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Phase change materials characterization (PCM) and thermochemical materials (TCM) development and characterization towards reactor design for thermal energy storage

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PhD Thesis

Phase change materials characterization (PCM) and thermochemical materials (TCM) development and characterization towards reactor design for thermal energy storage

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CERTIFIQUEN:

Que la memòria "Phase change materials (PCM) characterization and thermochemical materials (TCM) development and characterization towards reactor design for thermal energy storage" presentada per Aran Solé i Garrigós per optar al grau de Doctor s'ha realitzat sota la seva supervisió.

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Resum

Aquesta tesi s'emmarca en l'emmagatzematge d'energia tèrmica, concretament per a aplicacions en edificis. Les polítiques presents i de futur immediat passen per reduir el consum de combustibles fòssils i així promocionar l'ús d'energies renovables per proporcionar calefacció, fred i aigua calenta sanitària a les cases. Un inconvenient de les energies renovables, a part del cost d'inversió inicial el qual està decreixent, és la necessitat de bateries tèrmiques. L'emmagatzematge d'energia tèrmica és fonamental per quadrar la producció i la demanda, i així proporcionar fred o calor (energia tèrmica) als consumidors quan així ho requereixin, independentment de quan ha estat obtinguda. Hi ha diverses maneres de fer-ho, la més comuna és un tanc d'aigua. No obstant, hi ha maneres més compactes i eficients, com ara els materials de canvi de fase (PCM) i els materials termoquímics (TCM). Aquests materials han d'haver estat ben caracteritzats i llurs propietats termofísiques perfectament determinades per tal de poder dissenyar l'adequat sistema per calefacció, fred i aigua calenta sanitària el més òptimament possible. Els sistemes amb PCM ja estan disponibles al mercat, però encara manca estandarditzar la manera de caracteritzar-los i trobar el mètode adequat per fer-ho. A més a més, la ciclabilitat tèrmica, propietat importantíssima, ha estat poc estudiada i és la que ens assegura una llarga vida al sistema dissenyat. Els TCM estan encara en fase de recerca i desenvolupament. Aquests, presenten majors densitats energètiques que l'aigua i els PCM, el que comporta sistemes més compactes, i no presenten pèrdues tèrmiques amb l'ambient. Tot i això, encara hi ha punts a tractar com la corrosió, l'obtenció del rendiment teòric del reactor, les limitacions en els processos de transferència de massa i energia, la cinètica, i l'elecció del reactor i el sistema adequat. És per això, que l'objectiu de la present tesis és contribuir a la caracterització de PCM des d'un punt de vista de les tècniques d'anàlisi tèrmica, estabilitat fisicoquímica i morfològica, així com investigar experimentalment sobre la ciclabilitat tèrmica dels sucres-alcohols. Pel que fa als materials termoquímics l'objectiu és dur a terme un estat de l'art dels reactors utilitzats, així com aprofundir en els requeriments quan es procedeix a elegir un TCM. A més a més, també és presenten els resultats de tests de corrosió sota diferents atmosferes, simulant els reactors, i nous materials desenvolupats, basats en grafit, per millorar la transferència de calor.

Resumen

La presente tesis se encuadra en el campo del almacenamiento de energía térmica, en concreto para edificios. Las políticas actuales, así como de futuro inmediato se basan en reducir el consumo de carburantes fósiles y por lo tanto promocionar el uso de energías renovables para proporcionar calefacción, frío y agua caliente sanitaria. Uno de los inconvenientes de las energías renovables, a parte de la inversión inicial la cual está disminuyendo, es la necesidad de baterías térmicas. El almacenamiento de energía térmica es fundamental para hacer coincidir la producción y la demanda, para así proporcionar energía térmica cuando sea requerida por los inquilinos, independientemente de cuándo ésta ha sido obtenida. Existen diferentes maneras de hacerlo, la más común el agua. No obstante, hay maneras más eficientes y compactas, como los materiales de cambio de fase (PCM) y los materiales termoquímicos (TCM). Estos materiales deben ser caracterizados y sus propiedades perfectamente determinadas para proceder al diseño de un sistema de calefacción, frío y agua caliente lo más óptimo posible. Los sistemas con PCM están ya disponibles en el mercado, aun así falta estándares de caracterización al igual que el método adecuado para llevarlo a cabo. Además, la ciclabilidad térmica, propiedad importantísima, ha sido poco estudiada y es la que asegurará una vida útil larga al sistema. Los TCM están aún en fase de investigación. Éstos presentan mayores densidades energéticas que el agua y los PCM, lo que conllevaría sistemas más compactos, y no presentan pérdidas térmicas con el exterior. Sin embargo hay temas a abordar como la corrosión, la obtención esperada del rendimiento del reactor, las limitaciones en los procesos de transferencia de masa y energía, la cinética, y la elección del sistema y el reactor adecuado. Es por eso, que el objectivo de la tesi es contribuir a la caracterización de los PCM desde un punto de vista de las técnicas de análisis térmico, estabilidad fisicoquímica y morfológica, así como investigar experimentalmente sobre la ciclabilidad térmica de los azúcares-alcoholes. En relación a los TCM, el objetivo es llevar a cabo un estado del arte de los reactores utilizados, así como profundizar sobre los requerimientos para la elección de un TCM. Asimismo, se presentan resultados de ensayos de corrosión bajo diferentes atmósferas y materiales desarrollados en base a grafito para la mejora de la transferencia de calor.

Summary

This thesis is in the frame of thermal energy storage, specifically for building applications. It is well known that present and immediate future policies are focused on reducing fossil fuels consumption and thus to promote the use of renewable energy sources for heating, cooling and domestic hot water production. A resulting drawback of renewable energies use, besides the investment cost which is actually decreasing, is the need of thermal batteries. Thermal energy storage is essential to match production and demand, and therefore to provide heat or cold to the consumers when required independently of when it was obtained. Several ways exist to fulfil this requirement in buildings, the most common one is a water tank. But there are more compact and efficient ways, such as phase change materials (PCM) and thermochemical materials (TCM) storage. These materials need to be properly characterized and their thermophysical properties perfectly known in order to design the most appropriate and optimum system for heating, cooling and domestic hot water applications in dwellings.

PCM systems are already commercially available, but still properties characterization shows a lack on standardization and method to obtain them. Furthermore, important properties, like thermal cycling stability, have been studied very little and are very important to ensure long system performance. TCM are still at research level. These materials provide higher energy densities than water and PCM, which are translated into more compact systems and do not present heat losses to the ambient. Nevertheless, there are still big points to be overcome such as corrosion, achieving the expected reactor yield, heat and mass transfer limitations, kinetics, and choosing the appropriate reactor concept and system configuration.

Therefore, the main objective of this thesis is to contribute on PCM characterization from a material thermal analysis, physicochemical stability and morphological point of view, and experimentally investigate on thermal cycling stability of sugar-alcohols. Then, on TCM side the aim is to provide an overview among TCM available reactors and requirements to choose the suitable storage material. Moreover, corrosion tests under different atmospheres and enhancement of heat transfer by developing graphite based composites are performed and shown in detail in this thesis.

Nomenclature

TES	Thermal energy storage	**DSC**	Differential Scanning Calorimeter
PCM	Phase change material	**TGA**	Thermogravimetric Analysis
TCM	Thermochemical material	**SA**	Sugar alcohols
R&D	Research and development	**FT-IR**	Fourier Transformed Infrared Spectroscopy
DHW	Domestic hot water	$\mathbf{p_{eqSG}}$	Equilibrium gas pressure
UTES	Underground thermal energy storage	$\mathbf{T_{eqSG}}$	Equilibrium temperature of the solid
TA	Thermal analysis	**RH**	Relative humidity

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1 Introduction

1.1 Thermal energy storage

According to the European Commission the energy challenge is to support the energy transition from fossil fuels to reliable, sustainable and competitive energy systems [1]. One of the big focus areas within the work programme for "Secure, Clean and Efficient Energy" Horizon2020 is low carbon technologies (H2020-LCE-2014/2015) which main contribution lays on reducing the fossil fuels consumption to generate energy and thus turn to renewable energies. Research activities within this area cover: photovoltaic, concentrated solar power, wind energy, ocean energy, hydro power, geothermal energy, renewable heating and cooling, **energy storage**, biofuels and alternative fuels, carbon capture, and storage.

Another focus area of the mentioned work programme of the Hortizon2020 is **energy efficiency** (H2020-EE-2014/2015) which is focused on buildings, industry, heating and cooling, small and medium-sized enterprises (SMEs) and energy-related products and services, integration of information and communications technology (ICT), and cooperation with the telecom sector.

The European Commission requirements of increasing energy efficiency in systems and to store thermal energy can be fulfilled by **thermal energy storage** (TES) systems. TES opens up potential for reduced energy demand and reduced peak heating and cooling loads as well as possibilities for an increased share of renewable energy to cover the energy demand.

1.1.1 TES systems

Thermal energy storage (TES) is a technology that stores thermal energy by heating or cooling a storage medium so that the stored energy can be used at a later time for heating and cooling applications and power generation. TES systems are used particularly in buildings and industrial processes [2].

TES systems can be based on different principles of storing energy. Three main concepts exist: sensible, latent, and thermochemical.

The energy released or absorbed by a material as its temperature is reduced or increased is called sensible heat. The amount of heat stored is proportional to the density, specific heat, volume and variation of temperature of the storage material. The performance of a storage system depends mainly on density and specific heat of the substance used, that affects the necessary volume. Other important features are the material cost and the rate at which heat can be extracted. Typical materials used are water, rock beds, bricks and soils [3],[4].

Phase change materials (PCM) are those materials that are used to store energy by means of latent heat, thus phase change. PCM can be solid–solid, solid–liquid or liquid–gas transitions. The solid–liquid phase change is the most suitable for the building application, considered in this thesis. Typical PCM used are water/ice, salt hydrates/eutectics and paraffins [5].

The third kind of available TES systems, known as thermochemical energy storage, is based on reversible physical and chemical processes or reactions, named thermochemical materials (TCM). That entails absorption, adsorption and chemical reactions. Here, at least two substances are needed to undergo the physical or chemical process, also known as working pairs. Typical working pairs for building application are salt hydrates/water.

The above classified energy storage systems can be compared on the basis of [2]:

- Capacity: defines the energy stored in the system and depends on the storage process, the medium and the size of the system.
- Power: defines how fast the energy stored in the system can be charged and discharged.

- Efficiency: is the ratio of the energy provided to the user to the energy needed to charge the storage system. It accounts for the energy loss during the storage period and the charging/discharging cycle.
- Storage period: defines how long the energy is stored and lasts hours to months (i.e. hours, days, weeks and months for seasonal storage).
- Cost: refers to either capacity (€/kWh) or power (€/kW) of the storage system and depends on the capital and operation costs of the storage equipment and its lifetime (i.e. the number of cycles).

Sensible heat storage offers a storage capacity ranging from 10-50 kWh/t and storage efficiencies between 50-90%, depending on the specific heat of the storage medium and thermal insulation technologies. Power values range from 0.001 and 10 MW [2].

PCM can offer higher storage capacity and storage efficiencies than sensible heat, ranging from 50-150 kWh/t and 75-90%, respectively. In most cases, storage is based on a solid/liquid phase change offering power values between 0.001 and 1 MW [2].

Thermochemical storage systems can reach storage capacities of up to 120-250 kWh/t and efficiencies from 75% to nearly 100%. This technology can reach between 0.01 and 1 MW of power [2].

The storage capacity values of some TCM, PCM and water (as representative of the best sensible system) are depicted in Figure 1 and it can be clearly seen that TCM encompasses the highest values of storage capacity.

What can also be withdrawn from Figure 1 is that to obtain the same KWh (or GJ), and given the same material density, the required storage material volume is much lower for the TCM. This fact is also represented in Figure 2 which shows the necessary volume to cover the annual storage need of an energy efficient passive house [6]. It is obvious that thermochemical energy storage offers the best option if volume is a constraint, which usually it is in building applications.

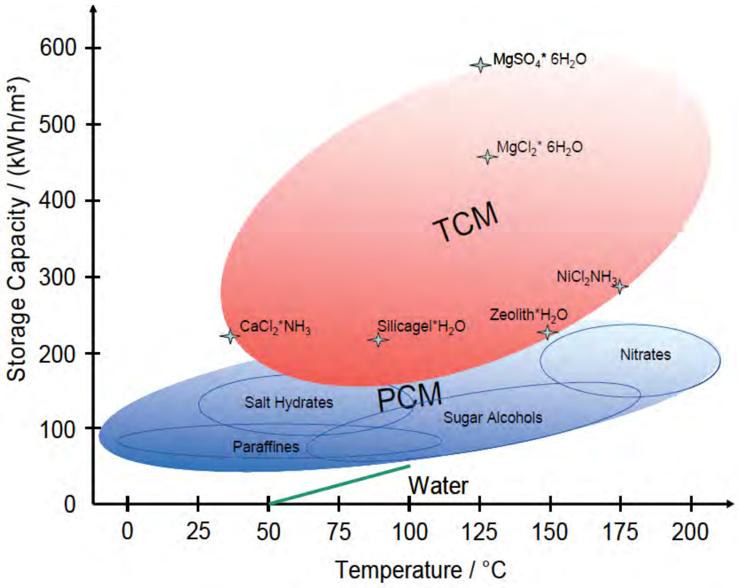

Figure 1. Storage capacity vs. Temperature for sensible (water), latent (PCM), and thermochemical (TCM) TES [2].

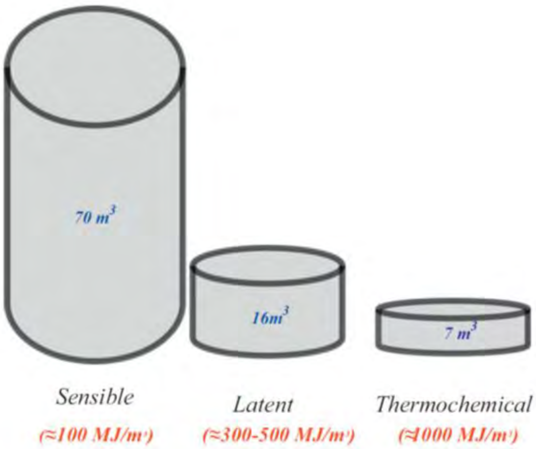

Figure 2. Volume needed to full cover the annual storage need of an energy efficient passive house (6480 MJ) [6].

Another important variable, which also affects industry and their viability on the market, is the cost of these technologies. The cost of a complete system for sensible heat storage ranges between 0.1-10 €/kWh, depending on the size, application and thermal insulation technology. The costs for PCM and TCM systems are in general higher. In these systems, major costs are associated with the heat (and mass) transfer technology, which has to be installed to achieve a sufficient charging/discharging power. Costs of latent heat storage systems based on PCMs range between 10-50 €/kWh while TCM costs are estimated to range from 8-100 €/kWh [2].

In most cases, cost is a major issue to market deployment. Table 1 shows the status market or R&D, of different systems, including sensible, PCM, and TCM. Also barriers and main R&D topics for each system are summarized. Among the available, hot water tanks represent the most mature technology, fully developed, available on the market, as can be seen in Table 1. In the PCM field, cold storage with ice is the most available in the market. On the contrary, waste heat with high temperature PCM is totally under research. PCM storage research is still needed, mainly on materials [7].

In the case of TCM all the available technologies still present a low percentage of implementation, around 5 %. High cost and complexity of the systems are the greatest barriers. Thermochemical storage systems need to become reliable and simple to use, since the largest potential seems to be in the residential market and especially in single family houses or other small buildings [7].

1.1.2 TES in the building sector

In the Energy Efficiency Plan 2011 [8], the European Commission states that the greatest energy saving potential lies in buildings. The 2010 Energy Performance of Buildings Directive and the 2012 Energy Efficiency Directive are the EU's main legislation when it comes to reducing the energy consumption of buildings. The building sector is expanding, which is bound to increase its energy consumption [9].

Buildings are responsible for 40% of energy consumption, as can be observed in Figure 3 (services and households), and 36% of CO_2 emissions in the EU [10]. Around 85 % of this energy is required for heating and domestic hot water. When focusing on the building sector, the consumption of energy for heating, domestic hot water (DHW), and cooling suggest that new policies and research are needed in this field to accomplish the new European policies and directives.

Table 1. State of development, barriers and Main R&D Topics for different TES technologies, adapted from [2].

Technology	Status (%) Market/R&D	Barriers	Main R&D topics
		Sensible TES	
Hot water tanks (buffers)	95/5	-	Super insulation
Large water tanks (seasonal)	25/75	System integration	Material tank, stratification
UTES	25/75	Regulation, high cost, low capacity	System integration
High temp. Solids	10/90	Cost, low capacity	High temp materials
High temp. Liq	50/50	Cost, temp<400 ºC	Materials
		PCM	
Cold storage (ice)	90/10	Low temp.	Ice production
Cold storage (other)	75/25	High cost	Material (slurries)
Passive cooling (buildings)	75/25	High cost, performance	Material (encapsulation)
High temp. PCM (waste heat)	0/100	High cost, Material stability	Materials (PCM containers)
		TCM	
Adsorption	5/95	High cost, complexity	Materials, and reactor/system design
Absorption	5/95	High cost, complexity	Materials, and reactor/system design
Chemical reactions	5/95	High cost, complexity	Materials, and reactor/system design

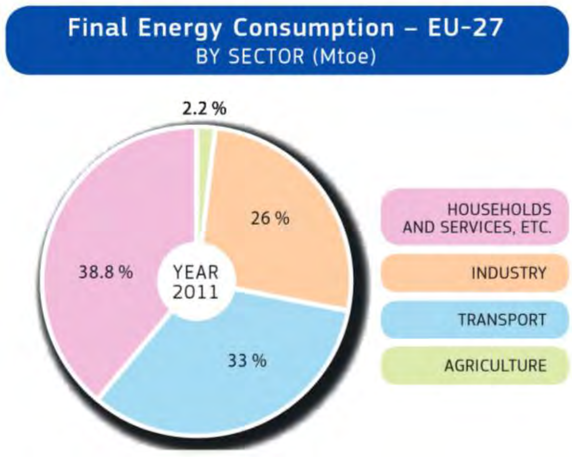

Figure 3. Final energy consumption by sector in EU 2011 [11].

In Figure 4, the stock of buildings in Spain can be seen. Since most of the buildings are already built and the perspective of new buildings construction is quite low, but still increasing, research can contribute in providing an optimum solution for the energy demand based in low carbon technologies and storage, and increasing energy efficiency of the systems of all building sector.

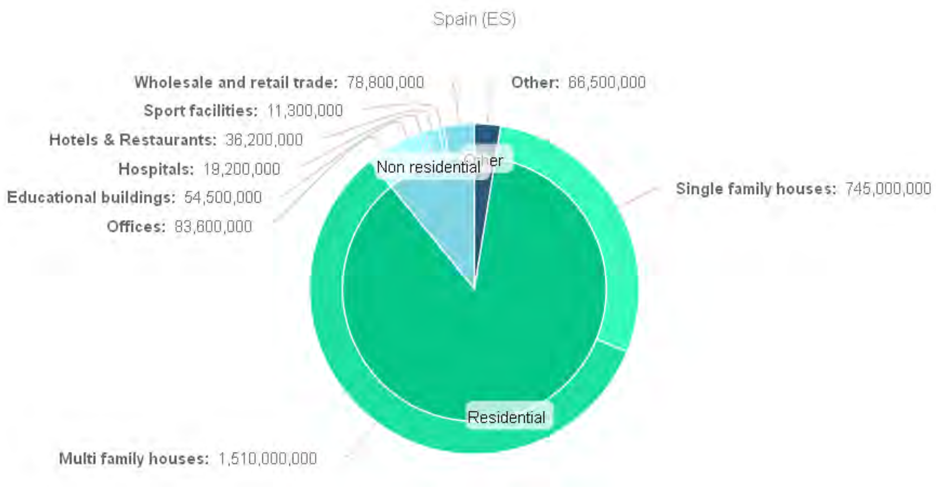

Figure 4. Breakdown of the building stock by building type in Spain [12].

Therefore, reduction of energy consumption and the use of energy from renewable sources in the buildings sector constitute important measures needed to reduce the Union's energy dependency and greenhouse gas emissions (GHG) [9].

The minimum energy savings in buildings can lead to a reduction of 60-80 Mtoe/year in final energy consumption by 2020, and make a considerable contribution to the reduction of GHG emissions. This will be achievable only if buildings are transformed through a comprehensive, rigorous and sustainable approach [8].

In that sense, renewable energies, like solar, geothermal, etc. are the most viable solution. It is well known that from the sun all the thermal energy needs (also electrical, but is out of scope of this thesis) can be fulfilled, being heating for winter times, cooling for summer times, and DHW for all seasons.

The big issue to overcome related to renewable sources is the storage. Thus thermal energy storage is essential for the full implementation of renewable energies. This would allow meeting the availability and the demand, to provide thermal energy when cloudy days (short-term), but also the possibility to "transport" the thermal energy between seasons (long-term), and to increase the overall efficiency of the energy system. The estimate of the European potential is based on a 5 % implementation rate of TES systems in buildings [2].

Within the compared TES technologies, this thesis will focus on the most efficient and the one offering the highest storage capacity values, leading to more compact systems: PCM and TCM.

1.2 Phase change materials

Any active latent heat thermal energy storage system is composed of a heat storage medium, namely PCM, that undergoes the phase change, a container for the storage medium and a heat exchanger for transferring heat to and from the storage medium [3]. There are several materials that can be used as PCM, and its phase change temperature is the one limiting the application. Here, the focus will be mainly on building applications which cover DHW, heating and cooling. There are other areas that also implement PCM, for instance, waste heat, concentrated solar power (CSP) plants, freezing, food transport, etc. [13], [14].

1.2.1 PCM classification

Although other phase changes are available (solid-solid, liquid-gas, etc.), here the focus will be on the most common ones, solid-liquid phase change. Many different types of solid–liquid PCMs are employed for thermal storage applications, such as water, salt hydrates, paraffins, and sugar-alcohols. In the following subsections, the various classes of solid–liquid PCMs will be described. A common way to distinguish PCM is by dividing them into organic, inorganic and eutectic PCM [15], as shown in Figure 5.

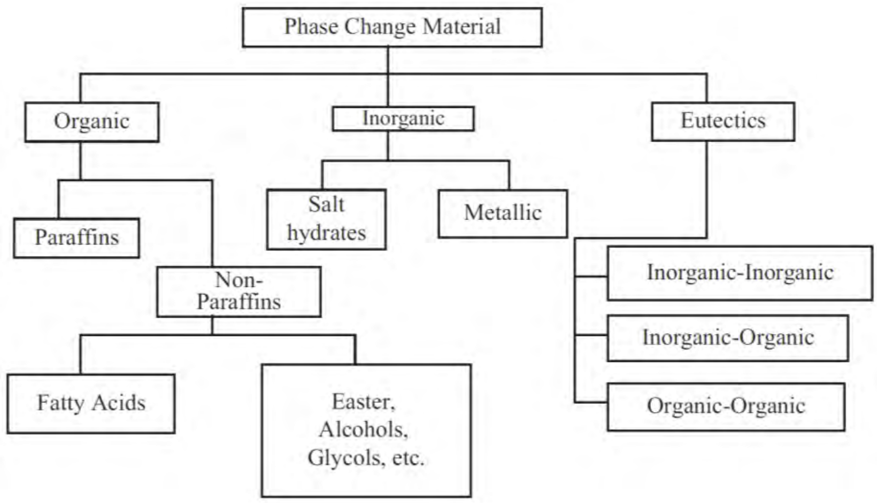

Figure 5. PCM classification in organic, inorganic, and eutectic [16].

Generally, inorganic compounds have almost double volumetric latent heat storage capacity (250–400 kg/dm^3) than the organic compounds (128–200 kg/dm^3) [17]. Inorganic compounds for energy storage also have a higher thermal conductivity than organic compounds. However, they are more corrosive to metallic materials (vessel containers) [18], [19] and subcooling may adversely influence their phase change properties although the use of nucleating and thickening agents may mitigate these disadvantages.

On the other hand, organic compounds are promising as low temperature PCM because they are chemically stable, non-corrosive and exhibit reproducible melting and crystallization behaviour after a high number of thermal cycles [20]. Nevertheless, some of them are flammable and present low thermal conductivity values [5].

A eutectic is a minimum melting composition of two or more components, each of which melts and freezes congruently. During the crystallization phase, a mixture of the components is formed, hence acting as a single component. The components freeze to an intimate mixture of crystals and melt simultaneously with-out separation [15]. Eutectics can be mixtures of organic and/or inorganic compounds.

Table 2. Advantages and disadvantages of organic and inorganic PCM [21].

	Organic	Inorganic
Advantages	No corrosives Low or no subcooling Chemical and thermal stability	High phase change enthalpy High thermal conductivity
Disadvantages	Low phase change enthalpy Low thermal conductivity Flammability	Subcooling Corrosion Phase separation Phase segregation, lack of thermal stability

Furthermore, in order to improve some of the PCM properties, or to prevent corrosion, composite PCM, or also called hybrid, are being developed: encapsulated, mixed with other materials, etc. [22]. Within the available hybrid PCM, several final products can be found, called: shape-stabilized, slurries, microcapsules, etc. [23],[24].

1.2.2 PCM characterization

To proceed in the design of a system implementing PCM, a good characterization of their properties is required.

1.2.2.1 PCM properties

The most remarkable requirements of a PCM, can be defined and classified as [17]:

- Thermal properties: suitable phase-transition temperature, high latent heat of transition, and good heat transfer (high thermal conductivity).
- Physical properties: favourable phase equilibrium, high density, small volume change, and low vapour pressure.
- Kinetic properties: no subcooling and sufficient crystallization rate.
- Chemical properties: long-term chemical stability, compatibility with materials of construction (no corrosive), no toxicity, and no fire hazard.
- Economics: abundant, available, and cost effective.

Both thermal analysis (TA) and calorimetric techniques provide data which can be further evaluated to obtain mainly thermal, kinetic and chemical properties.

1.2.2.2 Thermal analysis techniques

Arkar and Medved [25] and Cho and Choi [26] showed that a perfect knowledge of the thermal properties of the PCM and the way those properties are measured, is necessary to correctly design a latent heat storage system. These properties can be determined experimentally, usually by means of TA techniques, or found in database, chemical handbooks, etc. Tyagi and Buddhi [27] warn the reader about data provided by the manufacturer, which could be erroneous (usually over optimistic).

Several techniques are market available to determine thermal, kinetic and chemical properties of PCM, such as: specific heat, thermal conductivity, latent heat, phase change temperature, subcooling, and thermal cycling stability.

TA differs from calorimetry since the former investigates the behaviour of a sample as a function of temperature or time while calorimetry is based on recording the temperature, or heat of a sample when heating/cooling as a function of time. Differential scanning calorimetry (DSC) is within these two concepts, as the output property is the heat flow as a function of both time and temperature. Here, it will be included in the category of TA techniques [28].

Different thermal analysis techniques exist as shown in Table 3. The choice of the suitable one for experimental data acquisition depends on several variables such as the device outputs, measured values accuracy, experimental setup requirements as sample size, maintenance, etc.

Table 3. Comparison between the four most common TA to characterize PCM [28].

	Thermogravimetric analysis (TGA)	Differential thermal analysis (DTA)	Differential scanning calorimetry (DSC)	*T*-history
Sample size (mg)	10–150	10–150	1–50	15,000
Measurement time (min)	100	100	100	40
Maintenance	++	++	++	+
Equipment price	++	++	++	+
Phenomenon	Thermal stability/decompositio, sublimination/evaportation/dehydration	Decompositio, glass transition, melting	Melting, glass transition, subcooling degree, reaction (curing/polymerization)	Melting, visual phase change, subcooling degree
Thermophysical properties	−%sample mass loss $f(T,t)$	$-\Delta T$ $f(T,t)$ $-H$ $f(T,t)$	$-Cp$ f(T,t) $-H$ $f(T,t)$ $-T_m$	$-Cp$ $f(T,t)$ $-H$ $f(T,t)$ $-T_m$ $-k$

Within the four exposed TA techniques to characterize PCM in Table 3, the first three are commercially available, being DSC the most used one, while the last one, T-history is being developed since 1999 at research labs with increasing attraction [28].

Nowadays, there are still discussions about the accuracy and the appropriate use of these techniques for PCM. For instance, it is well known that DSC results vary as a function of sample mass and heating rate [29],[30]. Also, it is known that the DSC is a complex system and the direct use of the measured curves is not physically correct because some heat transfer phenomena are omitted, the convection in the sample (i.e. capsule), the non-uniformity of the temperature in the sample (conduction), the time needed to heat or cool the sample (inertia) [31]. Therefore, an inverse method to identify the thermodynamic parameters of the sample through a matching step between the experimental curves and theoretical ones has been developed [32]. It relies on the analysis of the experimental thermogram of the sample and its comparison with a numerical one, based on a thermodynamical and heat transfer modeling of the sample, whose thermodynamical parameters may be adapted by an inverse method.

Furthermore, another new DSC measurement method, called the partially melted DSC measurement method, was proposed to determine the ending melting temperature of PCM [[33]], since the determination of the melting temperature range of PCM means to find the starting melting temperature at which PCM starts melting and the ending melting temperature at which the melting process is finished.

T-History technique is not yet commercially available, but several research labs, have built up their own equipment. It allows obtaining fusion and solidification enthalpy and temperature, specific heat as well as conductivity for 10 times bigger samples than DSC. Furthermore, the equipment is less expensive and the maintenance too.

Thermal conductivity of PCM can be obtained with the hot-wire method, T-history method, hot plate measurements, and hot box measurements [34].

Characterization of PCM and hybrid or composite PCM is not always possible to carry out with conventional equipment, mainly due to the sample size. Cabeza et al. [35]

show several equipment developed in different research centres and universities to analyse thermophysical properties, such as specific heat, latent heat and melting temperature, and thermal conductivity and diffusivity of PCM and hybrid PCM materials.

Another very important PCM property that needs to be characterized is the thermal cycling stability [16],[36]. Cycling stability tests ensure long-term performance of a storage unit. A PCM is reliable if it is thermally, chemically and physically stable after a number of repeated thermal cycles [37]. Among the most used techniques to characterize the stability there is DSC. It has been seen that seventeen out of twenty-nine used DSC while the other 41 % were setups exclusively designed to cycle PCM [38].

Other important properties and devices used to characterize PCM and hybrid PCM are described by Fernandez et al. [36]. For instance, Fourier Transformed Infrared Spectroscopy (FT-IR), Raman spectroscopy, and X-ray diffraction are used to check the chemical structure, therefore ensure chemical stability, of the PCM before and after the cycling tests, and Atomic Force Microscopy (ATM) is used to study the morphology and mechanical integrity of microencapsulated PCM with temperature.

In general, one of the obstacles that hinder the development of PCM applied technologies is a critical lack of international technical standards for testing PCM. This has led to research groups employing their own methods for characterizing energy storage materials. Consequently it is difficult to directly compare thermophysical properties such as latent heat of fusion and thermal conductivity and this necessitates the repetition of experiments rather than focusing on the development of novel advanced materials for energy storage [20].

Regarding DSC, one working group experts on materials at the International Energy Agency storage IA (ECES IA), previous Annex 24, and today the follower Annex 29 is specifically working on developing DSC PCM testing standard [39]. Nevertheless, for thermal cycling stability is still missing [38].

1.3 Thermochemical materials

In section 1.1.1 the advantages and disadvantages of thermochemical energy storage have been pointed out. As TCM show promising figures, the research goal is to do steps forward to design optimum systems and make them market available. In that sense, the International Energy Agency Roadmap recommends focusing on R&D to improve control technologies for use in advanced storage systems, including thermochemical storage technologies for medium temperature (10 to 250 ºC) applications [40].

In [41] the authors conclude that although many research studies are ongoing, thermochemical technology is still not at a sufficiently developed stage for commercialisation. Some of the key factors which should be taken into consideration in order to achieve both an efficient and economically feasible system are: reactor design and materials study (i.e. developing new composites).

Other authors state that before being put into practice and commercialised, chemical storage needs to conquer several problems, including low overall efficiency, high cost, corrosion, swelling and clogging, long-term repeatability and stability. Additionally, exploring new materials that are advantageous in terms of storage density and power density is quite necessary [42].

The effective performance of a thermochemical energy system depends on several design parameters [41]:

- Thermochemical material.
- Ambient psychrometric conditions where the storage system will be used.
- System design.
- Reactor design.

Here the focus will be on thermochemical material side and system and reactor design.

1.3.1 TCM classification

TCM are reversible processes, generally known as chemical reactions, which are endothermic in one way, and thus can absorb energy (charge), store it while keeping the products separated (storage), and release the energy, thus exothermic way (discharge), when putting the products in contact again in the required conditions. A general view of the TCM working principle is drawn in Figure 6.

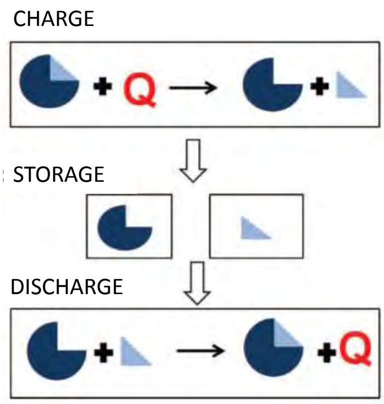

Figure 6. Scheme of thermochemical energy storage.

During the storage period, since the energy is kept in form of chemical bonds, no losses are expected. Only when inducing the exothermic reaction extra energy is needed to heat up the material to let the reaction takes place. This concept makes TCM viable for what is known as seasonal storage, meaning that heat can be stored from summer to be released in winter when heating is needed.

By the moment, there is no agreed classification when talking about TCM. When looking at the literature, the information is confusing and sometimes differs. There are different terms; one could find sorption, thermochemical, and chemical.

As an example, authors proposing different classifications are listed and gathered here:

N'Tsoukpoe et al. [43] consider that sorption comprises physical and chemical, absorption and adsorption. Also, chemical solid/gas reactions are considered as chemisorptions (chemical adsorption) as shown in Figure 7, where salt hydrates would belong to. Abedin and Rosen [44] suggest to refer to the entire category as chemical energy storage and to divide it into sorption and thermochemical reactions, where sorption includes adsorption and absorption. Here, salt hydrates would be in the thermochemical reactions group.

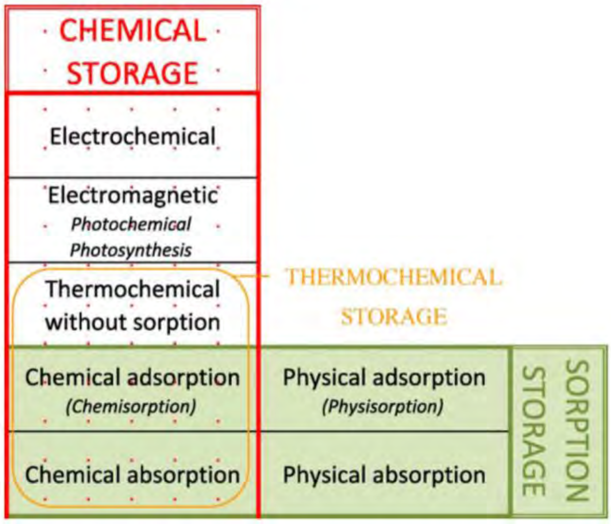

Figure 7. Chemical and sorption storage classification [43].

In Tatsidjodoung et al. [6], thermochemical heat storage materials comprise two big groups: sorption phenomena materials, in within adsorption and absorption are found, and chemical reaction materials, which is also divided into pure and composites thermochemical materials. Here, salt hydrates belong to chemical reactions, pure thermochemical materials. Xu et al. [42] purpose classification for chemical storage is to divide the materials into three big groups: adsorption, absorption, and chemical reaction. Salt hydrates are considered in the adsorption group.

While adsorption and absorption generally present bivariant equilibrium, and therefore two state variables are needed to describe the reaction equilibrium (i.e. temperature and pressure), the chemical reactions, present monovariant thermodynamic equilibrium, which means that one state variable is necessary [45].

The most accepted classification is shown in Figure 8. Adsorption would entail activated carbon/methanol, silica gel/H_2O, zeolites/ H_2O, etc. Absorption includes NaOH/ H_2O, LiCl/ H_2O, $CaCl_2$/ H_2O, LiBr/ H_2O, etc. And chemical or thermochemical reactions are the ones under study in this thesis, from where it can be seen that mostly are gas-solid reactions, where the solid is a salt hydrate and the gas is water vapour.

Recently, in order to enhance some of the materials properties and thus overcome some of the abovementioned TCM problems: overall efficiency, compaction and stability, new TCM are being developed named composites. The main idea is to incorporate the TCM, usually a salt hydrate in an adsorption material (zeolites, silica gel, etc.) [46] or to add an inert (graphite, metal foam, cellulose, etc.). Usually the first pairs are to sum both process energies (chemical and adsorption) and thus increase the storage capacity and the second pairs are thought to increase overall material conductivity and thus enhance mass and heat transfer inside the reactor.

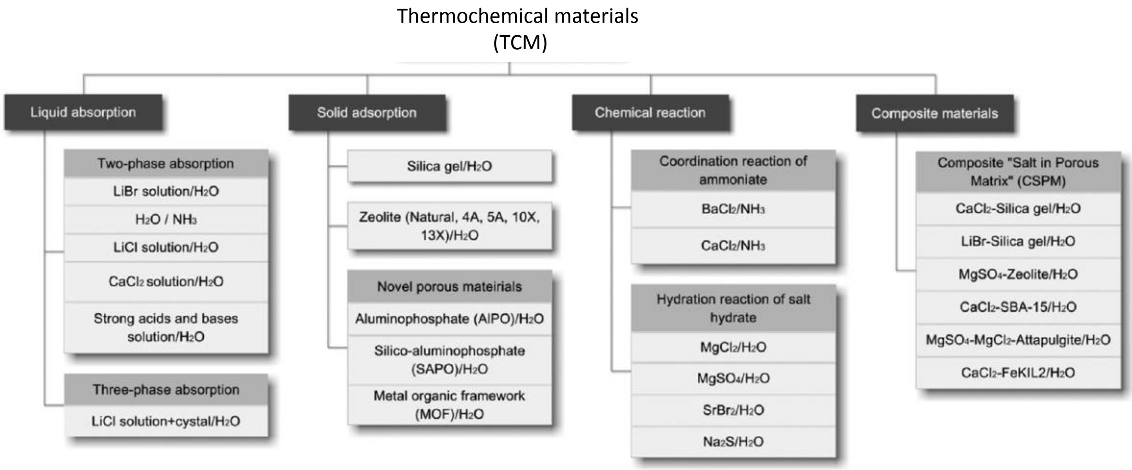

Figure 8. Thermochemical materials classification. Adapted from Yu et al. [47].

High temperature TCM (above 150 ºC) are out of scope of this thesis, since they are not usable for building applications. Nevertheless, there are also TCM under study in high temperature applications (i.e. inorganic oxides/hydroxides for chemical heat pumps, redox for concentrated solar power plants, etc.).

1.3.2 TCM properties

Regarding TCM for building applications, main properties requirements are [48]:

- High energy density: to store the maximum energy in the minimum volume.
- Reaction temperature reachable by a solar collector (below 150 ºC): the heat source to proceed with the endothermic reaction is the sun.
- Non-toxicity and non-flammability: since will be implemented in buildings and need to accomplish health and safety conditions.
- Non-corrosiveness: especially with the reactor material in contact.
- Stable after several hydration/dehydration reactions: to ensure long term performance of the system.
- Low cost: to be market competitive.

When choosing a TCM one of the properties that are the first to look at is the energy density and reaction temperature. The first is wanted to be as high as possible in order to store the maximum amount of energy in the lowest volume. Values of energy densities and reaction temperatures (charging/discharging) of the most common gas-solid TCM for building applications are gathered in Table 4. From this table it can also be observed that usually the experimental energy density is not as high as the theoretical.

Another key parameter is the durability and stability that should be examined under repetitive cycles to demonstrate their operability. With an increasing number of thermochemical cycles, a thermochemical material degrades and its behaviour may change. The stored heat and the overall efficiency of the storage system may decrease over time and numbers of cycles.

Table 4. Theoretical and experimental energy density, reaction temperature and water vapour pressure of several gas-solid TCM [49].

Reaction (TCM) (solid↔solid+gas)	Theoretical energy density (GJ/m^3)	Experimental energy density (GJ/m^3)	Reaction temperature (charging/ discharging) (°C)	$p(H_2O)$(mbar)
$MgCl_2 \cdot 6H_2O \leftrightarrow MgCl_2 \cdot H_2O + 5H_2O$	2.5	0.71	150/30–50	13
$MgCl_2 \cdot 4H_2O \leftrightarrow MgCl_2 \cdot 2H_2O + 2H_2O$	1.27	1.10	118/n.a.	13
$CaCl_2 \cdot 2H_2O \leftrightarrow CaCl_2 + 2H_2O$	1.1	n.a.	95	n.a.
$CaCl_2 \cdot 2H_2O \leftrightarrow CaCl_2 \cdot H_2O + H_2O$	0.60	n.a.	n.a./174	n.a.
	0.72		95/35	
$Al_2(SO_4)_3 \cdot 6H_2O \leftrightarrow Al_2(SO_4)_3 + 6H_2O$	1.9	n.a.	150	n.a.
$MgSO_4 \cdot 6H_2O \leftrightarrow MgSO_4 \cdot H_2O + 5H_2O$	2.37	1.83	72/n.a.	13
$MgSO_4 \cdot 7H_2O \leftrightarrow MgSO_4 \cdot H_2O + 6H_2O$	2.3	n.a.	150/105	n.a.
$MgSO_4 \cdot 7H_2O \leftrightarrow MgSO_4 + 7H_2O$	1.5	n.a.	122–150/122	n.a.
$CaSO_4 \cdot 2H_2O \leftrightarrow CaSO_4 + 2H_2O$	1.4	n.a.	n.a./89	n.a.
$Na_2S \cdot 5H_2O \leftrightarrow Na_2S \cdot 1/2H_2O + 9/2H_2O$	2.7	n.a.	80/65	13
Zeolites 4A	n.a.	0.58	130/65	n.a.
$SrBr_2 \cdot 6H_2O \leftrightarrow SrBr_2 \cdot H_2O + 5H_2O$	2.3	2.08	n.a./23.5	20
$SrBr_2 \cdot 6H_2O \leftrightarrow SrBr_2 \cdot H_2O + 5H_2O$ and vermiculite	n.a.	1.83	n.a./22.3	10
$Li_2SO_4 \cdot H_2O/Li_2SO_4 + H_2O$	0.92	0.80	103/n.a.	13
$CuSO_4 \cdot 5H_2O \leftrightarrow CuSO_4 \cdot H_2O + 4H_2O$	2.07	1.85	92/n.a.	13

Also corrosion is one of the drawbacks that TCM present and needs to be addressed. When working with salt hydrates, water is present and usually the vessel materials of the containers, heat exchangers, and reactors, are metals [50].

1.3.3 Gas-solid TCM reactors and systems

1.3.3.1 Working principle

The core of a thermochemical energy storage system is a reactor that contains a solid (S_0) which reacts with a gas (G) (where υ stands for stoichiometric coefficient), usually water vapour, following an exothermic reaction (where Δh^o_r (J/mol) is the standard enthalpy reaction), which products are another solid (S_1) and heat that can be used for instance for heating a house. This process is reversible as shown in Eq. 1. The endothermic way allows the absorption of thermal energy which will be stored until demanded.

$$S_0 + \upsilon G \leftrightarrow S_1 + \Delta h_r^0 \quad \textit{Eq.1}$$

The equilibrium conditions (p_{eqSG}, T_{eqSG}) of the solid/gas reaction follow the Clausius-Clapeyron relation. This relation is obtained by stating that the free Gibbs energy of this transformation is equal to zero at the thermodynamic equilibrium (Eq.2).

$$\Delta G_r = \Delta G_r^0 + RT_{eqSG} \ln K = \Delta h_r^0 - T_{eqSG} \Delta s_r^0 + RT_{eqSG} \ln K = 0 \quad Eq.2$$

Where G is the free Gibbs energy in ($Jmol^{-1}$), R the gas constant in ($Jmol^{-1}K^{-1}$), T the equilibrium temperature in (K), and K is the equilibrium constant for the solid/gas reaction. Δh_r^0 ($Jmol^{-1}$) and Δs_r^0 ($Jmol^{-1}\ K^{-1}$) are respectively the standard enthalpy and entropy of the solid/gas reaction and p^0 is the reference pressure (1 bar).

Assuming that the reactive gas behaves as a perfect gas, K follows Eq. 3.:

$$K = \left(\frac{p_{eqSG}}{p^o} \right)^{\upsilon} \quad Eq.3$$

Finally, the thermodynamic equilibrium conditions are determined by only one intensive variable: the equilibrium gas pressure p_{eqSG} or the equilibrium temperature of the solid T_{eqSG} (Eq. 4.).

$$\ln \left(\frac{p_{eqSG}}{p^0} \right) = -\frac{\Delta h_r^0}{\upsilon R T_{eqSG}} + \frac{\Delta s_r^0}{\upsilon R} \quad Eq.\ 4$$

The operating principle of a gas-solid reaction (working in a closed reactor see section 1.3.3.2) is represented in Figure 9, where both equilibriums L/V of water and S/G of TCM are depicted in black solid lines.

From Figure 9, Q_d represents the charging heat, from solar collectors and Q_a the available heat to provide heating or DHW to dwellings. Q_c and Q_e are the condensation and evaporation heats of the involved gas reactant, respectively. In closed systems (see section 1.3.3.2) the gas is condensed in order to keep it in liquid state for volume constraints.

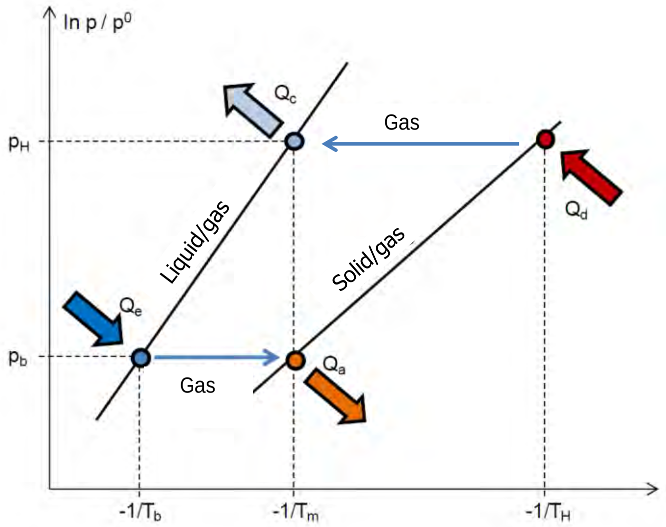

Figure 9. Diagram of Clausius–Clapeyron showing operation principle of a gas-solid TCM in a closed reactor [45].

It can be seen from Figure 9 that there are three levels of temperature, the high temperature (T_H) which is the one coming from solar collectors, usually between 50 and 150 °C. The medium temperature, T_m, is the one which will provide heating to dwellings (a minimum temperature of 35 ºC is needed). And finally, the low temperature, T_b, is the one necessary to evaporate the gas which was kept in liquid state. In this case direct ambient air or ground source, depending on the climate, are used [47]. For instance, for water as gas reactant 10 °C at 12 mbar would be required.

If the starting point is S_1 from Eq.1 and charging process (Q_d) starts, there is an increase of the pressure inside the reactor from initial p_b to p_H. Since gas is being produced, at this moment the reactor is connected to the condenser and condensation of gas (Q_d)

takes place. When the reaction finishes, the reactor is disconnected from the condenser and cools down until T_m, which makes decrease the pressure until p_b. The reactor is at T_m and p_b when the evaporation (Q_e) of gas is induced and connected to the reactor, then the discharging process gives Q_a to be used for heating.

Different lab scale and real scale systems following this principle are being tested with different TCM [42],[49],[51],[52]. Some of them are summarized in Table 5.

Although this technology presents promising advantages, there are still big issues regarding TCM reactor and system design. Mass and heat transfer are sometimes limiting steps [41], high pressure drops and kinetics are not always being addressed [53]. For this, more research is needed from material level to reactor design.

Reactors designed for thermochemical energy storage systems based on gas-solid reactions can be either open or closed. Also, the reactor can act as the container of all solid (integrated) or have it as another equipment, named separated.

1.3.3.2 Open/ Closed

Open systems, as the name suggests, are open to the environment. The gas involved is typically water vapour. For the sorption process during discharging is obtained directly from the ambient air, as shown in Figure 10 left, or in some cases from a moisture source such as a humidifier. This makes open systems weather dependent.

Table 5. Summary of the reviewed solid–gas thermochemical and sorption storage systems; reactors specifications and main outputs [49].

	Monosorp U. Stuttgart 2004	Modestore AEE INTEC 2006	Zondag 2008	PROMES 2008	ECN 2009	U. Stuttgart 2011	PROMES U. Perpignan 2012	Fraunhofer IGB ZeoSys GmbH 2012	PROMES U. Perpignan 2012	TNO 2012	ECN 2013
Applications	Space heating	Space heating	–	Heating and cooling	Properties characterization	Heating	Mass and heat transfer characteriza-tion/House heating	Heating	Solar air conditioning	–	Heating
TCM	Zeolite 4A/ water	Silica gel/ water	Zeolites (Köstrolith beads)/water	$SrBr_2$+ENG/ water	$MgCl_2$ $CaCl_2$ $AlSO_4$ $MgSO_4$ /water	Zeolites and salt impregnated zeolites (9%wt $MgSO_4$ and 1% wt LiCl)/water	$SBr_2 \cdot 6H_2O$/ water	Zeolites and composites (attalpugite and poolkohl+30% $CaCl_2$)/water	$BaCl_2$+ENG/ammonia	Zeolites/water	$MgCl_2$/ water
Reactor	n.a.	n.a.	Fixed bed or stirred	–	Fixed bed	Moving or fixed bed	Fixed bed	–	–	–	Fixed bed
Volume (L)	7850	350 (400 kg silica, 30 kg water)	0.015	1000	0.015	64	0.015	1.5, 15 and 750	19 tubes of 140 kg of anhydrous $BaCl_2$ and 35 kg of ENG	–	17
Water vapour pressure (mbar)	–	–	–	10/60	2.8	1/20	10/18	12/42	–	–	12
TCM system	con- figura- tion	Open and integrated	Closed and integrated	Closed and Integrated	Closed and integrated	Closed and integrated	Open and separated	Open and integrated	Closed and integrated	Closed and integrated	Closed and integrated
Open and	inte-	grated									
Conclusions	12 kW h measured storage capacity	Low storage energy density 13 kW h for heat	Heat transfer inside the reactor is improved when stirring	Stores 60 kW h and 40, for heating and cooling, respectively	Higher temperature lifts are achieved by chlorides. $MgCl_2$ is recommended	Simulation results show constant power of 400 W	Energy densities of about 430–460 kW h/m^3	Specific Heat storage capacity ~200 W h/ kg. Scaling effects were observed	Daily cooling productivity at 4 °C of about 0.8–1.2 kW h of cold per m^2 of flat plate solar collector	Output power of about 0.6 kW/kg of active material	Effective energy storage density of 0.5 GJ/m^3
Reference	14	14	11	41	22	9, 42	21	43	8	44	45

Where n.a. stands for not available.

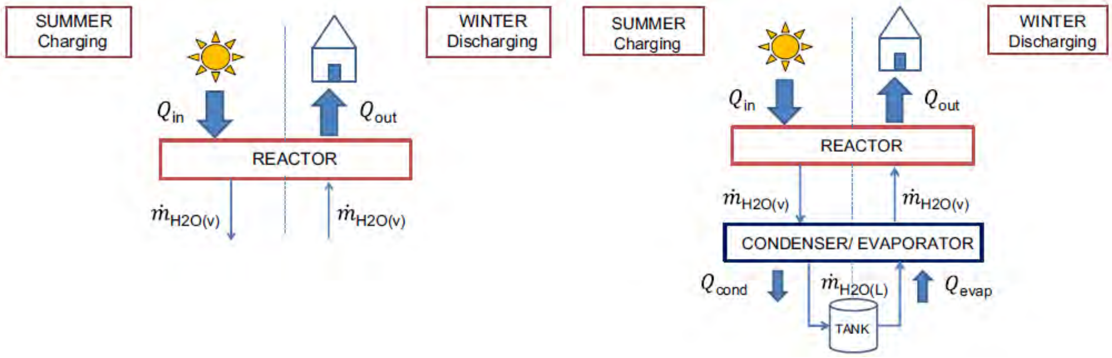

Figure 10. Open (left) vs. closed (right) systems with integrated reactor [49].

A closed system has no mass exchange with the environment and requires and evaporator/condenser for the evaporation of water when required as a reactant and to condense it when storage, as can be seen in Figure 10 right. During discharge, evaporation of the working fluid is necessary and therefore a low heat source (T_b in Figure 9) is required. As the most common working fluid is water the temperature of this heat source commonly needs to be at least 5 ºC in order to evaporate water under vacuum conditions. Usually closed systems operate under vacuum conditions for optimal mass transport in the reactor [54]. How this heat should be supplied to the system during the heating season is not always mentioned in research papers but is still a key point that can make decide if as system is feasible or not [7].

On the contrary, the open system allows a simpler manufacturing of the reactor. The evaporator/condenser is not necessary, which does not affect negatively the apparent energy density of the storage system. Nevertheless, this working mode results in a flow of vapour and air through the bed, and the total flow is significantly higher than in the previous case. Thus, mass transfer must be carefully considered [55]. Moreover, although at the beginning of the reaction there is good vapour diffusion within these systems, as the time passes, the diffusion shows a decreasing trend and results in a corresponding drop in ΔT. This causes instability during heat generation, which is not evidenced in closed sorption systems. In closed cycles, the generated heat can be stored sensibly and the amount extracted can be altered by changing the parameters of the heat transfer fluids (e.g. mass flow rate) [41].

A comparison between open and closed systems has been published by Michel et al. [55], who concludes that for the closed system, the heat transfer is the main limitation, and a small increase of the thermal conductivity strongly improves the reaction rate. For example, a conductivity which is two times higher than the reference bed conductivity decreases the reaction time of about 14%. For the open system, the mass transfer is the main limitation and the hydration rate can be improved by acting on the bed permeability: doubling the permeability leads to a half reaction time. Both operating modes lead to close global performances. Thus, the open thermochemical reactor, which presents technical advantages (easier conception and management, lower cost, etc.), is a promising way to implement a thermochemical process as long-term heat storage.

Other authors also compared open and closed systems but for physical adsorption (zeolites 13X). The overall system energy and exergy efficiencies, respectively, are determined to be 50% and 9% for the closed storage, and 69% and 23% for the open storage. The results suggest that there is a significant margin for loss reduction and efficiency improvement for closed and open thermochemical storages, since the exergy efficiencies of both are significantly lower than the energy efficiencies [56].

1.3.3.3. Integrated/Separated

Another possible configuration is to have an integrated or separate reactor. In the integrated reactor system (Figure 11 b), the absorption/release of energy (reaction) occurs within the storage vessel, while the separate reactors (Figure 11 a) concept consists in transporting the TCM from the storage vessel to the reactor and to another storage vessel, after reacting, as illustrated in Figure 11.

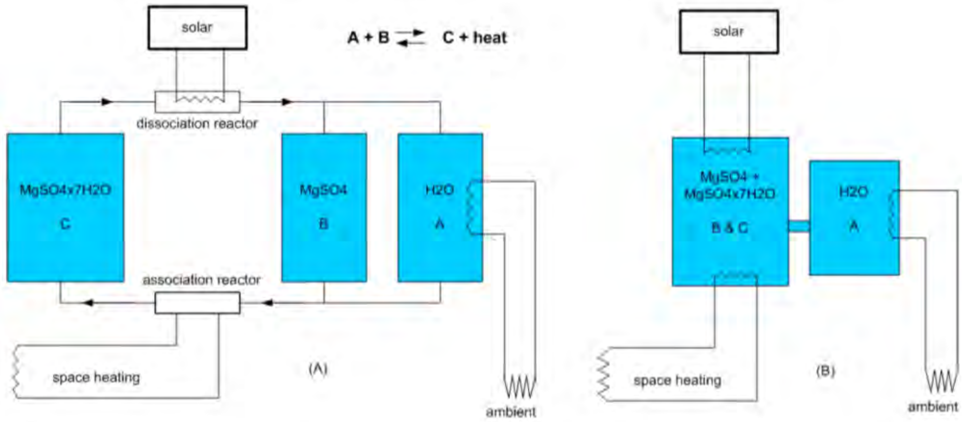

Figure 11. (a) separated reactor, (b) reactor integrated in storage [57].

If the TCM material is a solid, preferably integrated reactors are used. This has the advantage that it is not necessary to transport the solid material, thus less power consumption. However, for large storages such as seasonal storage, this also has disadvantages such as a larger sensible heat loss, since then the whole reactor content has to be heated up before dehydration occurs [57]. Furthermore, the required heat exchange area is much larger than for a separate reactor. In a separate reactor, it is possible to heat up only the required amount of TCM, thereby making the charging process much more efficient. Also, the heat and vapour transfer can be optimised within a separate reactor by stirring of the material.

2 Objectives

The present thesis aims to contribute in providing new knowledge to the thermal energy storage field. Two available TES technologies will be the focus of this thesis: PCM and TCM. The first technology has been widely researched and it is used domestically and industrially, but there are still some issues related to material level and design to be improved. The second technology is a promising one and a lot of research is focused on it today. However, it is still at research level and no commercial systems are available yet. Therefore, the main objective of this PhD thesis is to provide a step forward in PCM characterization, specifically going in depth in quite new techniques, and placing a special emphasis on thermal cycling studies. Furthermore, in the TCM field, the main aim is to look for synergies between material and reactor scale towards overcoming the observed obstacles that this technology presents and thus contribute on the commercialization of it.

To fulfil this global objective, several sub-objectives are detailed for each part of the thesis.

In the PCM part:

- To provide an overview on non-conventional, self-developed PCM characterization techniques.
- To bring together all the information about a non-commercial thermal analysis technique to characterize PCM, named T-history, from its development (1999) to present.
- To study thermal cycling stability of sugar alcohols in deep and provide solutions if degradation is observed.

In the TCM part:

- To look for synergies between material and reactor level in order to provide knowledge to improve the low experimental reactor yields of the present setups.

- To go a step forward in TCM reactor design by bringing together the chemical engineering knowledge of reactor design and the already tested TCM reactors and systems for building applications.
- To study one of the main drawbacks of TCM, this is corrosion between them and the material vessel in contact under different conditions (pressure, temperature, and atmosphere). To do so, a new experimental set up has been designed and built.
- To provide solutions to prevent corrosion of a selected TCM under vacuum conditions.
- To develop new TCM composites based on graphite in order to obtain high conductive storage materials and thus enhance heat transfer in the reactor.

3 PhD thesis structure and methodology

The PhD thesis counts with eight papers; six of them have already been published in SCI journals while the other two have been submitted.

The thesis is within the frame of thermal energy storage mainly for building applications. It is organized in two big parts PCM and TCM as can be seen in Figure 12. These two available TES technologies have already been presented and explained in detail in the introduction and the main objectives stated in the objective section.

In the PCM part, the focus is put on material characterization, being an essential step to select the optimum PCM for a given application and also for accurate system simulations and design. **Paper 1** provides a review of the available thermal analysis techniques to characterize PCM, especially one which is not commercial, and it is being quite use at the present, named T-history. Then, **paper 2** is also a review of characterization techniques, but the focus is more on physico-chemical and mechanical stability and morphological techniques, especially the non-conventional ones.

Paper 1 and paper 2 approach analytical techniques which can be used to characterize all kinds of PCM. Although T-history is mainly used to characterize PCM with melting temperatures below 100 ºC, new setups are being built for higher temperatures.

In **paper 3** a study about thermal cycling stability, one key property, most times forgotten, when characterizing a PCM is presented. In particular, it is an experimental study of thermal cycling stability of sugar alcohols as PCM. Sugar alcohols melting temperatures make them viable for waste heat and solar cooling, being between 100 and 200 ºC.

The TCM part is in the line of looking forward to come with an optimum system to be market competitive. To do so, several issues need to be addressed. First, from the literature it was observed that the theoretical reactor yield containing TCM was far to be experimentally achieved. One of the missing studies in TCM papers is an accurate kinetic model of each TCM reaction. In that sense, **paper 4** is a compilation and a guide to provide tools at material level for the TCM scientific community to obtain a reliable kinetic model for TCM reactions. One other possibility that can be an obstacle to obtain the desired reactor output is the reactor and system design. In **paper 5**, a first attempt towards the reactor and process design is provided. Therefore, a review of what has been done seeking for the main experimental reactors outputs and to bring knowledge from the chemical engineering reactors is presented.

From the material level research and reactor level review it was observed that two big issues could be studied which would contribute in useful results for the TCM technology development: corrosion between the TCM and vessel material and the enhancement of some properties of the TCM itself to promote heat and mass transfer.

Corrosion has been studied simulating open and closed TCM reactors, thus under different ambient conditions, and is presented in **paper 6** and **paper 7,** respectively. In **paper 8**, the aim is to contribute in improving the overall system efficiency, but mainly in the reactor, by enhancing thermal conductivity of TCM. Graphite has been selected as high conductive material to develop new and enhanced TCM and thus increase principally heat transfer in the reactor.

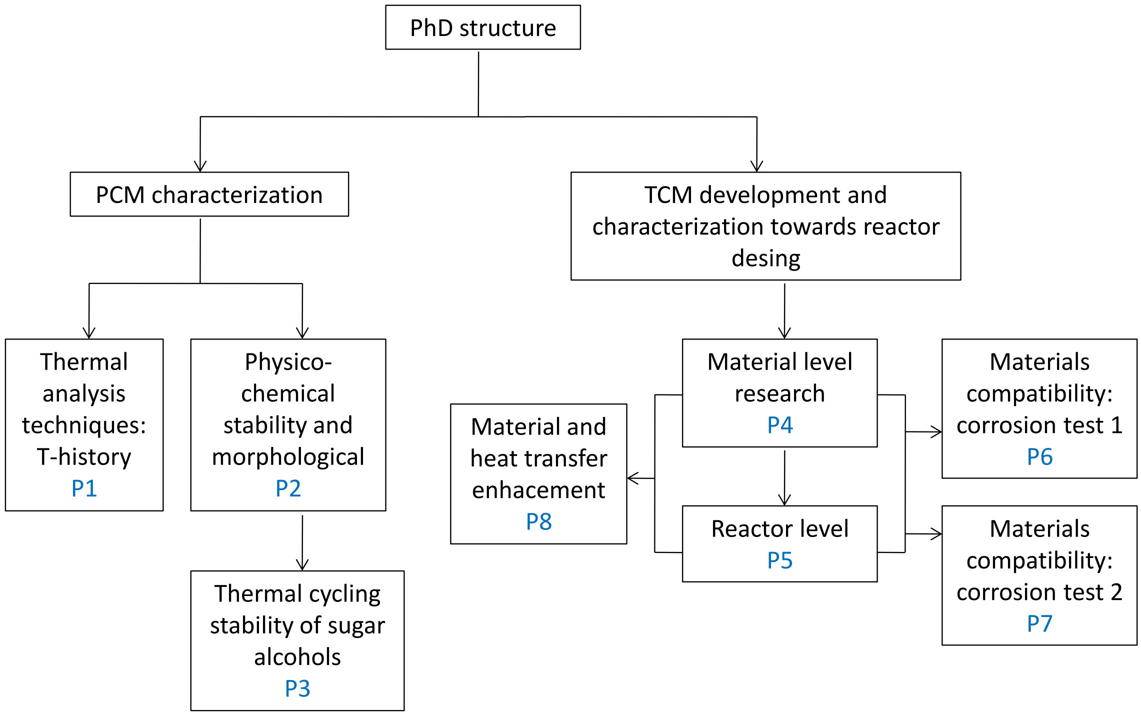

Figure 12. PhD structure.

4 P1: Review of the T-history method to determine thermophysical properties of phase change materials (PCM)

4.1 Introduction

In order to design a system for thermal energy storage based on PCM, this material needs to be perfectly characterized. There are several important thermophysical material properties to take into account, as described in section 1.2.2.1. To do a first material screening, mainly phase change enthalpy (latent heat) and temperature are needed.

Thermal analysis techniques allow obtaining the desired properties which are temperature dependent, such as phase change enthalpy. Within the techniques that allow measuring, at least, the latent heat and phase change temperature there are the differential scanning calorimeter (DSC), differential thermal analysis (DTA), T-history, 3-layer calorimeter, and self-developed devices [35]. Only the first two are commercial. The need to develop new techniques which are more suitable to test PCM exists. Therefore, in 1999 Yinping [58] developed T-history method to determine PCM thermophysical properties. This method presents certain advantages when compared to the already available ones, for instance large sample testing (around 10 mg), optimized measuring time, simple and economic setup and less equipment maintenance.

4.2 Contribution to the state-of-the-art

The main contributions to the state-of-the-art of the T-history review are to do a review about the method itself and to provide details and establish comparisons between all the published contributions from 1999 to 2012. From 1999 to the present, several papers have been published contributing on the improvement of this method. Those contributions are reviewed and classified while providing details in different sections such as experimental setup, mathematical model, and data evaluation improvements and is published in one paper:

- A. Solé, L. Miró, C. Barreneche, I. Martorell, L.F. Cabeza. Review of the T-history method to determine thermophysical properties of phase change materials (PCM). Renewable and Sustainable Energy Reviews 26 (2013) 425-436.

The main contributions achieved during these years are a better accuracy of the results, temperature dependent properties data evaluation instead of time, setup robustness, controlled cooling and automation, and implementation of control elements (PID).

Moreover, a contextualization with previous similar methods is provided. The basis of T-history method might lay on different previous methods. Three publications about self-developed devices to measure phase change thermophysical properties based on the same principle were found and are described here.

This paper provides a step forward into the standardization and possible commercialization of this technique. Still nowadays research groups are building up new setups suggesting new modifications.

In these two years, since this paper was submitted up to the present day, other papers related to T-history technique have been published. Then, it has been thought useful to provide an update of the state-of-the-art. One paper has been found which suggest improvements and present a new setup of T-history method.

Rathgeber et al. [59] present a new T-history setup which main improvement is in the temperature range. This new setup allows testing from 40 to 200ºC. Then water cannot be used as a reference due to its boiling point and instead copper is used. Rathgeber remarks that the new T-history is based on their experience with an existing T-history instrument that has an operating temperature range of approximately -15 °C to 80 °C [60]. It is also continued the suggestion of insulating the tests tubes and place them in horizontal position.

This publication aims to improve the measuring accuracy of the T-history method. A three-part procedure, consisting of an indium calibration, a measurement of the specific heat of copper and measurements of three solid–liquid PCMs (stearic acid, dimethylterephthalate and D-mannitol), was performed and an advanced procedure for the correction of enthalpy curves was developed. Thus, this design of a T-history calorimeter together with the developed calibration procedure provides the measuring accuracy that is required to identify the most suitable PCM for a given application (± 0.001 for enthalpy and ± 0.02 for specific heat capacity).

4.3 Journal paper

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Review of the *T*-history method to determine thermophysical properties of phase change materials (PCM)

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ABSTRACT

Phase change materials (PCM) are able to store thermal energy when becoming liquid and to release it when solidifying. Latent heat storage has gained importance due the applications towards increasing energy efficiency in several systems. Thus, a correct and accurate thermal characterization of these materials should be achieved. Among all possible thermal analysis methods to determine PCM thermophysical properties, the *T*-history method presents certain advantages. The *T*-history method is known to be suitable to obtain fusion enthalpy, specific heat and thermal conductivity for large phase change materials samples. On the other hand, no experimental *T*-history equipment is commercially available yet. Therefore, the goal of this paper is moving towards a consensus. To achieve this goal, a collection of similar methods previous to *T*-history are exposed and different proposals based on improving the original *T*-history method are discussed and reviewed.

The pages 37 to 48 contain the article:

A. Solé, L. Miró, C. Barreneche, I. Martorell, L.F. Cabeza. Review of the T-history method to determine thermophysical properties of phase change materials (PCM). Renewable and Sustainable Energy Reviews 26 (2013) 425-436.

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5 P2: Unconventional experimental technologies used for phase change materials (PCM) characterization: part 2 – morphological and structural characterization, physico-chemical stability and mechanical properties

5.1 Introduction

Characterization of PCM and hybrid PCM composites (see Introduction section 1.2.2) is of great interest for the scientific community, because it is of extreme importance for the deployment of such materials into the market. In previous articles [28], [35] special attention was paid to the characterization of thermophysical properties showing the difficulties of using commercial equipment with composite materials and/or samples size above few milligrams.

Although the thermophysical properties are the main selection criteria for the use of PCM, other important properties such as chemical stability, crystalline structure or mechanical properties are extremely important to predict the performance of the PCM and hybrid PCM composites. Characterization of hybrid materials has different approaches depending on the scale (nano- and micro-to bulk and macro- scale). The morphological and structural characterization gives information on crystalline characteristics, and how the micro-structure may be affected by cycling the hybrid material. PCM crystalline structure is evaluated when cycling the material and with temperature changes. Matrix structure or even the encapsulating coating materials may also be evaluated in terms of volume expansion while melting and also the change in their mechanical properties. Chemical stability of the hybrid materials is also a key issue. Cycling organic materials may lead to a partial degradation that is reflected then in thermal properties (see paper 3). Related with the chemical stability there is the compatibility of the composite, how the PCM is affecting the matrix properties, that is, chemical, mechanical or even fire resistance properties.

5.2 Contribution to the state-of-the-art

The main contribution to the state-of-the-art is to present different non-conventional methods for the analysis of morphological and structural characterization of hybrid PCM composites, physico-chemical stability and mechanical properties available in different institutions around Europe. This is presented in the following paper:

- A. I. Fernández , A. Solé, J. Giró-Paloma, M. Martínez, M. Hadjieva, A. Boudenne, M. Constantinescu, E. M. Anghel, M. Malikova, I. Krupa, C. Peñalosa, A. Lázaro, H. O. Paksoy, K. Cellat, J. Vecstaudža, D. Bajare, B. Sumiga, B. Boh, T. Haussmann, S. Gschwander, R. Weber, P. Furmanskim, M.Jaworskim, L. F.Cabeza. Unconventional experimental technologies used for phase change materials (PCM) characterization: part 2 – morphological and structural characterization, physico-chemical stability and mechanical properties. Renewable and Sustainable Energy Reviews 43 (2015) 1415-1426.

This review was carried out in the frame of the European COST Action TU0802, with different institutions involved, developing a stable network of scientists. As part of the University of Lleida, the contribution is mainly in the physico-chemical stability part, specifically in the compatibility between PCM and container materials.

The described techniques in the paper are classified in three main topics as follows:

- Morphological and structural characterization of hybrid PCM composites:
    - X-ray
    - Optical and thermal microscopies
    - Scanning electron microscopy
    - Atomic force microscopy
    - Molecular spectroscopies
- Physico-chemical stability:
    - Chemiluminiscence
    - Chemical stability related to fire testing
    - Compatibility between PCM and container materials
    - Rheological behaviour

- Thermal stability investigation
- Physical stability of slurries

- Mechanical properties:
  - Mechanical characterization at nanometric scale
  - Loss of mechanical properties of polymers in contact with paraffin evaluation using nanoindentation

In addition to provide a list of non-conventional techniques for PCM and hybrid PCM characterization, there is useful information for the researchers working in this topic such as: measurement parameters, experimental tests results, and the main outputs from each technique applied to PCM. The major outcomes from each technique are:

- Changes after cycling may be followed by X-ray diffraction. Moreover, it is possible to calculate the crystallite size, and with additional data the degree of crystallinity and the time of the fastest crystallization.
- The optical microscopy is used to control crystal formation, size, allocation and modification before and after thermal cycling in PCM slurries.
- Scanning electron microscopy (SEM) is useful to evaluate PCM particle shape, the quality of the cover in the case of slurries, and the dispersion of fillers inside. The thickness of the microcapsules can be evaluated as well.
- Atomic force microscopy (AFM) is used to evaluate the morphology and mechanical integrity of microencapsulated PCM with temperature.
- Raman spectroscopy is a very useful technique in studying chemical structure and morphology of heterogeneous materials as the PCM composites.
- Fourier Transformed Infrared Spectroscopy (FT-IR) with an attenuated total reflectance (ATR) accessory was used to characterize wood-PCM composites. Degradation of composites after fire testing can also be evaluated by coupling these two techniques.
- FT-IR analysis is used to test the chemical stability. The approach is to carry out FT-IR analysis before and after thermal cycling and to compare the characteristic peaks obtained in the spectra.

- Chemiluminiscence is suitable for the detection and measuring of thermal oxidation of polymers or thermal decomposition.
- Chemical compatibility between the PCM, the shape stabilized PCM, PCM slurries and the materials containing them are usually carried out following protocols of corrosion tests.
    - For inorganic PCM corrosion of metallic containers is given as a rate of corrosion.
    - When plastic containers are considered, migration of PCM within the container and water sorption through the plastic wall is usually evaluated by gravimetric analysis after cycling the PCM.
- A controlled stress rheometer is used to study the rheological behaviour of PCM. For those materials that will be pumped in real applications, the viscosity versus share rates and the viscosity versus temperature curves are obtained. For those materials that will remain at rest, viscosity versus temperature curves are obtained with share rates close to zero.
- A calorimeter for fast tests of the stability of thermal properties of PCM during consecutive cycles of melting and solidification was designed and its scheme is shown in the paper.
- A test rig to test Phase Change Slurries (PCS) is described. It contains plate type heat exchangers, centrifugal pumps, a 500 L storage tank and sensors to measure all relevant volume flows and temperatures.
- The grid indentation technique has been employed to isolate the mechanical properties of a composite material or graphite foam and salt. The mechanical properties (hardness and Young's modulus) for individual phases can be isolated, as well as their surface volume fractions at nanometric scale.
- Nanoindentation technique is adequate to evaluate mechanical changes in the surface and in the internal properties of polymers when exposed to paraffin for a long time.

Compatibility tests between PCM and metals and polymers were carried out at the University of Lleida [61]. The tested PCM are used for cold storage applications (between -22 and -16 ºC) where they are normally encapsulated in containers, i.e. in food processes.

Nine of the tested PCM are own formulations and three are commercial [62]. Four of the PCM contain gelatine (CMC) in their formulation in order to enhance the PCM viscosity and to prevent leaks from the container to the storage/transport unit. Copper, aluminium, stainless steel, and carbon steel were the metals considered as containers and polypropylene (PP), high density polyethylene (HDPE), polyethylene terephthalate (PET) and polystyrene (PS) were the polymers tested.

Corrosion evaluation between metals and PCM follows the standard ASTM G1 and compatibility evaluation between polymers and PCM is done by calculating the mass change percentage looking for absorption or dilution of the polymer.

Results are gathered in Table 6 and Table 7 for metals and polymers, respectively. To sum up, the most suitable metal to act as a cold storage container to encapsulate PCM containing salts solution is stainless steel. Moreover, the addition of little quantities of a thickening material (CMC) in the PCM formulations reduces significantly the corrosion rate. On the other hand, PP, PS, PET and HDPE can be perfectly used as cold storage container to encapsulate the studied PCM.

Table 6. Results of PCM and metals compatibility [36].

	Aluminium	Brass	Copper	Steel	Stainless steel	Carbon steel
$NaOAc \cdot 3\ H_2O$	R	CR	CR	R	R	–
$Na_2S_2O_3 \cdot 5\ H_2O$	R	NR	NR	R	R	–
$CaCl_2 \cdot 2\ H_2O$ (TH29)	NR	R	R	NR	R	–
TH29 + $MgCl_2 \cdot 6\ H_2O$	NR	R	R	NR	R	–
$NaNO_3 + H_2O$ + additives(C-18)	NR	–	NR	–	R	NR
$NaCl + H_2O$ (E-21)	NR	–	NR	–	R	CR
$NaCl + H_2O$ + 1% CMC	NR	–	NR	–	R	CR
19% $NH_4Cl + H_2O$	NR	–	NR	–	R	NR
19% $NH_4Cl + H_2O$ + 1% CMC	CR	–	NR	–	R	NR
19% $NH_4Cl + H_2O$ + 3% AlF_3	NR	–	NR	–	R	NR
19% $NH_4Cl + H_2O$ + 3% AlF_3 + 1% CMC	NR	–	NR	–	NR	NR
19% $NH_4Cl + H_2O$ + 3% NaCl	NR	–	NR	–	R	NR
19% $NH_4Cl + H_2O$ + 3% NaCl + 1% CMC	R	–	CR	–	R	CR

CMC: thickening agent, R: Recommended, CR: Caution Recommended, NR: Not Recommended.

Table 7. Percentages of mass change of tested polymers with PCM [36].

PCM used	PP			HDPE		PET			PS			12 wk
	1 wk	4 wk	12 wk	1 wk	4 wk	12 wk	1 wk	4 wk	12 wk	1 wk	4 wk	
$NaNO_3+H_2O$+additives (C-18)	0.04	0.01	0.03	0.01	0.00	0.01	0.20	0.12	0.19	0.13	0.00	0.10
$NaCl+H_2O$ (E-21)	0.02	0.01	0.03	0.01	0.00	0.01	0.20	0.09	0.22	0.01	0.00	0.00
$NaCl+H_2O$+ 1% CMC	0.00	-0.01	0.02	0.01	0.00	0.01	0.20	0.12	0.21	0.05	0.03	0.03
19% NH_4Cl+H_2O	0.00	-0.01	0.01	0.01	0.00	0.01	0.22	0.15	0.30	0.02	0.01	0.02
19% NH_4Cl+H_2O+ 1% CMC	0.01	-0.01	0.02	0.02	0.00	-0.01	0.23	0.17	0.29	0.03	0.00	0.02
19% NH_4Cl+H_2O+ 3% AlF_3	0.00	0.01	0.01	0.00	0.02	0.01	0.11	0.22	0.28	0.01	0.00	0.00
19% NH_4Cl+H_2O+ 3% AlF_3+ 1% CMC	0.00	0.02	0.01	-0.01	0.01	0.02	0.12	0.24	0.28	0.00	0.02	0.01
19% NH_4Cl+H_2O+ 3% NaCl	0.01	-0.01	0.01	0.01	0.00	0.00	0.21	0.14	0.26	0.01	0.00	0.00
19% NH_4Cl+H_2O+ 3% NaCl+ 1% CMC	0.00	-0.01	0.01	0.01	0.00	0.01	0.21	0.15	0.28	0.02	0.01	-0.02

5.3 Journal paper

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Unconventional experimental technologies used for phase change materials (PCM) characterization: part 2 – morphological and structural characterization, physico-chemical stability and mechanical properties

CrossMark

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ABSTRACT

Due to the high interest of appropriate characterization of PCM and hybrid PCM composites, different research centres and universities are using several material characterization techniques not commonly used with PCM, to study the structure and morphology of these materials. Likewise, physico-chemical stability is a crucial parameter for the performance of latent storage materials during time and its evaluation has been done by using molecular spectroscopy, chemiluminiscence or calorimetric tests. Atomic force microscopy and nanoindentation are also reported to characterize hybrid PCM composites.

The pages 56 to 67 contain the article:

A. I. Fernández , A. Solé, J. Giró-Paloma, M. Martínez, M. Hadjieva, A. Boudenne, M. Constantinescu, E. M. Anghel, M. Malikova, I. Krupa, C. Peñalosa, A. Lázaro, H. O. Paksoy, K. Cellat, J. Vecstaudža, D. Bajare, B. Sumiga, B. Boh, T. Haussmann, S. Gschwander, R. Weber, P. Furmanskim, M.Jaworskim, L. F.Cabeza. Unconventional experimental technologies used for phase change materials (PCM) characterization: part 2 – morphological and structural characterization, physico-chemical stability and mechanical properties. Renewable and Sustainable Energy Reviews 43 (2015) 1415-1426.

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6 P3: Stability of Sugar alcohols as PCM for thermal energy storage

6.1 Introduction

Thermophysical properties of PCM, such as phase change enthalpy and temperature, need to be experimentally determined by thermal analysis techniques. A comparison of these techniques is given in [28], [35]. Moreover, other important properties like morphological and structural characterization, physic-chemical stability and mechanical properties can be characterized by other techniques gathered in [36]. Within these last properties, cycling stability is a crucial factor for the long term performance of the system containing the storage material, in this case PCM. That implies that after a repeated number of melting and freezing cycles, thermophysical properties and chemical structure of the selected PCM remain the same.

Rathod and Banerjee [16] showed in a recent review, about thermal stability of phase change materials used in latent heat energy storage systems, all cycling test results that have been carried out concerning different types of PCM. Sugar alcohols, except erythritol, had not been studied yet in terms of cycling stability.

Sugar alcohols melting temperatures make them suitable for medium temperature applications for solar process heat or waste heat recovery. Furthermore, sugar alcohols are very interesting PCM due to their advantages referring to high enthalpy values, no toxicity, and low cost, but they have not been studied as much as paraffin and salt hydrates. Nevertheless, one disadvantage of sugar alcohols is high hysteresis (temperature difference between melting and solidification).

6.2 Contribution to the state-of-the-art

The contribution of this paper to the state-of-the-art is to study three potential sugar alcohols (SA), D-mannitol, myo-innositol, and galactitol, by performing thermal cycling stability test to see if they are suitable to be implemented in real systems. In the case that the selected sugar alcohols present degradation, a solution is investigated and suggested. The publication showing these results is:

- A. Solé, H. Neumann, S. Niedermaier, I. Martorell, P. Schossig, L. F. Cabeza. Stability of sugar alcohols as PCM for thermal energy storage. Solar Energy Materials & Solar Cells 126 (2014) 125-134.

Desired phase change temperature was set between 100 and 250 ºC for application requirements since this study was in the frame of a European project called SAMSA. A high phase change enthalpy (ΔH) and material density are determining when choosing a PCM as a first screening. For all these reasons, D-mannitol, myo-inositol and galactitol were selected to perform stability tests (see specific values in the paper).

Twenty and fifty cycles were performed, with two samples of each (to ensure repeatability), in a DSC at 10 K/min and their thermophysical properties determined before and after the test, also by DSC at 1 K/min. FT-IR was carried out also before and after the cycling test to study their chemical stability and changes in the molecular scale, bonds and functional groups. Moreover, tests trying to control some parameters affecting SA cycling stability, i.e. the oxygen presence and temperature range, were performed.

The main results obtained in this paper explain that myo-inositol and D-mannitol present different polymorphic phases formation depending on the temperature range that the PCM was cycled. That effect should be taken into account when designing the system minimum and maximum permissible operating temperatures, since the change in one polymorph to another has a negative effect on the energy stored or released.

On one hand, myo-inositol shows good cycling stability besides the FT-IR results depict changes in the chemical structure which does not seem to affect its thermophysical properties. On the other hand, galactitol shows poor cycling stability since before the 20th cycle, solidification temperature had decreased by almost 50 %.

Also, D-mannitol showed poor cycling stability. FT-IR results show vibrations of CO (carbon oxide) double bonds of ketones, acids or aldehydes. This is a hint for oxidation during cycling. D-mannitol was studied more in depth and the most remarkable result is the effect of the oxygen presence which was found to be the cause of this SA poor cycling stability. Figure 13 shows clearly that when the atmosphere is controlled (no oxygen presence: totally filled crucible) D-mannitol shows the desired cycling stability for a PCM. When oxygen is in contact with this SA, not only the phase change temperature decreases but also the phase change enthalpy.

Therefore, when designing a system containing D-mannitol, vacuum or inert atmosphere are suggested in order to ensure no oxygen presence and thus good cycling stability.

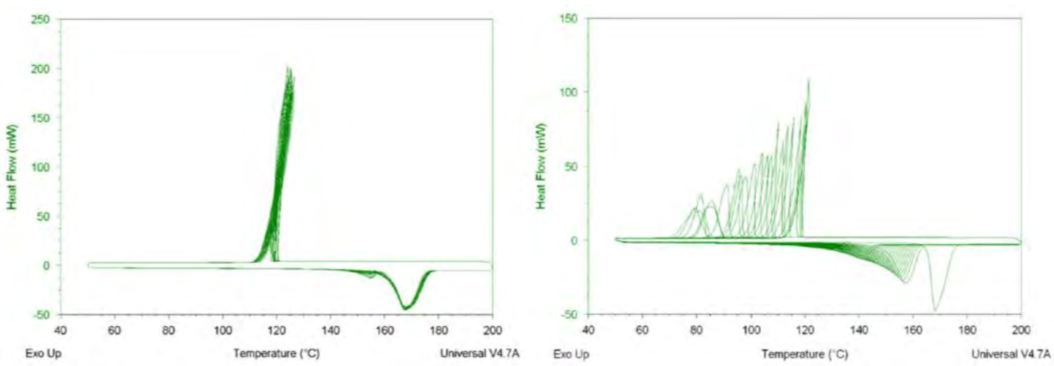

Figure 13. DSC response comparison between totally filled D-mannitol crucible (left) and partially filled D-mannitol crucible (right)[1].

[1] In the published paper there is an error and it is written in the other way (left and right).

6.3 Journal paper

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Stability of sugar alcohols as PCM for thermal energy storage

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ABSTRACT

Sugar alcohols as phase change materials (PCM) are very promising due to their high storage capacity, safety and economic reasons. Their phase change temperatures make them suitable for medium temperature storage, which is needed for solar process heat or waste heat recovery applications. To guarantee a long PCM working lifetime they should be tested under a repeated number of freezing/melting cycles to check whether the thermophysical properties remain constant or not. The cycling stability of D-mannitol, myo-inositol and galactitol has been studied with DSC and the chemical stability with FT-IR. Myo-inositol shows a good cycling stability under the chosen measuring parameters. The cycling and chemical stability of D-mannitol up to 20 cycles can be achieved by controlling some parameters. The variable affecting it the most is the amount of oxygen in contact with it. Hence, in the storage unit this could be prevented with an inert or vacuum atmosphere.

The pages from 72 to 81 contain the article:

A. Solé, H. Neumann, S. Niedermaier, I. Martorell, P. Schossig, L. F. Cabeza. Stability of sugar alcohols as PCM for thermal energy storage. Solar Energy Materials & Solar Cells 126 (2014) 125-134.

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7 P4: Requirements to consider when choosing a thermochemical material for solar energy storage

7.1 Introduction

On the contrary to PCM, TCM technology is still at research level and not available at commercial scale. This is the reason why this thesis focuses on both the material level and also the reactor level, looking for synergies between these two big knowledge areas to be able to provide a step forward in the scientific community for TCM technology development.

Focusing on TCM material level, development and characterization of chemical reactions is one of the areas under research. Different systems have been studied so far, with applications in different climates [63]. The most researched systems are those where the material change from oxide to hydroxide, like CaO–$Ca(OH)_2$ and MgO–$Mg(OH)_2$, and those that change from a hydrated form to another, like $CaSO_4 \cdot xH_2O$, $MgSO_4 \cdot xH_2O$, $CaCl_2 \cdot xH_2O$, and $MgCl_2 \cdot xH_2O$ (x = 0, 1/2, 1,... , n). All mentioned systems belong to solid–gas reactions, involving the release of water. For these considered reactions, several features regarding the solid should be taken into account when characterizing the system. Nevertheless, a complete study on solid reactants and products is missing when designing a technology based on TCM which could lead to an unexpected, lower, reactor yield.

7.2 Contribution to the state-of-the-art

The present paper is the first step towards the second big part of this thesis entitled thermochemical (TCM) development and characterization towards reactor design. The motivation and contribution to the state-of-the-art of this paper is to provide a pathway to finally obtain a reliable kinetic model which would be useful for an accurate reactor design. Different concepts when choosing a suitable TCM are evaluated and exemplified. The research is described in the following publication:

- A. Solé, X. Fontanet, C. Barreneche, A. I. Fernández, I. Martorell, L. F. Cabeza. Requirements to consider when choosing a thermochemical material for solar energy storage. Solar Energy 97 (2013) 398-404.

To conduct this objective, six of the most studied solid-gas TCM have been selected to study three aspects from bibliographic data to be followed when performing kinetic computations; first the solid characterization, second the quality kinetic data analysis, and finally the evaluation of experimental data. This paper brings the knowledge which should be applied in solid-gas TCM in order to properly design a solar thermochemical reactor and thus to obtain the theoretical reactor yield.

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

- The crystal structure changes and the coordination of water molecule with the involved compound were studied. Regarding calcium and magnesium oxides, the covalent bond is directly influencing the enthalpy values. This group of TCM should be distinguished from the ones that change from an hydrated form to another, as this last one is strong influenced by water molecule stability within the crystalline solid structure. These features are related to the enthalpy value of the reaction which is directly related to the storage capacity of the technology implementing TCM.

- SEM images of solids participating in the reaction are recommended to be taken before and after reacting to obtain more information. If nucleation, growth, or gas diffusion take place and their effects are observable at microscopic scale, such an observation can support the kinetic model when evaluating experimental data. Also, the solubility of materials in water is an important property to consider because if the solid presents less solubility, the probability of achieving the expected reactor yield is higher.

- To achieve reliable kinetic data by means of thermal analysis techniques, experiments should be performed under several heating rates and under different operating conditions. Plus, reproducibility of data obtained is important to enable the accuracy of kinetic parameters. Moreover, data may be obtained by performing isothermal or non-isothermal experiments. A truly good model should simultaneously fit both types of runs with the same kinetic parameters.

- To evaluate the obtained kinetic data there are mainly two computational methods. First the isoconversional or model-free methods which give the reaction rate at constant extent of conversion being only a function of temperature. Unlike model-free, the model-fitting methods are capable of identifying multi-step reaction models suitable for the description of complex kinetics.

The main conclusion is that before the selection of the suitable reversible reaction for a specific application in a reactor, the material must be first properly characterized in the specific operation conditions. If the theoretical reactor yield is wanted to be achieved, first the size and morphology of the solid particles involved (before and after reaction) is required, as it is influencing the kinetic model and will support the limiting step identification. Also, the material appearance (pellets, powder, etc.) and the impurities found in the material will affect durability of TCM. Last but not least, kinetic data obtained by means of thermal analysis techniques should be based on different heating rates, isothermal and non-isothermal experiments and under different conditions leading to the same kinetic parameters. Then these data can be evaluated by two different computational methods, model-free and model-fitting, depending on the complexity of the reaction and the information that is required.

7.3 Journal paper

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Requirements to consider when choosing a thermochemical material for solar energy storage

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Abstract

Solar thermochemical reactors offer good potential for production of heat for residential space heating and cooling and domestic hot water. The materials able to store solar energy are called thermochemical materials which are based on reversible chemical reactions, focusing here on solid–gas ones. These materials are capable to store solar thermal energy in one direction and to release it in the other, whenever is needed, with almost no heat losses. In the literature several materials have been successfully analyzed and tested at lab scale, but the expected heat storage capacity, or yield, of the reactor implementing these materials is not achieved. This paper shows that in order to reach the calculated operation conditions, a detailed and proper characterization of solid materials involved is needed (including solubility of the reactants and products, and evaluation of the crystallographic structure changes). Furthermore, a reliable kinetic model should be obtained to predict further behavior and to design the suitable reactor. The main goal of this paper is to provide a correct pathway to obtain the reliable kinetic model regarding important solid features that should be considered when working on thermochemical energy storage.

Keywords: Solar thermochemical reactor; Thermochemical materials (TCM); Solid state kinetics; Solubility; Crystallographic structure change

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8 P5: State of the art on gas-solid thermochemical energy storage systems and reactors for building applications

8.1 Introduction

TCM technology still presents several drawbacks which are needed to be addressed to make it market competitive. For instance, low overall efficiency, high cost, corrosion, swelling and clogging, long-term repeatability and stability [42].

The core of a TCM system is the reactor, where the absorption and release of energy takes place by means of the TCM. The reactor design highly influences the overall energy efficiency as well as the power output. Moreover, in the reactor is where kinetics, heat and mass transfer processes take place. Literature shows that mainly heat and mass transfer are limiting steps in TCM technology [41], [64]. The reactor design has an active play role to promote these processes in order to overcome some of the TCM drawbacks. Therefore, it is interesting to bring what is available in the chemical engineering field to better select the appropriate reactor type for each TCM selected.

Up to now, TCM prototypes are divided into open or closed, and integrated or separated (also called external). The first classification would concern the entire system configuration, where in the closed one the gas (water vapour) needs to be condensed in the charging phase and then evaporated in the discharge phase, Open systems deal with the water (moisture) from the ambient air being generally integrated into the ventilation system of buildings. The second classification concerns the reactor and storage vessel, so in the external reactor concept the material charging and discharging is performed in a reactor separated from the material storage vessel whereas in the integrated reactor concept the charging and discharging take place directly in the material vessel itself [65]. Recently, publications regarding comparisons between open and closed [55], [56], and integrated and separated [65] can be found in the literature.

8.2 Contribution to the state-of-the-art

The main contributions to the state-of-the-art are, first, to define and classify the available systems for TCM storage as well as the reactors types. Then, a literature review of the existing gas-solid chemical engineering reactors with their advantages and disadvantages is provided with the aim to bring both areas of knowledge together. Also, the promising candidates for thermochemical energy storage are listed and the thermal analysis technique, applied methodology and obtained results of some characterized TCM tabulated. Finally, a review of all the tested prototypes from laboratory to real scale, from 0.015 to 7850 dm^3, has been done and the main characteristics shown along with the selected gas-solid chemical reactor type. This research has been published in:

- A. Solé, I. Martorell, L. F. Cabeza. State of the art on gas-solid thermochemical energy storage systems and reactors for building applications. Renewable and Sustainable Energy Reviews 47 (2015) 386-398.

Main conclusions are that fixed bed reactors are the most used ones. Moreover, mass transfer is the main limiting process in TCM reactions, and thus further research may be based on optimizing the geometry of the reactor and contact flow pattern between phases. Nevertheless, from very new publications it has been seen that for closed systems, the heat transfer is the main limitation, whereas for the open system the mass transfer is the main limitation [55].

8.3 Journal paper

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State of the art on gas–solid thermochemical energy storage systems and reactors for building applications

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Thermal energy storage (TES) is moving towards thermochemical materials (TCM) which present attractive advantages compared to sensible and phase change materials. Nevertheless, TCM are more complex to characterize at lab scale and also the implied technology, which belongs to the chemical engineering field, needs to be contextualized in the TES field. System configurations for thermochemical energy storage are being divided into open/closed storage system and separate/integrated reactor system. Reactors, which are the core of the system, are the focus of this paper. Different gas–solid thermochemical and sorption reactors for building applications are reviewed from lab to pilot plant scale, from 0.015 to 7850 dm^3. Fixed bed reactors are the most used ones. Mainly, mass transfer is limiting to achieve the expected energy density. The geometry of the reactor and contact flow pattern between phases are key parameters for a better performance.

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9 P6: Corrosion of metals and salt hydrates used for thermochemical energy storage

9.1 Introduction

From the literature review, and as stated in the presented paper "State of the art on gas-solid thermochemical energy storage systems and reactors for building applications", one can conclude that technologies based on TCM present several advantages compared to the other available and most studied ones like sensible and latent heat storage systems for TES.

One of the main TCM advantages is their high theoretical energy storage density, which makes viable the development of compact systems for dwellings applications. As shown in the Introduction, the volume needed to full cover the annual storage need of an energy efficient passive house (6480 MJ) with a TCM system is ten times lower than the sensible [6]. Energy densities of some TCM based on reversible chemical reactions are one order of magnitude higher than water (sensible heat storage) [66]. Furthermore, despite the need to heat the TCM up to reach the discharging reaction temperature, heat losses when storing are almost zero. This last advantage makes TCM suitable for long-term thermal energy storage also known as seasonal storage. These listed advantages make them potential candidates for thermal energy storage and thus encourage research to go in depth with TCM. Nonetheless, drawbacks are found, especially when working experimentally. One of the main drawbacks is corrosion between the vessel (reactor/heat exchanger) and the TCM, specifically when using salt hydrates (solid-gas reactions).

Only few pure salts can be directly used because of their corrosive properties [46]. Corrosion tests are needed to know TCM and vessel material compatibility. N'Tsoukpoe et al. [67] state that $Na_2S{\cdot}9H_2O$ and $KOH{\cdot}H_2O$ are classified as corrosive, although the first presents an attractive energy density. De Boer et al. [68] presented the Sweat module with Na_2S/H_2O salt hydrate used as TCM. They highlighted the corrosive effect of the Na_2S/H_2O when it is in contact with metal parts. Cuypers et al. [69] showed preliminary experiments of a glass laboratory-scale zeolite reactor containing copper heat exchangers, where one of the downsides is the corrosion produced by the TCM.

On the other hand, regarding TCM technology, there are two main different system concepts to implement TCM materials: open and closed. When focusing on gas-solid reactions and being water the gas reactant, the main difference between these two systems is that the closed system works with pure vapor, while the open system uses moist air as the reactive gas and heat transfer fluid [55]. Besides the differences in equipment requirements (see Introduction and paper 5), basically open systems work at atmosphere pressure and moist air is in direct contact with the TCM, therefore oxygen. On the contrary, in closed systems the atmosphere can be controlled, then inert or vacuum can be implemented and the working pressure can be chosen.

No data is found regarding corrosion test between solid salt hydrates, nor in closed neither in open systems configuration, under real conditions considering the working temperature, the relative humidity as well as pressure. These results are totally necessary for the optimal development of a TCM system and to solve practical aspects to make them suitable for market implementation [44].

9.2 Contribution to the state-of-the-art

The contribution to the state-of-the-art of this study is to perform corrosion test between metals and TCM in open system configuration under moist air and atmosphere pressure. Furthermore, the aim is to provide suitable working pairs, TCM/metal, from the material compatibility point of view. The experimental results and details about this research are presented in:

- A. Solé, L. Miró, C. Barreneche, I. Martorell, L. F. Cabeza. Corrosion of metals and salt hydrates used for thermochemical energy storage. Renewable Energy 75 (2015) 519-523.

To do so, four common metals: copper, aluminum, stainless steel 316, and carbon steel, and five TCM: $CaCl_2$, Na_2S, CaO, $MgSO_4$, and $MgCl_2$, were combined and tested following the standard ASTM-G1. A humidity and temperature controlled chamber was designed to pursue this study.

Main results are that stainless steel is the most resistant metal to all the tested TCM under the experimental conditions being recommended to be used to contain all the TCM under study. Copper is only recommended with caution when combined with $CaCl_2$ and $MgCl_2$. This metal is mostly used as the heat exchanger material because of its high thermal conductivity. Carbon steel is slightly corroded with $CaCl_2$ and Na_2S, forming a brittle corrosion layer on the surface. Aluminum is recommended with caution to be in contact with all the TCM, except with Na_2S. Table 8 gathers the obtained results following a recommendation table elaborated by the industrial sector based on the obtained corrosion rates. Depending on which interval is the obtained corrosion rate a recommendation is given.

Table 8. Main results of open systems corrosion tests between metals and TCM [50].

	Copper	Stainless steel	Carbon steel	Aluminium
$CaCl_2$	Recommended with caution	Recommended for long term service	Recommended with caution	Recommended with caution
Na_2S	Completely destroyed	Recommended for long term service	Recommended with caution	Completely destroyed
$Ca(OH)_2$	Not recommended (>1 yr)	Recommended for long term service	Not recommended (> 1 yr)	Recommended with caution
$MgCl_2$	Recommended with caution	Recommended for long term service	Not recommended (> 1 yr)	Recommended with caution
$MgSO_4$	Not recommended (>1 yr)	Recommended for long term service	Not recommended (> 1 month)	Recommended with caution

9.3 Journal paper

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Corrosion of metals and salt hydrates used for thermochemical energy storage

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ABSTRACT

Solar energy can be efficiently used if thermal energy storage systems are accordingly designed to match availability and demand. Thermal energy storage by thermochemical materials (TCM) is very attractive since these materials present a high storage density. Therefore, compact systems can be designed to provide both heating and cooling in dwellings. One of the main drawbacks of the TCM is corrosion with metals in contact. Hence, the objective of this study is to present the obtained results of an immersion corrosion test following ASTM G1 simulating an open TCM reactor, under humidity and temperature defined conditions. Four common metals: copper, aluminum, stainless steel 316, and carbon steel, and five TCM: $CaCl_2$, Na_2S, CaO, $MgSO_4$, and $MgCl_2$, were studied. Aluminum and copper show severe corrosion when combined with Na_2S, aluminum corrosion is more significant since the specimen was totally destroyed after 3 weeks. Stainless steel 316 is recommended to be used as a metal container material when storing all tested TCM.

The pages from 113 to 117 contain the article:

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10 P7: Corrosion evaluation and prevention of reactor materials to contain thermochemical material for thermal energy storage

10.1 Introduction

As mentioned in sections 1.3 and chapter 9, corrosion is one of the issues to be overcome to reach the commercialization of TCM technology. Since most of the gas-solid TCM for building applications are salt hydrates and the vessel container, heat exchanger or reactor are made of metal, it is highly possible that corrosion takes place. Furthermore, some problems can be encountered depending on the deliquescence relative humidity of the salt [70], which should be higher than the relative humidity in order to avoid the formation of the salt solution. The forming of liquid film on the surface of salt crystal will not only prevent the hydration reaction from proceeding, but also cause corrosion problems due to the dripping of solution to other metal components [47]. Therefore it is important to control temperature and pressure of the reactor to prevent water condensation inside and hence allow the expected reaction to take place (hydration/dehydration) to obtain the desired overall performance.

Only one study has been published concerning corrosion tests between TCM and metals [50]. Solé et al. 2015 performed corrosion tests for open configuration TCM systems between four common metals (copper, aluminium, stainless steel 316, and carbon steel) and five TCM ($CaCl_2$, Na_2S, CaO, $MgSO_4$, and $MgCl_2$). Compatibility data between salts and metals is found in the literature [71], but with salts in solution with water and in atmospheric pressure. No literature has been found providing results of closed reactors, where preferred pressure condition is vacuum for optimal mass transport in the reactor [54].

10.2 Contribution to the state-of-the-art

The main contribution to the state-of-the-art is to design and build a new setup to be able to perform corrosion tests in a closed configuration, being able to control temperature and pressure. Accordingly, the subsequent methodology has been developed. To test and validate the setup and methodology, a TCM was selected and several metals and coated metals were tested seeking for material compatibility in the given conditions. This research is published in the following paper:

- A. Solé, C. Barreneche, I. Martorell, L. F. Cabeza. Corrosion evaluation and prevention of reactor materials to contain thermochemical materials for thermal energy storage. Applied Thermal Engineering 94 (2016) 355-363.

The developed device is a 5 L glass jacketed reactor, connected to a heating unit, an evaporator (round-bottom flask), and a vacuum pump. One temperature sensor is giving the TCM temperature, and another is placed in the atmosphere. Relative humidity (RH) is also measured. A general view of the setup is shown in Figure 14 left and a scheme of the reactor and evaporator in the right part. The details of the design process and the start-up of the setup are explained in this chapter in 10.2.1 section.

The selected TCM is Na_2S/water pair promising TCM for building comfort applications due to its high theoretical energy density (between 1.3 and 3 GJ/m^3 depending on the hydrates) and appropriate reaction temperature that can be achieved by a solar collector [67], [72]. This TCM has also been selected since it is part of the European Project MERITS, in where a combisystem based in TCM is being developed and the selected TCM is Na_2S/H_2O. Nonetheless, Na_2S reacts with oxygen and is corrosive to metals, especially with those used to build up heat exchangers or reactors that contain the TCM [73]. Given the Na_2S corrosiveness and that reacts with oxygen, it is a good candidate to test and validate the developed setup along with the methodology, since it is a worst case scenario situation.

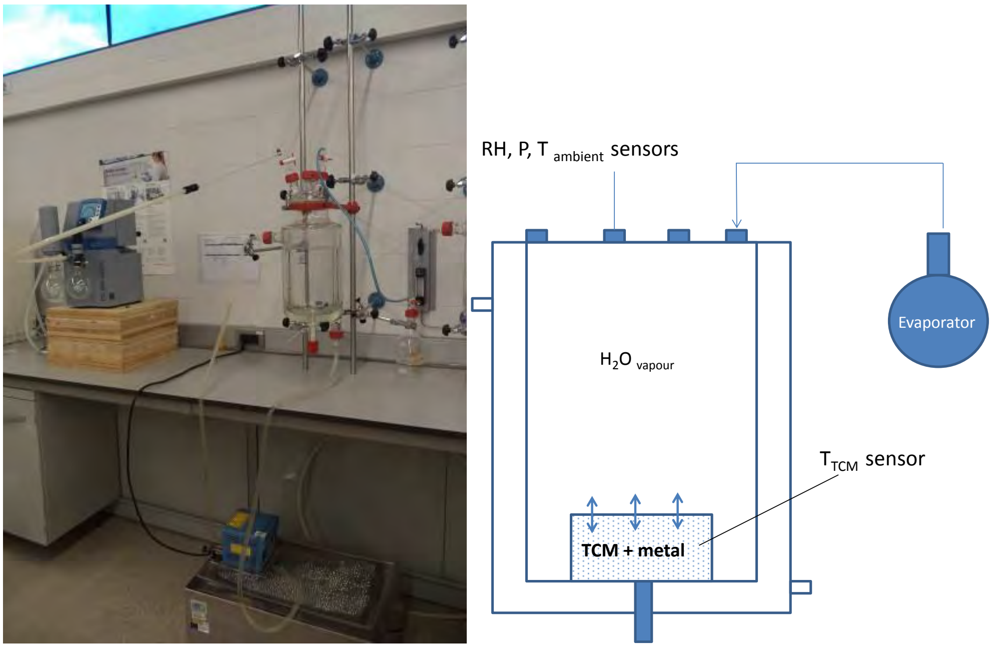

Figure 14. Self-developed setup to test TCM corrosion for closed configuration systems. Left: general view, right: scheme of the reactor and evaporator.

In this paper single metals under study are stainless steel 316 and copper. Moreover, coatings are considered to protect copper and aluminium from Na_2S corrosion. Two different coatings were chosen, halar (organic coating) and electroless nickel (inorganic coating).

The single metal samples follow the ASTM G1 standard in order to evaluate the corrosion rate and the coated samples are evaluated by SEM technique which allows measuring the coating thickness before and after the test.

Therefore, corrosion tests in vacuum conditions, 13 mbar, and 32.5 ºC, conditions given by $Na_2S{\cdot}9H_2O/5H_2O$ reaction and two metals: copper and stainless steel 316 have been performed in the described setup. These two metals were also tested previously in the open configuration tests (see chapter 9). Results show that in closed configuration, corrosion rate value for copper metal is reduced by 30 times when compared to the open configuration. In the case of stainless steel 316 results show that is recommended for long term service in both configurations.

One option to prevent corrosion is to apply coatings on the metal surfaces. Halar and electroless nickel, have been applied onto copper and aluminium specimens. From the results it can be said that halar is a potential candidate to protect both copper and aluminium heat exchangers/reactor that may contain Na_2S/H_2O pair for thermochemical energy storage or other applications under these conditions.

10.2.1 Process design and start-up

This section aims to explain how were the design process and the start-up of the developed system to test corrosion under vacuum conditions. This is not reflected in any published paper and this is why is detailed here. Middle steps while designing and the challenges that arise since it was not a straight forward process are presented next.

Testing materials compatibility under vacuum is interesting since it is the first time that is performed in TES field. This part is also in the frame of the European project called MERITS where the present author has been involved since the beginning of the PhD thesis.

The initial stage was either to buy a commercial available setup, as Büchiglasuster [74] or Mettler-Toledo [75] provide, or to design it and built up in our laboratory by pieces. Several aspects were taken into account to compare within the available setups and the possibility to build up our own setup:

- The main body of the test setup needs to be made of glass in order to minimalize the contact area between corrosive elements from the TCM (gases or the TCM itself) and metal components. Also, glass has been selected for being an inert material able to stand high temperatures, low pressures, and allowing direct visual inspection.
- The TCM should be situated in an independent support, inside the reactor, which is heated by convection.

The best option was to design and build up the setup in our laboratory due to several reasons. One of them was the price since the commercial ones were around 7 times more expensive than the own made. On top of that, it was a key factor in the decision process to have a versatile equipment to be able to perform further tests and this is basically why the own made equipment option was the one selected. Of course, there are always disadvantages and in this case the most important one was the complexity of building and mainly assembling a vacuum system.

The ordered components were two jacketed glass reactors able to place another glass cup with the TCM and metal samples inside, a thermostatic bath, and a vacuum pump. Building two test setups was thought to enable parallel test runs that will significantly reduce the overall time that is needed for testing. The vacuum pump, permitting lower values of pressure (3 stages, 3.4 m^3/h, and 1.5 mbar), was purchased from Vacuubrand. This vacuum pump is chemically resistant since its interior parts are coated to prevent them from corrosion. It also presents a filter to prevent the entrance of solids in the inlet flow.

The piping and assembling were purchased looking for compatibility with the gases and vacuum tightness. The pipes are polyamide based and the clamps to assemble to the inlet/outlets are metal based. Then other aspects like outgasses that could present toxic compounds, the entrance of the gases to the vacuum pump that could bring some solids and therefore damage the pump, the evaporator, the sensors, and the assurance of the vacuum tightness were also key points that were taken into account.

A round flask as an evaporator was connected with a polymeric pipe to the reactor to provide the water vapour necessary to let the reaction take place. Previously, the necessary water to react was thought to be placed in the same vessel, but a temperature of 10 ºC is needed to evaporate water at vacuum pressures (13 mbar), and since the reactor is set to higher temperatures, this possibility was discarded.

The initial methodology was to vacuum the reactor, place the TCM and metal samples and measure the pressure rise due to corrosion gasses products formation while analysing them. The bought reactors presented a leakage rate of around 0.01 mbar l^{-1} s^{-1}

which is 3 orders of magnitude higher than the established by the project consortium (10^{-5} mbar l^{-1} s^{-1}), even after sending the reactor lid to the manufacturer two times to treat the surface in contact with the reactor body. Therefore, the initial approach was shifted to run the pump in continuous mode which permits to control the water vapour pressure over the TCM, to maintain the established pressure and to avoid vacuum leakage. Moreover, the venting gases are continuously driven to the fume hood, being previously cooled and condensed at the pump outlet by a water tap circuit.

With these changes, the setup was then thought to conduct screening corrosion tests rather than quantifying the gasses formation due to possible corrosion products. Screening tests under real operating conditions are necessary to start the selection of the optimum reactor vessel material. Moreover, the gas produced by corrosion process concentration is quite low that could be very difficult to analyse it by sampling air from the setup, which will also has a negative effect on the vacuum conditions.

First, the sensors of temperature, pressure and relative humidity were thought to be connected to a datalogger and acquire data in a computer. However, to prevent vacuum leakage, the sensors were wireless and placed inside the cavity. Data was read visually since glass permit to see the inside. One thermometer to measure the TCM temperature and one HygroPalm HP22 equipment for the temperature and the relative humidity of the atmosphere were used, as can be seen in Figure 15. Although the vacuum pump was set at the water vapour pressure set value, the relative humidity data was used to verify the expected water vapour pressure following equation 5 from Clausius-Clapeyron and equation 6.

$$e_s = 6.11 \cdot 10^{\left(\frac{7.5 \cdot T}{T + 237.3}\right)} \quad Eq.\ 5$$

$$HR = \frac{e}{e_s} \quad Eq.\ 6$$

Where e_S (hPa) is the saturated vapour pressure at a given temperature (ºC), *HR* the relative humidity, and *e* the partial vapour pressure (hPa).

Figure 15. Reactor setup with the sensors inside.

Several preliminary tests were planned and performed to test the system. First, only the setup was tested seeking for the proper operation and in order to establish the start-up. The start-up is composed by eight steps listed here:

1. Turn on the thermostatic bath at the set temperature.

2. Place the TCM + metal samples, which are inside a glass cup, inside the reactor.

3. Place the sensors, temperature TCM and atmosphere and relative humidity.

4. Close all the outlets, valves, and reactor lid.

5. Switch on the vacuum pump having programmed the set pressure value before.

6. Turn on the refrigeration circuit of the vacuum pump.

6. Fill the evaporator with distilled water, connect it to the reactor and once the pressure inside the reactor is the established, open the valve to the evaporator.

8. Switch on the fume hood.

Furthermore, more tests were performed only with the TCM to have a reference without possible corrosion. Finally, corrosion tests were carried out, some of them are published in paper 7 and other are part of the MERITS project, being confidential results. A total of around 13 experiments were performed with this setup. At the present, we are still using it.

10.3 Journal paper

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Research Paper

Corrosion evaluation and prevention of reactor materials to contain thermochemical material for thermal energy storage

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H I G H L I G H T S

- Corrosion tests are needed for thermochemical reactor components and system design.
- Corrosion tests between Na_2S/H_2O working pair as TCM and metals have been performed.
- Copper is corroded and should be coated if used as reactor material containing Na_2S.
- Halar and nickel coatings have been applied onto metals for corrosion prevention.
- Ss 316 and Halar coated copper and aluminium are corrosion resistant to Na_2S/H_2O.

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A B S T R A C T

Thermochemical materials (TCM) can be used for seasonal heat storage, storing high amounts of thermal energy coming from the sun in summer and releasing it in winter, when heating for houses is needed. One promising TCM for building comfort applications is the Na_2S/water pair due to its high energy density and appropriate reaction temperature that can be achieved by a solar collector. Nonetheless, Na_2S reacts with oxygen and is corrosive to metals, especially with those used to build up heat exchangers or reactors that contain the TCM. Therefore, corrosion tests in a self-developed experimental setup under vacuum conditions, 13 mbar, between $Na_2S \cdot 9H_2O/5H_2O$ and two reactor metals – copper and stainless steel 316 – have been performed. Since copper is corroded and is highly used for thermochemical reactors, two promising coatings, Halar and electroless nickel, have been applied. Furthermore, aluminium has also been tested coated with these coatings. Halar is a potential candidate to protect both copper and aluminium heat exchangers/reactor that may contain Na_2S/H_2O pair for thermochemical energy storage. Stainless steel 316 is also corrosion resistant to the selected TCM.

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11 P8: High conductive Thermochemical material (TCM) and graphite composites for thermal energy storage

11.1 Introduction

As stated in the introduction and along this thesis, the main goal of researchers working with TCM systems is to come with an optimum system to be market competitive. To do so, several problems need to be addressed, such as: low overall efficiency, high cost, corrosion, swelling and clogging, long-term repeatability and stability [42]. In order to increase overall efficiency there are several features that can be researched [41]: Thermochemical material itself, ambient conditions, process design, and reactor design. To improve the overall system efficiency, but mainly reactor efficiency, heat and mass transfer need to be promoted. There are mainly two ways to promote heat transfer: by increasing the surface area in contact (fins, etc.) [76] and/or by increasing the overall material thermal conductivity by adding a superconductive material (i.e. graphite).

Moreover to promote heat transfer but also mass transfer, matrix materials with a high porous structure with TCM dispersed inside are being developed and implemented and is one major direction of this research activity [6].

Several composite TCM have been tested at laboratory and reactor scale [46], [77], [78]. TCM composites can be divided in two groups: adsorption + thermochemical and inert + thermochemical. The first group consists in a porous material like vermiculite, zeolites, etc. in which the TCM is impregnated. These composites have the advantage of providing the heat released by the TCM reaction together with the heat from the adsorption material. Furthermore, by using these composites, agglomeration can be prevented and thus better mass transfer can be achieved in the reactor. The other group are mainly thought to increase the overall material conductivity which would enhance heat transfer by means of using an inert material such as graphite. Moreover, the inert material prevents compaction or clogging of the TCM and thus increases mass transfer, too. A literature review of the available TCM composites is provided in the paper introduction and also can be seen in Aydin et al. [41].

Some of the published studies show promising results, for instance Fujioka et al. [77] show that conductivity of $CaCl_2$ is enhanced by 10-30 times by adding expanded graphite. Nevertheless, Michel et al. [64] show that vermiculite + $SrBr_2$ composite does not allow any reduction of the reaction time, and, as a result, it does not lead to any enhancement of the thermal power.

In another study where open and closed system configurations are compared, Michel et al. [55] have highlighted heat transfer mainly limits the hydration reaction for the closed system, and a small increase of the thermal conductivity strongly improves the reaction rate. For example, a conductivity which is two times higher than the reference bed conductivity decreases the reaction time of about 14%. [55]. In open configurations, mass transfer is the limiting step and permeability is the parameter affecting the most.

11.2 Contribution to the state-of-the-art

The main contribution to the state-of-the-art is to enhance TCM which are promising for building applications, from a temperature reaction and enthalpy point of view, but show poor reactor performance. The aim is to add graphite to increase the overall material conductivity while maximising the storage energy density. Furthermore, time of the reaction to achieve a 100% conversion has been determined to be compared to single TCM and to evaluate the influence of the graphite addition. All the research carried out with the obtained results and the methodology is presented in this publication, which is in process:

- A. Solé, A. Palacios, C. Barreneche, A. I. Fernández, I. Martorell, L. F. Cabeza. High conductive thermochemical material (TCM) and graphite composites for thermal energy storage. Solar Energy Materials & Solar Cells. Submitted.

Two promising TCM, sodium sulphide nonahydrate ($Na_2S·9H_2O$) and magnesium sulphate heptahydrate ($MgSO_4·7H_2O$), have been selected to undergo these tests. From the literature [67] both selected salts are between the most promising materials from an energy density point of view, within a group of 125 TCM. Moreover, both of them fit in an active HVAC closed system to provide heating and DHW for dwellings, from a temperature reaction point of view.

Graphite has been selected as high conductive material to be incorporated in TCM and thus increase material conductivity. By adding graphite, also clogging and swelling might be prevented since it will act as a matrix avoiding salt compaction. Therefore, at the same time, graphite can contribute in avoiding salt agglomeration which inhibits mass transfer. Two graphite kinds, expanded and flakes, were chosen and two composite preparation techniques, direct wet and vacuum impregnation, were followed obtaining a total of eight different combinations. The amount of added graphite has been the maximum seeking to achieve the highest overall material conductivity, while maximizing enthalpy reaction.

Kinetics, time to reach 100 % of dehydration reaction conversion, has been evaluated for each composite and single TCM to see if it is affected by this inert addition. Also, conductivity, enthalpy reaction and density (both bulk and real) have been experimentally determined which at the end would have an effect on the overall material energy density and reactor efficiency. Also, porosity has been calculated since it is an influencing parameter on permeability and mass transfer.

Main conclusions are that thermal conductivity is improved when graphite is included in the formula independently of the addition technique used and the TCM impregnated. Percentages of conductivity increase vary from 61 to 679% (when compared to each single TCM). In addition, kinetics remains the same despite adding an inert material like graphite. In some composites the energy density is seen to be increased when compared to the single TCM. A better stability of $Na_2S·9H_2O$ has been achieved by the effect of adding graphite.

11.3 Journal paper

Elsevier Editorial System(tm) for Solar Energy Materials and Solar Cells

Manuscript Draft

Manuscript Number:

Title: High conductive thermochemical material (TCM) and graphite composites for thermal energy storage

Article Type: Regular Manuscript

Keywords: Thermal energy storage (TES); Thermochemical material (TCM); Composite; Graphite; Conductivity; Kinetics

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Abstract: Thermochemical materials (TCM) are being implemented in active HVAC systems to store thermal energy in dwellings and therefore provide heating and domestic hot water when demanded. The heat transfer rate from the storage material to the heat transfer fluid needs to be improved. One way to contribute in that sense is by means of increasing the TCM conductivity. This would also enhance the overall system performance. Two promising TCM, Na_2S/H_2O and $MgSO_4/H_2O$, have been selected to develop eight different composites, varying the manufacturing technique and the graphite form. The aim is to add graphite to increase the overall material conductivity while maximising the TCM storage energy density. Furthermore, time of the reaction has been evaluated in order to determine the influence of the graphite addition on dehydration reaction kinetics. Results show that effective thermal conductivity is improved in all cases, regardless the technique used and the form of selected graphite. Percentages of conductivity increase vary from 61 % to 679 % (when compared to each pure TCM), depending on the composite. Kinetics remains the same despite adding an inert material like graphite. Other important material properties have been determined to be implemented in a future reactor predictive model.

The pages from 135 to 162 contain the article in process:

A. Solé, A. Palacios, C. Barreneche, A. I. Fernández, I. Martorell, L. F. Cabeza. High conductive thermochemical material (TCM) and graphite composites for thermal energy storage. Solar Energy Materials & Solar Cells. Submitted. November 2015.

12 Conclusions and recommendations for future work

12.1 Conclusions of the thesis

This PhD thesis has contributed to the thermal energy storage field. In particular the focus has been on two available technologies, PCM and TCM, which present very different status of market availability, but both fulfil the requirements of thermal energy storage and thus provide a solution to do a step forward in the usability of renewable energies.

PCM commercial systems and materials are already available, but there is still a lack of research in the materials characterization field. First standards to characterize these materials have been created during this PhD period and are still on-going nowadays. In addition, new techniques are being developed at laboratory scale in different research centres to better characterize PCM. The development of new techniques and the improvement on the existing ones answer the shortage of suitable results with the already available ones.

Moreover, important properties like thermal cycling stability of PCM were not widely studied in the beginning of this PhD and now, 3 years later, it can be seen that it has growth an interest since it is essential to assure the PCM system work in a suitable way.

The main achievements and conclusions concerning PCM characterization techniques are:

- T-history is a suitable candidate technique to characterize larger samples of PCM, around 1000 times larger than DSC, and it is a simple setup that researchers can build in their own laboratory compared to the widest and expensive used technique, DSC.
- The review of the T-history provides tools to the researchers that want to build up a new one. It gives clues about the useful improvements that have been done since the original setup was published. These improvements should be in agreement and implemented in the new setups.

- Main suggested improvements compared to the original T-history concern data evaluation, mainly to turn to temperature dependent variables instead of time dependent and therefore obtain enthalpy-temperature curves instead of temperature-time curves.
- Furthermore, a big effort has been put in T-history data accuracy; sensors are being replaced for better ones and PID controllers installed to control the homogeneity of the ambient temperature.
- Almost all new T-histories are placed inside an insulated chamber. Most of them are being prepared to perform heating and cooling experiments and widening the temperature range.
- Likewise, there are also suggestions to change the position of the test tubes from vertical to horizontal and to cover them with insulating material to ensure the same temperature at the same time along all the PCM which are not being adopted for other researchers developing a new T-history.
- To move towards a commercial available T-history it is important to get consensus among all researchers to suggest a common instrumental setup, data analysis and presentation of final results. A review has been provided to the scientific research community to contribute in this sense.
- Internal reviews like the one presented concerning the unconventional techniques to characterize PCM are good ways to encourage interrelations between laboratories, but mainly enlighten what is missing from the commercially available characterization techniques.
- Moreover, this review provides techniques and the conditions to characterize PCM and composite PCM from a morphological, structural, physic-chemical and mechanically point of view to the research community. Modified techniques and how to use the available ones to characterize both PCM and composite PCM is described.

The main outputs from thermal cycling stability studies performed with sugar alcohols are:

- From the three cycled sugar alcohols it can be deduced that the open carbon chains, such as the case of D-mannitol and galactitol, are not thermally stable after repeated cycles under air atmosphere. Both sugar alcohols present oxidation. Galactitol is totally degraded after 19 cycles, and D-mannitol shows decrease percentages of 50 % in its melting/solidification enthalpy after 50 cycles.
- It has been experimentally demonstrated that D-mannitol is thermally stable after cycles if the atmosphere can be controlled, specifically when no oxygen is present. A possible solution is to work with a heat exchanger containing this PCM under vacuum or inert atmosphere to ensure long term system performance.
- The closed carbon chain sugar alcohols, or at least myo-inositol is thermally stable after cycling it, besides some changes are seen in the molecular structure.
- Different polymorphs are foreseen depending on the applied temperature range, which can lead to unexpected thermophysical properties. This has been proven with myo-inositol and D-mannitol.
- All these sugar alcohols present high hysteresis values. Differences from 45 ºC in the case of myo-inostiol to 79 ºC, in the case of galactitol, are detected between melting and solidification temperature.

The other technology tackled in this thesis is TCM. This one compared to the PCM, is not available at commercial scale because more research is needed in several issues. Materials development, reactor and system design, and costs are some of the major constraints to be addressed in order to let TCM become market competitive. In this sense, the present PhD thesis has contributed in several aspects from material to reactor level. Moreover, knowledge from other fields (i.e. chemical engineering) has been brought to TES field since sometimes the knowledge is available but not interrelated. What is more important is that this thesis has looked for synergies between material and reactor level seeking for better overall system performance. Main achievements have been reached by enhancing TCM itself, by adding graphite and thus enhancing material conductivity and so heat transfer in the reactor. And also by providing results of real conditions corrosion tests, which is also a big drawback in TCM technology. Solutions are given to solve corrosion problem if copper and aluminium metals are desired in closed systems working with Na_2S/H_2O pair.

The main general conclusions from material and reactor level for gas-solid TCM are:

- When designing a thermochemical gas-solid reactor a reliable kinetic for each TCM under the real operating conditions should be obtained to achieve an accurate design.
- When using thermal analysis techniques to obtain the kinetic model, data would be required to be obtained by different heating rates and always supported by microscopic information. A good characterization of the solid is needed before and after the reaction to corroborate the kinetic model.
- Within the available laboratory scale reactors for thermochemical energy storage, the most used reactor type is fixed bed. This kind of reactors present low heat and mass transfer. Fluidized bed and moving beds promote heat transfer between solid and gas. Nevertheless, for the same reactor volume, less TCM will be available in fluidized reactors compared to fixed, thus less storage capacity.
- Better reactor yields can be achieved by enhancing some of the TCM properties like conductivity for closed reactors and permeability for open reactors.
- Both open and closed configurations provide similar performances and should be carefully chosen depending on the selected TCM and application. If the selected TCM can work with both configurations, then the open is preferred from a total cost system and complexity point of view.

The conclusions related to corrosion tests with TCM are:

- For open configurations, stainless steel 316 is the only metal recommended to be in contact with all the studied TCM: $CaCl_2$, Na_2S, CaO, $MgSO_4$, and $MgCl_2$.
- There are other combinations that can be used with caution if corrosion rate values from 10 to 49 $mg \cdot cm^{-2} \cdot yr^{-1}$ can be assumed: $CaCl_2$ and $MgCl_2$ with

copper, $CaCl_2$ and Na_2S with carbon steel, $CaCl_2$, CaO, $MgCl_2$, and $MgSO_4$ with aluminium.

- The first setup to test corrosion for closed configuration has been successfully designed and built up in our laboratory. A methodology to carry out corrosion tests for metals and coated metals has been developed and used to test Na_2S/H_2O pair under vacuum and 32.5 ºC. From these tests, only stainless steel 316 is a candidate to be used to contain this TCM.
- It has been demonstrated that when halar coating is applied onto copper or aluminium it is a great solution to prevent corrosion against Na_2S if those metals are desired for the reactor design.
- Nickel coatings are not appropriate coatings for Na_2S/H_2O under these conditions.

Regarding the enhancement of TCM properties and thus overall heat transfer in the reactor, main achievements and conclusions are:

- It has been demonstrated that the fact of adding graphite not only contributes in increasing overall material conductivity but also in stabilizing the Na_2S/H_2O working pair.
- Conductivities of all the developed composites $MgSO_4{\cdot}7H_2O$ and Na_2S/H_2O with flakes and expanded graphite increase. Great achievements in percentages of increase when compared to the single TCM have been reached which vary from 85 to 679 % in the case of Na_2S/H_2O composites, and from 61 to 574 % in the case of $MgSO_4{\cdot}7H_2O$.
- $MgSO_4{\cdot}7H_2O$ composites present lower energy density values, from 0.11 to 0.49 GJ/m^3, compared to the single TCM, 1.05 GJ/m^3. Percentages of decrease vary from 50 % to 90 %, depending on the composite.
- Energy densities of the composites based on Na_2S/H_2O are sometimes higher than the single TCM, which is 1.14 GJ/m^3, but in some cases are lower. The values range from 0.27 to 1.38 GJ/m^3.

- Kinetics is unchanged when adding graphite.

12.2 Recommendations for future work

From the research carried out and presented in this thesis, some points arise which are not addressed in this thesis and are relevant in the PCM and TCM field to continue in the contribution of the optimum technology development. Identified recommendations for further work are listed below.

From the PCM part:

- To start the standardization of the T-history technique. This could be held within the materials group meeting where we belong to, named Annex 29 from the IEA.
- To design and built up our own T-history at GREA laboratory.
- More research is needed to ensure whether a PCM can be used for long-life time. This can be achieved by studying thermal cycling stability of PCM when performing enough freezing/melting cycles and under the real operating conditions. Also, since oxygen is known to react with sugar alcohols, other atmospheres like vacuum or nitrogen are candidates to perform further tests with these PCM.
- To develop or contribute in developing a standard methodology to perform thermal cycling stability tests. In that sense, a review of the methodology used by all researchers that have published results concerning thermal cycling stability of PCM has been recently published.
- To study the hysteresis of sugar alcohols at laboratory scale and see if this phenomena is also happening at higher scale.

From the TCM part:

- To do a research and study the availability depending on the weather of the suitable low heat source for closed TCM systems for building applications.
- To perform a life cycle analysis (LCA) of a real TCM system and compare it with a reference system.
- To perform corrosion test between composite TCM and metals or coated metals.
- To model numerically the heat and mass transfer processes in thermochemical materials since it will improve the understanding of how these systems work and make possible their optimization.
- To do a sensitive parameter analysis of material composite properties which affect the overall system efficiency, such as conductivity, density, and permeability.
- To study the long-term stability of the developed graphite based TCM composites which show promising results.
- To build up or adapt the available laboratory setup to be able to test different reactor geometries and thus improve reactor design when working with TCM.

13 Contribution of the candidate to each paper

The candidate belongs to GREA research group, expert in thermal energy storage and lead by Prof. Dr. Cabeza. This is a multidisciplinary group where exchange of information between co-workers and interesting discussions are happening every day. At least 6 PhD thesis have been defended in the last 5 years, all of them supervised by Prof. Dr. Cabeza.

Periodical meetings with my two supervisors, Dr. Martorell and Prof. Dr. Cabeza, have been very important to define the scope of my PhD. All the papers of this thesis have been done under the supervision and revision of both PhD supervisors. If critical decisions were needed to be taken at some points there were done by the three of us. Both supervisors have a chemical engineering background, as well as the candidate, which helps in having a good perspective and knowledge of both, materials and reactors, especially in the case of TCM. Luisa F. Cabeza, the head of the group, is always in charge of the final approval of the papers and submissions to the journals, but is the candidate doing the answer to reviewers, if any.

- T-History method

In one of the first group research meetings I attended at the beginning of my PhD it was discussed the idea of writing a review regarding T-history method. The candidate started collecting information and writing a manuscript in the benchmark of one of the subjects (taught by Dr. Martorell) of MCAE, Master in Applied Science in Engineering. The master thesis was defended in June 2012. My supervisors considered that the information presented was very completed and interesting for the scientific community and with their supervision and advice I rewrote and adapted it to the final published paper. There is one part, called previous methods, which was written by another co-author of the paper, Laia Miró.

- Unconventional techniques Part 2

This is a paper fruit of the collaboration between several universities, research centers, and other research institutions participating in the frame of COST Action TU0802. As explained in the PhD thesis, UDL participates in the compatibility tests between PCM and metals and polymers, where the candidate performed the experimental part in collaboration with other lab co-workers and evaluated and analysed obtained data, as well as writing.

- Stability of sugar alcohols

Thanks to the international experience of GREA I had the unique opportunity to work during three months at Fraunhofer ISE. During this period Dr. Schossig was in contact with my two supervisors and me in order to determine and design the work of the candidate. The candidate contributed in the design of the experimental part, conducted the experimental part itself, and wrote a first draft of the final paper that was reviewed and completed by the supervisors. It is important to highlight that fruit of the collaboration with the Fraunhofer, Sophia Niedermaier, as a chemist, contributed in the FTIR part, in performing the experimental tests and analysing data.

- TCM requirements

The idea of this paper rose from the head of the research group with the aim to start this research line. This paper has been done in collaboration with University of Barcelona. The more chemistry part of the paper, crystallographic structure change, was performed at that University, whereas the other parts, solubility and kinetic pathway were undergone at the University of Lleida. Several coordination meetings were needed with all the participants in order to design the best experimental protocol. The candidate played a key role in the part conducted at UdL, the supervision of the part conducted at UB as well as the bibliographic research, and writing.

- State of the art TCM reactors

Following the TCM research line in the group and with the experience and background of the supervisors and candidate, a review of TCM reactors was thought to be carried out. Bibliographic research, data processing, and writing were led by the candidate while several meetings were done during the preparation of the paper in order to decide the structure and organization of the paper and the way to better present the information.

- Corrosion test 1: humidity chamber

This study is in the frame of a European project, MERITS, were the supervisors and candidate were in charge and played an active role in WP4 related to storage materials. The TCM studied in this paper were preselected by the consortium. One of the strong points of this paper is the design of a new experimental setup. The candidate led this part with the collaboration of the lab team. Periodical meetings were conducted during months in order to decide the final setup as well as the equipment to be bought. Collaboration of coauthors was also important during the validation of the experimental setup. Experimental tests to be done in the laboratory were discussed in different meetings with the supervisors. Once the setup was working properly the candidate supervised the experiments, analysed data, and prepared a first version of the manuscript to be reviewed by all the coauthors. The experimental part coincided with the first research stay, thus was supervised from there and was mainly performed by Laia Miró and Dr. Camila Barreneche.

- Corrosion tests 2: vacuum conditions

This testing was done in the frame of MERITS project. The TCM and some coated metals were preselected by MERITS consortium, but some samples (metal+coating) were decided by our lab team. After discussing with the supervisors how the experimental part would be performed, the candidate was in charge of the setup design, the built up, and the start-up. Furthermore, all the experimental part (around thirteen one week tests) and chemical cleaning was done by the candidate, except the SEM tests that were done at the University of Barcelona by Dr. Camila Barreneche. Nevertheless, the candidate also contributed to perform some of the SEM images at the University of Barcelona. All data was processed and evaluated by the candidate as well as first version of the paper that was reviewed and completed by all the co-authors.

- High conductive TCM

This last paper is also in the frame of the MERITS project, therefore one of the TCM was given by partners decision. The idea of this paper arose in one of the lab meetings. The bibliographic research, part of the experimental part, data evaluation and part of the writing was done by the candidate. University of Barcelona, especially Anabel Palacios and Dr. Camila Barreneche performed the density, and conductivity measurements as well as the corresponding written part. Several meetings with the supervisors were done during this period in order to follow-up the experimental process and discuss the scope of the paper and the way results were going to be presented. As done with the other papers, once a first version of the paper was written, a review process conducted by all the authors was performed.

14 Other contributions

14.1 Journal contributions

- **Materials characterization (4)**

– Barreneche C, Solé A, Miró L, Martorell I, Fernández AI, Cabeza LF. New methodology developed for the differential scanning calorimetry analysis of polymeric matrixes incorporating phase change materials. Measurement Science & Technology 23 (2012) 085606-1-085606-5.

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- **Systems (1)**

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

- **TES materials and equipment material compatibility (2)**

– Moreno P, Miró L, Solé A, Barreneche C, Solé C, Martorell I, Cabeza LF. 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.

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14.2 International conferences

- **Thesis related conference contributions (13)**

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– Solé A, Fontanet X, Barreneche C, Fernández AI, Martorell I, Cabeza LF. Parameters to take into account when developing a new thermochemical energy storage system. SHC 2012, USA.

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- Solé A, Martorell I, Cabeza LF. Review on thermochemical reactors for building comfort applications. Eurotherm 2014, Spain.
- Solé A, Barreneche C, Cabeza LF, Fernández AI, Martorell I, Miró L. Corrosion test of salt hydrates and vessel metals for thermochemical energy storage. SHC 2013, Germany.
- Solé A, Cabeza LF, Neumann H, Niedermaier S, Palomo E. Thermal stability test of sugar alcohols as phase change materials for medium temperature energy storage applications. SHC 2013, Germany.
- Solé A, Barreneche C, Martorell I, Cabeza LF. A new setup to test thermochemical material (TCM) corrosion under vacuum conditions. GREENSTOCK 2015, China.
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- **Other (14)**

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