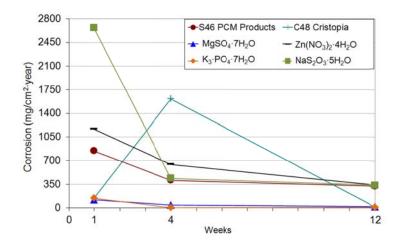


Figure 17. Corrosion rate of PCM for heating application with copper.

The results of this study are summarised in Table 4, where the recommendation of using the metals and metal alloys with the PCM tested is presented.

Table 4. Recommendation of use of metals and metal alloys with the studied PCM for heat pump

applications.

PCM	Copper	Stainless steel	Carbon steel	Aluminium				
PCM for cooling application								
S10	Not recommended	Recommended	Not recommended	Caution recommended				
C10	Not recommended	Recommended	mmended Not recommended for long term service					
ZnCl ₂ ·3H ₂ O	Recommended	Recommended	Not recommended for long term service	Not recommended				
NaOH·1.5H ₂ O	Not recommended	Recommended	Caution recommended	Not recommended				
K ₂ HPO ₄ ·6H ₂ O	Caution recommended	Recommended	Not recommended	Not recommended				
PCM for heating application								
S46	Not recommended	Recommended	Not recommended for long term service	Caution recommended				
C48	Not recommended	Recommended	Recommended	Recommended				
MgSO ₄ ·7H ₂ O	Not recommended	Recommended	Not recommended	Recommended				
$Zn(NO_3)_2 \cdot 4H_2O$	Not recommended	Recommended	Not recommended	Not recommended				
K ₃ PO ₄ ·7H ₂ O	Not recommended	Recommended	Recommended	Not recommended				
Na ₂ S ₂ O ₃ ·5H ₂ O	Not recommended	Recommended	Caution recommendation	Caution recommendation				



Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

7.3 Journal paper

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Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications



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Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications

The paper "Corrosion of metal and metal alloy containers in contact with phase change materials (PCM) for potential heating and cooling applications" (doi:10.1016/j.apenergy.2014.03.022) is included from page 66 to page 73.















Conclusions and recommendations for future work

8 Conclusions and recommendations for future work

8.1 Conclusions of the thesis

This PhD thesis deals with the utilisation of TES units in domestic heat pumps for energy management. The studies presented here were carried out as a consequence of a FP7 project which included the construction and experimentation of a TES-heat pump system.

The major achievements of this PhD are the following:

- From the state-of-the-art review it was seen that not only the PCM storage units
 can be used for load shifting in heat pumps but also some studies have
 demonstrated their potential utilisation as heat recovery or defrosting system
 support.
- The results from the experimental set-up indicate that the PCM was able to store 35.5 % more cold on average than the water tank but needed 4.55 times longer to charge. Moreover, the PCM tank supplied 14.5 % more cold than the water tank but the discharge efficiency (cold supplied/cold stored ratio) was higher for the water tank.
- The space cooling tests indicated that the system working with the PCM tank was able to maintain the indoor temperature by 20.65 % longer than using the water tank.
- The mathematical model presented in this thesis predicts the discharge of the PCM tank showing good agreement with the experimental data. Furthermore, using the parameter $c_{PCM;old}$ or constant HTF properties as simplifying approximation was demonstrated to be a good solution for reducing the computational time with acceptable error.
- Regarding the corrosion study, stainless steel is the most appropriate material to be used in contact with any of the PCM tested since it showed very low corrosion rate in all the tests.

Conclusions and recommendations for future work

The main conclusions from the state-of-the-art review part are listed below:

- One of the main advantages of using TES is the potential utilisation together with renewable energies with the consequent environmental benefits that this implies.
- TES units working as defrosting system of the outdoor unit are able to reduce the energy consumption and the defrosting time.
- Ice is a well-known substance which can be used as PCM in air-conditioning devices for cold storage. However, the use of ice in domestic air-conditioning is dependent on the evaporator temperature since standard cooling equipment does not usually reach temperatures below zero.

The conclusions that came out from the experimental study of the thesis are presented next:

- The initial HTF temperature inside the tank influences the cold storage and charging time. For the water tank lower initial temperatures lead to lower cold storage and longer charging time since the minimum HTF temperature in the evaporator, set to prevent damage, is reached earlier. On the other hand, higher cold storage is stored in the PCM tank when initial HTF temperatures are higher, due to lower heat gains during the charging process.
- The melting of the PCM was not clearly reflected on the temperature profile during the discharge. This can happen because of the low heat transfer between PCM and HTF due to the low thermal conductivity of the PCM and the plastic encapsulation.

From the theoretical study it is concluded that:

• The optimisation of the model concluded that taking $N_x=N_y=10$ and $\Delta t=30$ s provided good accuracy and acceptable computing time. Moreover, this was considered the most appropriate configuration to compare the results with the experimental data.

Conclusions and recommendations for future work

- The variables which presented the highest influence of uncertainties were the inlet HTF temperature, melting PCM temperature, PCM density and PCM specific heat.
- The validation of the theoretical model demonstrated good agreement between simulations and experimental results. However, an improvement of the accuracy can be achieved by increasing the PCM thermal conductivity. Taking higher conductivity should be understood as considering all the heat transfer phenomena occurring inside the PCM package (including convection in the liquid phase of the PCM), and not only the thermal conduction itself.

Finally, the main conclusions from the corrosion test are listed below:

- Both commercial PCM for cooling applications (S10 and C10) are recommended to work in contact with aluminium as well; however the utilisation of S10 needs to be evaluated for the specific application.
- NaOH·1.5H₂O is also suitable to work with carbon steel depending on the application, while ZnCl₂·3H₂O and K₂HPO₄·6H₂O can work also with copper, although the last one depends on the application.
- Regarding the commercial PCM for heating applications, S46 is also recommended to be used with aluminium according to the application. On the other hand, C48 presented low corrosion rate with carbon steel and aluminium as well.
- MgSO₄·7H₂O is recommended to be used with aluminium, K₃PO₄·7H₂O presented low corrosion rate with carbon steel and Na₂S₂O₃·5H₂O can also be used with carbon steel and aluminium according to the specific application.

8.2 Recommendations for future work

The tests carried out with the experimental set-up provided interesting results comparing the use of PCM and water as TES systems. The next research will be focused on the thermal behaviour of the PCM tank used for space heating application.



Conclusions and recommendations for future work

Related to the performance of the TES-heat pump system, the study of the COP during charging and discharging processes is also an important issue to carry out in further studies. The results could be compared with the utilisation of the heat pump without the TES system or other heat pumps from the market.

The PCM tested in the experimental set-up were commercial products. It would be interesting to test different PCM and packages, such as balls or cylindrical encapsulation, in the same tanks and compare the thermal behaviour of each configuration with the results presented in this thesis. In this sense, the utilisation of bulk PCM in a shell-and-tubes tank was also taken into account to be tested in the experimental set-up; this was in part the reason to carry out the corrosion study.



Other research activities

9 Other research activities

9.1 Other publications

Other scientific research about thermal energy storage was carried out during this thesis. The publications resulted are listed below:

1. A. Gil, C. Barreneche, P. Moreno, C. Solé, A.I. Fernández, L.F. Cabeza. Thermal behaviour of d-mannitol when used as PCM: comparison of results obtained by DSC and in a thermal energy storage unit at pilot plant scale. Applied Energy 111 (2013) 1107-1113.



Summary

The use of thermal energy storage (TES) systems for solar heating and cooling applications has received considerable attention in recent decades because it has a high potential in energy savings. Phase change materials (PCMs) can store large amount of energy per mass unit compared with other TES materials. Nevertheless, the selection of the suitable PCM for each application is a key issue in any TES system design. The most important properties to take into account to select a PCM are the melting and solidification temperature, the phase change enthalpy and the stability after several thermal cycles. In this paper, D-mannitol was a candidate material to be tested as PCM in a solar cooling application due to its melting point (167 °C) and a relatively high enthalpy (316.0 kJ/kg). The experiments performed by DSC have shown that the D-

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mannitol presents polymorphic structural changes and, therefore, its thermal properties are not always the same. Depending on the polymorphic phase obtained, D-mannitol has different melting temperature. This behaviour was corroborated in a storage tank, where it may be seen that the cooling rate of the D-mannitol is a key parameter in the formation of the different polymorphic phases.

2. T. Nuytten, P. Moreno, D. Vanhoudt, L. Jespers, A. Solé, L.F. Cabeza. Comparative analysis of latent thermal energy storage tanks for micro-CHP systems. Applied Thermal Engineering 59 (2013) 542-549.



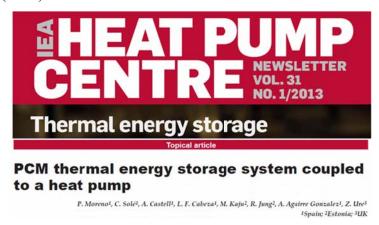
Summary

The efficiency of micro-combined heat and power (micro-CHP) systems can be increased by decoupling the production of electricity and heat by means of thermal energy storage (TES) systems where heat that is not needed during the production period can be stored for later use. The aim of this article is to evaluate the use of different TES units when coupled to micro-CHP systems. An experimental study was carried out to evaluate the thermal behavior of different TES units for coupling with a micro-CHP system. A cylindrical TES tank was used to compare the performance of two phase change materials (PCMs) with different melting temperature and encapsulation method, while using a water-filled unit as a reference scenario. The first concept consists of cylindrical PCM tubes while the second uses small spherical PCM capsules, both commercially available products. The analysis involves three different

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tests: constant inlet temperature, constant power, and partial capacity loading. The results are evaluated on the basis of a comparison between inlet and outlet temperatures, charging time and thermal energy stored by the TES units. The PCM tubes are characterized by a higher capacity when a low thermal power is applied while the PCM capsules are able to store more energy at higher power. The operating temperatures in partial loading tests indicate that the incorporation of PCM storage units in a smart grid environment may be beneficial from a thermal systems point of view.

3. P. Moreno, C. Solé, A. Castell, L.F. Cabeza, M. Kaju, R. Jung, A. Aguirre, Z. Ure. PCM thermal energy storage system coupled to a heat pump. IEA Heat Pump Centre Newsletter 31 (2013) 33-35.



Summary

The University of Lleida (Spain) has an experimental set-up consisting of a thermal energy storage (TES) system coupled to a heat pump. Phase-change materials (PCM) are used in the TES system as latent heat storage material. The system operates with a load-shifting strategy, so the two TES units installed supply the entire cooling or heating demand while shifting the electricity demand of the HVAC system to off-peak hours. The system prototype has been tested under summer conditions in Spain and is being tested for winter conditions in Estonia. This article describes the system and the first results of the trials.



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9.2 Contribution to conferences

The PhD candidate also contributed to several international conferences:

- 1. C. Barreneche, A. Gil, P. Moreno, C. Solé, L.F. Cabeza. Thermal behaviour of d-mannitol when used as PCM: comparison of results obtained by DSC and in a pilot plant storage tank. Innostock 2012, Lleida (Spain).
- 2. P. Moreno, C. Solé, A. Castell, L.F. Cabeza. Design of PCM thermal storage unit for a HVAC system. Innostock 2012, Lleida (Spain).
- 3. A. Castell, L.F. Cabeza, C. Solé, P. Moreno. Thermal energy storage potential for energy savings and climate change mitigation. Innostock 2012, Lleida (Spain).
- 4. P. Moreno, C. Solé, A. Castell, L.F. Cabeza. Heat pump integrated PCM thermal energy storage system. Eurosun 2012, Rijeka (Croatia).
- 5. P. Moreno, C. Solé, A. Castell, G. Zsembinski, L.F. Cabeza. Experimental analysis of TES tanks using PCM in space cooling system. ICAE 2013, Pretoria (South Africa).
- 6. G. Zsembinski, P. Moreno, C. Solé, A. Castell, L.F. Cabeza. Mathematical modelling of a phase change material TES tank for space cooling applications. Sustainable Energy Storage in Buildings the 2nd IC-SES, Dublin (Ireland).
- 7. P. Moreno, C. Solé, A. Castell, L.F. Cabeza. PCM thermal energy storage tanks in heat pump system for space heating. ISBE 2014, Doha (Qatar).

9.3 Scientific foreign exchange

The PhD candidate did a 3-month exchange during the realisation of this thesis in the Flemish Institute for Technological Research (VITO), in Belgium. This research stay demonstrates the ability of the candidate to perform high level scientific work in a different environment and in another international well-known and highly renowned institution, as well as it allows the candidate to aim for the European/International PhD.

The research carried out was also related with thermal energy storage but it was meant to be applied in micro-CHP systems. Experimental studies were developed using a cylindrical TES tank to compare the performance of two phase change materials (PCM) with different melting temperature and encapsulation method, while using a water-filled unit as a reference scenario. The first concept used cylindrical PCM tubes (58 °C as

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melting temperature) while the second one used small spherical PCM capsules (52 °C as melting temperature), both commercially available products. The analysis involved three different tests: constant inlet temperature, constant power, and partial capacity loading. The results were published in the scientific article listed in *Other publications* "Comparative analysis of latent thermal energy storage tanks for micro-CHP systems".





References

- [1] European Commission. Technology assessment SWD (2013) 157.
- [2] International Energy Agency (IEA). Technology Roadmap. Energy-efficient Buildings: Heating and Cooling Equipment, 2011.
- [3] On-line data services, International Energy Agency http://data.iea.org/ieastore/default.asp (accessed 2013).
- [4] European Parliament & Council. Directive 2009/28/EC.
- [5] I. Dinçer, M.A. Rosen, Thermal energy storage. Systems and applications, first ed., John Wiley & Sons, Baffins Lane, England, 2002.
- [6] I. Dincer. On thermal energy storage systems and applications in buildings. Energy and Buildings 34 (2002) 377-388.
- [7] F. Agyenim, N. Hewitt, P. Eames, M. Smyth. A review of materials, heat transfer and phase change problem formulation for latent thermal energy storage systems (LHTESS). Renewable and Sustainable Energy Reviews 14 (2010) 615-628.
- [8] B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. Applied Thermal Engineering 23 (2003) 251-283.
- [9] L.F. Cabeza, A. Castell, C. Barreneche, A. de Gracia, A.I. Fernández. Materials used as PCM in thermal energy storage in buildings: a review. Renewable and Sustainable Energy Reviews 15 (2011) 1675-1695.
- [10] A. Sharma, V.V. Tyagi, C.R. Chen, D. Buddhi. Review on thermal energy storage with phase change materials and applications. Renewable and Sustainable Reviews 16 (2009) 318-345.
- [11] E. Osterman, V.V. Tyagi, V. Butala, N.A. Rahim, U. Stritih. Review of PCM based cooling technologies for buildings. Energy and Buildings 49 (2012) 37-49.
- [12] A. Abhat. Low temperature latent heat thermal energy storage. Heat storage materials. Solar Energy 30 (1983) 313-32.



- [13] A. Arteconi, N.J. Hewitt, F. Polonara. Domestic demand-side management (DSM): Role of heat pumps and thermal energy storage (TES) systems. Applied Thermal Engineering 51 (2013) 155-165.
- [14] Y. Hamada, J. Fukai. Latent heat thermal energy storage tanks for space heating of buildings: Comparison between calculations and experiments. Energy Conversion and Management 46 (2005) 3221-3235.
- [15] F. Agyenim, N. Hewitt. The development of a finned phase change material (PCM) storage system to take advantage of off-peak electricity tariff for improvement in cost of heat pump operation. Energy and Buildings 42 (2010) 1552-1560.
- [16] C. Leonhardt, D. Müller. Modelling of Residential Heating System using a Phase Change Material Storage System. Proceedings 7th Modelica Conference, Como, Italy, 2009 Sep. 20-22.
- [17] IEA Heat Pump Centre Newsletter 1990;8(2):10.
- [18] D. Jiankai, J. Yiqiang, Y. Yang, A. Xue-dan. Operating performance of novel reverse-cycle defrosting method based on thermal energy storage for air source heat pump. J Cent South Univ Technol 18 (2011) 2163-2169.
- [19] Q. Minglu, X. Liang, S. Deng, J. Yiqiang. Improved indoor thermal comfort during defrost with a novel reverse-cycle defrosting method for air source heat pumps. Build Environ 45 (2010) 2354-2361.
- [20] J. Mazo, M. Delgado, J.M. Marin, B. Zalba. Modeling a radiant floor system with Phase Change Materials (PCM) integrated into a building simulation tool: Analysis of a case study of a floor heating system coupled to heat pump. Energy and Buildings 47 (2012) 458-466.
- [21] L. Cabrol, P. Rowley. Towards low carbon homes A simulation analysis of building-integrated air-source heat pump systems. Energy and Buildings 48 (2012) 127-136.
- [22] K. Kaygusuz. Investigation of a combined solar-heat pump system for residential heating. Part1: experimental results. International Journal of Energy Research 23 (1999) 1213-1223.



- [23] F. Niu, L. N, Y. Yaio, Y. Yu, H. Li. Performance and thermal charging/discharging features of a phase change assisted heat pump system in heating mode. Applied Thermal Engineering 58 (2013) 536-541.
- [24] Z. Han, M. Zheng, F. Kong, F. Wang, Z. Li, T. Bai. Numerical simulation of solar assisted ground-source heat pump heating system with latent heat energy storage in severely cold area. Applied Thermal Engineering 28 (2008) 1427-1436.
- [25] G. Fang, X. Liu, S. Wu. Experimental investigation on performance of ice storage air-conditioning system with separate heat pipe. Experimental Thermal and Fluid Science 33 (2009) 1149-1155.
- [26] G. Fang, S. Wu, X. Liu. Experimental study on cool air-conditioing system with spherical capsules packed bed. Energy and Buildings 42 (2010) 1056-1062.
- [27] E. Mettawee, I. Eldesouki, S. Amin. Experimental study on space cooling with PCM thermal storage. Journal of Applied Sciences Research 8 (2012) 3424-3432.
- [28] X. Zhang, S. Yu, M. Yu, Y. Lin. Experimental research on condensing heat recovery using phase change material. Applied Thermal Engineering 31 (2011) 3736-3740.
- [29] Z. Gu, H. Liu, Y. Li. Thermal energy recovery of air conditioning system heat recovery system calculation and phase change materials development. Applied Thermal Engineering 24 (2004) 2511-2526.
- [30] K. Nagano K, S. Takeda, T. Mochida, K. Shimakura, T. Nakamura. Supply of a floor air conditioning system using granular phase change material to augment building mass thermal storage Heat response in small scale experiments. Energy and Buildings 38 (2006) 436-446.
- [31] M. Yamaha, S. Misaki. The evaluation of peak shaving by a thermal storage system using phase-change materials in air distribution systems. HVAC&R Research Special Issue 12 (2006) Number 3c.
- [32] I. Dincer, M.A. Rosen. Energetic, environmental and economic aspects of thermal energy storage systems for cooling capacity. Applied Thermal Engineering 21 (2001) 1105-1117.



- [33] PCM Products, www.pcmproducts.net.
- [34] J. Fukai, Y. Hamada, Y. Morozumi, O. Miyatake. Improvement of thermal characteristics of latent heat thermal energy storage unit carbon-fiber brushes: experiments and modelling. International Journal of Heat and Mass Transfer 46 (2003) 4513-1525.
- [35] A. Felix Regin, S.C. Solanki, J.S. Saini. An analysis of a packed bed latent heat thermal energy storage system using PCM capsules: Numerical investigation. Renewable Energy 34 (2009) 1765-1773.
- [36] S.M. Vakilaltojjar, W. Saman. Analysis and modelling of a phase change storage system for air-conditioning applications. Applied Thermal Engineering 21 (2001) 249-263.
- [37] P. Dolado, J. Mazo, A. Lázaro, J.M. Marín, B. Zalba. Experimental validation of a theoretical model: Uncertainty propagation analysis to a PCM-air thermal energy storage unit. Energy and Buildings 45 (2012) 124-131.
- [38] H. Mehling, L.F. Cabeza. Phase change materials and their basic properties. In: H.O. Paksoy, editor. Thermal energy storage for sustainable energy consumption: fundamentals, case studies and design. Springer, 2007. p. 257–278.
- [39] A. Gil, E. Oró, L. Miró, G. Peiró, A. Ruiz, J.M. Salmerón, L.F. Cabeza. Experimental analysis of hydroquinone used as phase change material (PCM) to be applied in solar cooling refrigeration. International Journal of Refrigeration 39 (2014) 95-103.
- [40] A. Gil, E. Oró, A. Castell, L.F. Cabeza. Experimental analysis of the effectiveness of a high temperature thermal storage tank for solar cooling applications. Applied Thermal Engineering 54 (2013) 521-527.
- [41] E. Oró, L. Miró, C. Barreneche, I. Martorell, M.M. Farid, L.F. Cabeza. Corrosion of metal and polymer containers for use in PCM cold storage. Applied Energy 109 (2013) 449-453.
- [42] L.F. Cabeza, J. Illa, J. Roca, F. Badia, H. Mehling, S. Hiebler, F. Ziegler. Middle term immersion corrosion tests on metal-salt hydrate pairs used for latent heat



- storage in the 32 to 36 °C temperature range. Materials and Corrosion 52 (2001) 748–754.
- [43] L.F. Cabeza, J. Roca, M. Nogués, , H. Mehling, S. Hiebler. Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58 °C temperature range. Materials and Corrosion 53 (2002) 902-907.
- [44] A.J. Farrell, B. Norton, D.M. Kennedy. Corrosive effect of salt hydrate phase change materials used with aluminium and copper. Journal of Materials Processing Technology 175 (2006) 198-205.