

17. PHASE CHANGE MATERIALS AND THEIR BASIC PROPERTIES

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Abstract. This section is an introduction into materials that can be used as Phase Change Materials (PCM) for heat and cold storage and their basic properties. At the beginning, the basic thermodynamics of the use of PCM and general physical and technical requirements on perspective materials are presented. Following that, the most important classes of materials that have been investigated and typical examples of materials to be used as PCM are discussed. These materials usually do not fulfill all requirements. Therefore, solution strategies and ways to improve certain material properties have been developed. The section closes with an up to date market review of commercial PCM, PCM composites and encapsulation methods.

Keywords: PCM; phase change; latent heat; melting; heat storage; cold storage; corrosion; phase separation; incongruent melting; subcooling; nucleator; products.

17.1. Basic Thermodynamics

Heat and cold can be stored using different physical and chemical processes. These processes have different, distinct advantages and disadvantages.

17.1.1. HEAT STORAGE AS SENSIBLE HEAT

By far the most common way of heat storage is as sensible heat. As Figure 100 shows, heat transferred to the storage medium leads to a temperature increase of the storage medium. The ratio of stored heat to temperature rise is the heat capacity of the storage medium.

This temperature increase can be detected by a sensor and the heat stored is thus called sensible heat. Sensible heat storage in most cases uses as storage materials solids (stone, brick, ...) or liquids (water, ...). Gasses have

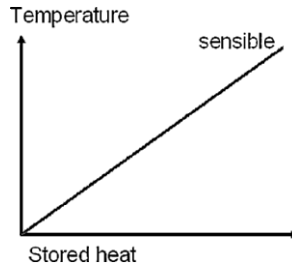


Figure 100. Heat storage as sensible heat leads to a temperature increase when heat is stored

very low heat capacity and are therefore usually not used for heat or cold storage.

17.1.2. HEAT STORAGE AS LATENT HEAT

If heat is stored as latent heat, a phase change of the storage material is used. Different options are:

1. *Evaporation of the storage material.* Evaporation is a phase change with usually large phase change enthalpy; however the process of evaporation strongly depends on the boundary conditions:
 - *Constant volume:* evaporation leads to a temperature and large pressure change within that volume and is therefore technically not applied.
 - *Constant pressure in closed systems:* this leads to a large volume change, which is therefore also technically not applied.
 - *Constant pressure in open systems:* upon loading the storage with heat, the storage material is evaporated and lost to the environment (open system). To unload the storage, the storage material has to be retrieved from the environment. The only technically used material is therefore water.
2. *Solid–liquid phase changes (melting).* Melting is a phase change with large phase change enthalpy, if a suitable material is selected. Melting is characterized by a small volume change, usually less than 10%. If a container can fit the phase with the larger volume, usually the liquid, the pressure is not changed significantly. Then melting and solidification of the storage material proceeds at a constant temperature. solid–liquid phase changes are therefore suitable for many technical applications.
3. *Solid–solid phase changes.* Solid–solid phase changes have the same characteristics as solid–liquid phase changes, but usually do not possess a large phase change enthalpy. However, there are exceptions.

The melting of the storage material is shown in Figure 101.

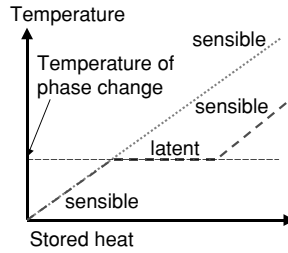


Figure 101. Heat storage as latent heat for the case of melting (solid–liquid phase change)

Upon melting heat is transferred to the storage material while the material keeps its temperature constant at the melting temperature. If the melting enthalpy has been transferred to the storage material the melting is completed and further transfer of heat results in sensible heat storage. The storage of the heat of melting cannot be detected from the temperature and the heat stored (melting enthalpy) is called latent heat. Materials with a solid–liquid (or solid–solid) phase change, which are suitable for heat or cold storage, are commonly referred to as “latent heat storage material” or simply “phase change material” (PCM).

17.1.3. POTENTIAL APPLICATIONS

Potential fields of application for PCM can be found directly from the basic difference between sensible and latent heat storage as explained in Figure 102.

17.1.3.1. Stabilization of Temperature

As Figure 102 shows, heat can be supplied or extracted from a latent heat storage material without significant temperature change. PCM can therefore be applied to stabilize the temperature in an application, for example the indoor temperature in a building or the temperature of the interior of transport boxes.

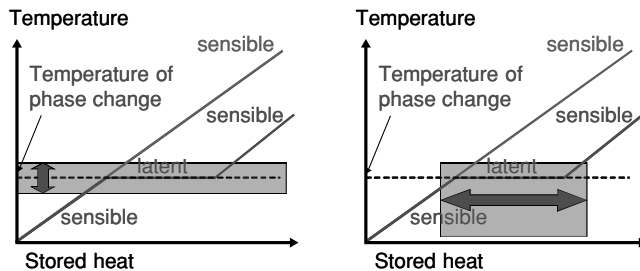


Figure 102. Potential fields of application of PCM: temperature stabilization (left) and storage of heat or cold with small temperature change (right)

TABLE 17. Comparison of typical storage densities of different energy storage methods

	kJ/l	kJ/kg	Comment
<i>Sensible heat</i>			
Granite	50	17	$\Delta T = 20^\circ\text{C}$
Water	84	84	$\Delta T = 20^\circ\text{C}$
<i>Latent heat of melting</i>			
Water	330	330	0°C
Paraffin	180	200	$5\text{--}130^\circ\text{C}$
Sulphate	300	200	$5\text{--}130^\circ\text{C}$
Salt	600–1,500	300–700	$300\text{--}800^\circ\text{C}$
<i>Latent heat of evaporation</i>			
Water	2,452	2,450	Ambient conditions
<i>Chemical energy</i>			
H gas	11	120,000	300 K, 1 bar
H gas	2,160	120,000	300 K, 200 bar
H liquid	8,400	120,000	20 K, 1 bar
Gas (petroleum)	33,000	44,600	
<i>Electrical energy</i>			
Battery		200	Zinc/manganese oxide

17.1.3.2. Storage of Heat or Cold with High Storage Density

As Figure 102 shows, PCM are also able to store large amounts of heat or cold at comparatively small temperature change. PCM can therefore be applied to design heat or cold storages with high storage density, for example in domestic heating. A comparison of energy storage densities achieved with different methods is shown in Table 17. PCM can store about 3–4 times more energy per volume as is stored as sensible heat storage in solids or liquids in a temperature interval of 20°C . This can be a significant advantage in many applications. Chemical energy storage in petroleum however shows a storage density about 100 times larger than that of PCM.

17.2. Physical, Technical and Economical Requirements on Phase Change Materials

A suitable phase change temperature and a large melting enthalpy are the requirements that have always to be met by a PCM. However, there are more requirements that have to be met for most, but not all applications. These are:

Physical requirements:

- Suitable phase change temperature \Rightarrow to assure storage and extraction of heat in an application with a fixed temperature range.
- Large phase change enthalpy $\Delta H \Rightarrow$ to achieve high storage density compared to sensible storage.

- Large thermal conductivity \Rightarrow to be able to extract the stored heat or cold with sufficiently large heat flux.
- Reproducible phase change \Rightarrow to use the storage material many times (also called cycling stability).
- Little subcooling \Rightarrow to assure that melting and solidification proceed at the same temperature.

Technical requirements:

- Low vapor pressure \Rightarrow to reduce requirements of mechanical stability on a vessel containing the PCM.
- Small volume change \Rightarrow to reduce requirements of mechanical stability on a vessel containing the PCM.
- Chemical and physical stability \Rightarrow to assure long lifetime of the PCM.
- Compatibility with other materials \Rightarrow to assure long lifetime of the vessel containing the PCM and surrounding materials in case of leakage.

Economic requirements:

- Low price \Rightarrow to be competitive with other options for heat and cold storage.
- Non toxicity \Rightarrow for environmental and safety reasons.
- Recyclability \Rightarrow for environmental and economic reasons.

A first selection of materials is usually done with respect to phase change temperature, enthalpy and reproducible phase change. The state of the art with respect to that selection is discussed in the following section “Classes of materials”. Usually a material is not able to fulfill all the above mentioned requirements. For example the thermal conductivity is generally small and an encapsulation is always needed. Therefore strategies and approaches have been developed to cope with these problems. These are discussed after the section “Classes of materials” in “Approaches to solve material problems”.

17.3. Classes of Materials

17.3.1. OVERVIEW

By far the best known PCM is water. It occurs naturally and has been used for cold storage for more than 2000 years. Today, cold storage with ice is state of the art and even cooling with natural ice and snow is used again.

For applications where the melting point of water at 0 °C is not useful, different material classes have been investigated in the past. Figure 103 shows the typical range of melting enthalpy over melting temperature for the most promising material classes.

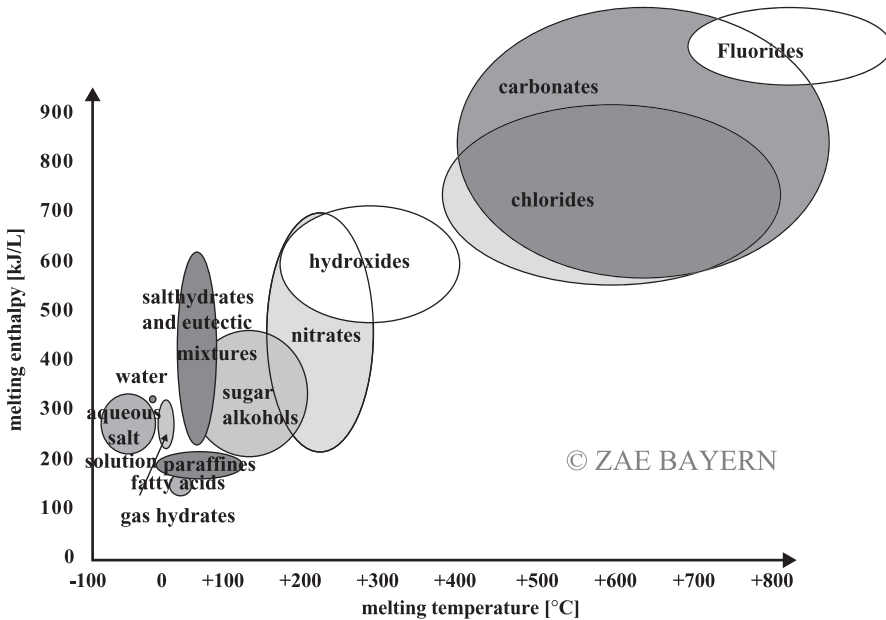


Figure 103. Classes of materials that can be use as PCM with regard to their typical range of melting temperature and melting enthalpy (graph: ZAE Bayern)

17.3.2. EXAMPLES OF MATERIALS INVESTIGATED AS PCM

A complete treatment of materials investigated as PCM is out of the scope of this book. The following text focuses on important and typical examples of materials. A more detailed treatment is found in Zalba et al. (2003) and Lane (1983).

17.3.2.1. Inorganic Materials

Inorganic materials, as Figure 103 shows, cover a wide temperature range. They include water at 0 °C, aqueous salt solutions at temperatures below 0 °C, salt hydrates between about 5 °C and 130 °C and finally different salts at temperatures above about 150 °C. Thanks to their density, usually larger than 1 g/cm³, they have larger melting enthalpies per volume than organic materials. Material compatibility with metals can be problematic as some PCM-metal combinations show severe corrosion. Table 18 shows a selection of a few typical examples which are the basis for many commercial PCM. Where several data are given, they reflect the typical variation of literature date.

In order to get new PCM, mixtures of 2 or more inorganic materials have also been investigated. Table 19 shows some examples of mixtures that

TABLE 18. Selection of inorganic materials that have been investigated for use as PCM

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
H ₂ O	0	333	0.612 (liquid, 20 °C)	998 (liquid, 20 °C) 917 (solid, 0 °C)
LiClO ₃ ·3H ₂ O	8	253	Not available	1,720
CaCl ₂ ·6H ₂ O	29	171, 192	0.540 (liquid, 39 °C)	1,562 (liquid, 32 °C), 1,496 (liquid), 1,802 (solid, 24 °C) 1,710 (solid, 25 °C)
LiNO ₃ ·3H ₂ O	30	296	Not available	Not available
Na ₂ HPO ₄ ·12H ₂ O	35–44	265	0.476 (liquid)	1,522
		280	0.514 (solid)	
Na ₂ S ₂ O ₃ ·5H ₂ O	48–55	187, 209	Not available	1,670 (liquid) 1,750 (solid)
Na(CH ₃ COO)·3H ₂ O	58	226, 264	Not available	1,280 (liquid) 1,450 (solid)
Ba(OH) ₂ ·8H ₂ O	78	265, 280	0.653 (liquid, 86 °C) 1.255 (solid, 23 °C)	1,937 (liquid, 84 °C) 2,180 (solid)
Mg(NO ₃) ₂ ·6H ₂ O	89	149, 163	0.490 (liquid, 95 °C)	1,550 (liquid, 94 °C)
	90		0.669 (solid, 55.6 °C)	1,636 (solid, 25 °C)
MgCl ₂ ·6H ₂ O	117	165, 169	0.570 (liquid, 120 °C)	1,450 (liquid, 120 °C)
			0.704 (solid, 110 °C)	1,569 (solid, 20 °C)
NaNO ₃	307	172	0.5	2,260
KNO ₃	333	266	0.5	2,110
KOH	380	145	0.5	2,044
MgCl ₂	714	452	Not available	2,140
NaCl	800	492	5	2,160
Na ₂ CO ₃	854	276	2	2,533
KF	857	452	not available	2,370
K ₂ CO ₃	897	236	2	2,290

are base on materials from Table 18. In the case of CaCl₂·6H₂O, small amounts of NaCl and KCl are added to achieve a better melting behavior without significant change of the melting temperature. The combination of Mg(NO₃)₂·6H₂O and MgCl₂·6H₂O results in a much lower melting point.

17.3.2.2. Organic Materials

Organic materials, as Figure 103 shows, cover a smaller temperature range from about 0 °C to 150 °C. They include mainly paraffins, fatty acids and sugar alcohols. In most cases, their density is smaller than 1 g/cm³. Thus paraffins and fatty acids usually have smaller melting enthalpies per volume than inorganic materials. They tend to be more expensive, but usually do

TABLE 19. Examples of inorganic mixture that have been investigated for use as PCM

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
48% CaCl ₂ + 4.3% NaCl + 0.4% KCl + 47.3% H ₂ O	27	188	Not available	1,640
58.7% Mg(NO ₃) · 6H ₂ O + 41.3% MgCl ₂ · 6H ₂ O	58, 59	132	0.510 (liquid, 65 °C) 0.678 (solid, 53 °C)	1,550 (liquid, 50 °C) 1,630 (solid, 24 °C)
66.9% NaF + 33.1% MgF ₂	832	Not available	Not available	2,190 (liquid), 2,940 (solid, 25 °C)

not subcool. Table 20 shows examples of paraffins and sugar alcohols that have been investigated for use as PCM. Examples of fatty acids are shown in Table 21.

Organic materials can also be mixed to modify the melting point.

17.3.2.3. *Mixtures of Organic and Inorganic Materials*

In the last few years, also mixtures of organic and inorganic materials have been investigated. However, at present not many results have been published.

TABLE 20. Examples of paraffins and sugar alcohols that have been investigated for use as PCM

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
Paraffin C14	4	165	Not available	Not available
Paraffin C15–C16	8	153	Not available	Not available
Paraffin C16–C18	20–22	152	Not available	Not available
Paraffin C18	28	244	0.148 (liquid, 40 °C), 0.358 (solid, 25 °C)	774 (liquid, 70 °C) 814 (solid, 20 °C)
Erythritol	118	340	0.326 (liquid, 140 °C), 0.733 (solid, 20 °C)	1,300 (liquid, 140 °C), 1,480 (solid, 20 °C)
High density polyethylene (HDPE)	100–150	200	Not available	Not available

TABLE 21. Examples of fatty acids that have been investigated for use as PCM

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
Caprylic acid	16	149	0.149 (liquid, 38 °C)	901 (liquid, 30 °C) 981 (solid, 13 °C)
Butyl stearate	19	140 123–200	Not available	Not available
Capric acid	32	153	0.153 (liquid, 38 °C), 0.149 (liquid, 40 °C)	886 (liquid, 40 °C), 1,004 (solid, 24 °C)
Lauric acid	42–44	178	0.147 (liquid, 50 °C)	870 (liquid, 50 °C), 1,007 (solid, 24 °C)
Myristic acid	49–58	186, 204	Not available	861 (liquid, 55 °C), 990 (solid, 24 °C)
Palmitic acid	61, 64	185, 203	0.162 (liquid, 68 °C), 0.159 (liquid, 80 °C),	850 (liquid, 65 °C) 989 (solid, 24 °C)

17.4. Approaches to Solve Material Problems

Usually, a material selected to be used as PCM does not fulfill all of the above requirements. Therefore, different strategies have been developed to solve or avoid potential problems. Some of these strategies are now discussed. A more detailed discussion of this subject can be found in Lane (1983) and Lane (1986).

17.4.1. PHASE SEPARATION

The effect of phase separation, also called semicongruent or incongruent melting, is a potential problem with PCM consisting of several components. Phase separation is explained in Figure 104 with a salt hydrate as example.

A salt hydrate consists of two components, the salt (e.g. CaCl_2) and water (e.g. $6\text{H}_2\text{O}$). The single phase of the salt hydrate is first heated up from point 1 (solid) to point 2. At point 3 the liquidus line is crossed and the material would be completely liquid. Upon heating or cooling, between point 2 and 3, 2 phases are formed, the liquid and a small amount of a phase with less water (point 4). If these phases differ in density, this can lead to macroscopic separation of the phases and therefore concentration differences of the chemicals forming the PCM material (points 5 and Figure 104 right).

When the temperature of the sample is reduced to below the melting point, the latent heat of solidification can usually not be released. This would require

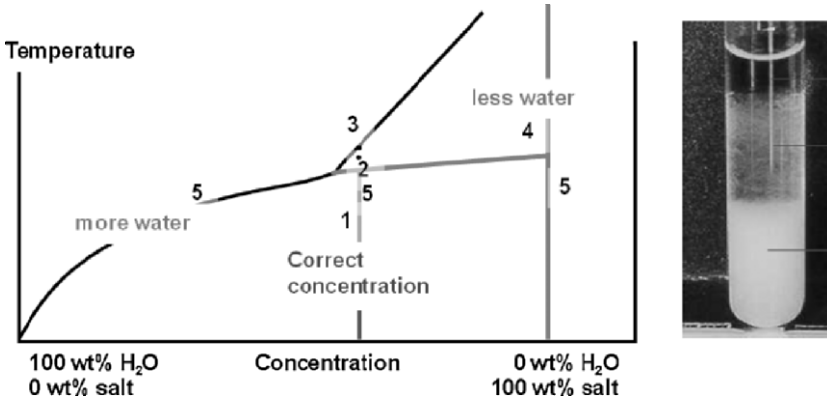


Figure 104. Phase separation of a salt hydrate (e.g. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) into three distinct phases with different water concentration and density (right) and corresponding phase diagram (left)

the correct concentration of the chemical components throughout the whole sample to form the solid PCM again. When the sample is heated up to a temperature where the phase point of the whole sample is in the liquid region (point 3) the different phases should mix again by molecular diffusion. If the sample is not mixed artificially, this can however take many hours or even days.

In most cases phase separation can be overcome using a gelling additive. A gelling additive forms a fine network within the PCM and thereby builds small compartments which restrict phases with different density to separate on a macroscopic level (Figure 105). If the sample is then heated to a temperature

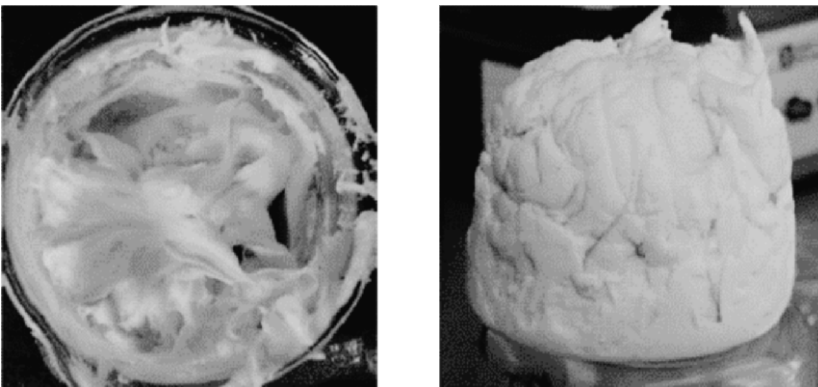


Figure 105. Gelling of a salt hydrate to prevent phase separation: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ gelled with cellulose

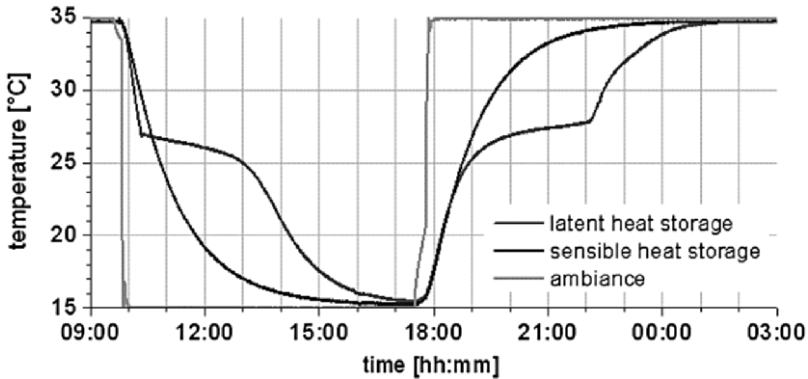


Figure 106. Solidification and melting of a PCM that is nearly ideal

somewhat above the melting point molecular diffusion can homogenize the PCM material again.

In some cases, phase separation can also be overcome by adding other chemicals to the original PCM and thus changing the phase diagram in a way that phase separation is prevented completely.

17.4.2. SUBCOOLING

An ideal PCM would solidify and melt at the same temperature as shown in Figure 106.

Many PCM however do not get solid right away if the temperature of the PCM is below the melting temperature (Figure 107).

This effect is called subcooling or supercooling. During subcooling, the PCM is in a metastable state, which means it is not in thermodynamic equilibrium. Subcooling is typical for many inorganic PCM. To reduce or

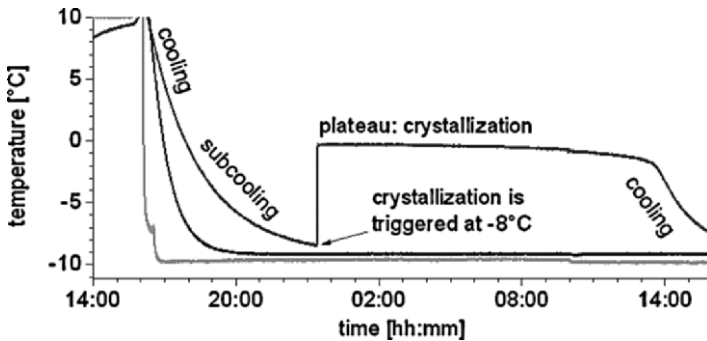


Figure 107. Subcooling of water

suppress subcooling, a nucleator has to be added to the PCM to ensure that the solid phase is formed with little subcooling. Potential nucleators are:

- *Intrinsic nucleators*: particles of solid PCM. They have to be kept separately from the PCM as they would otherwise melt with the PCM and thereby become inactive.
- *Extrinsic nucleators*: often chemicals that show very similar crystal structure as the solid PCM. This usually means that they have similar melting temperatures as the PCM itself and thus become deactivated at temperatures very close to the melting point of the PCM itself.

Nucleators have been developed for many, but not all, well investigated PCM. For a new PCM however, the search for a nucleator is usually time consuming and often not successful, as there is still no reliable theoretical approach for the search for a nucleator.

17.4.3. LOW THERMAL CONDUCTIVITY

The low thermal conductivity of PCM is an intrinsic property of nonmetallic liquids in general (Table 18–21). It poses a problem, because PCM store a large amount of heat in a small volume and this heat has to be transferred through the surface of this volume to the outside to be used in a system.

There are generally two ways to improve heat transfer:

- Improvement of heat transfer using mass transfer, which is convection. Convection only occurs in the liquid phase and therefore only acts when heat is transferred to the PCM. When heat is extracted, the solid phase forms at the heat exchanging surface.
- Improvement of heat transfer through increasing the thermal conductivity. This can be achieved by the addition of objects with larger thermal conductivity to the PCM. A special case are fins which are attached directly to the heat exchanger. Figure 108 shows two examples.

17.4.4. ENCAPSULATION AND COMPOSITE MATERIALS

Encapsulation and composite materials are a key issue in PCM technology. Because some of their positive effects can result from similar microscopic properties, they are discussed together (Figure 109). In almost all cases a PCM has to be encapsulated for technical use, as otherwise the liquid phase would be able to flow away from the location where it is applied. Macro

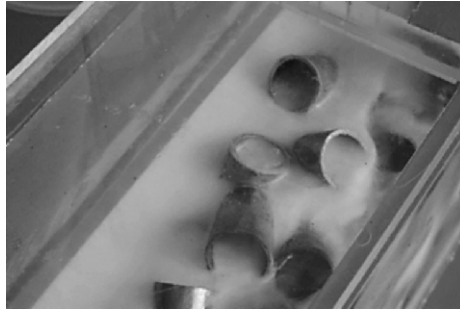


Figure 108. Improvement of heat transfer in a storage model through increasing the thermal conductivity with copper pieces (left) and graphite (right)

encapsulation, which is encapsulation in containments usually larger than 1 cm in diameter, is the most common form of encapsulation.

Besides holding the liquid PCM and preventing changes of its composition through contact with the environment, macro encapsulation also

- improves material compatibility with the surrounding, through building a barrier.
- improves handling of the PCM in a production.
- reduces external volume changes, which is usually also a positive effect for an application.

Micro encapsulation, which is encapsulation in containments smaller than 1 mm in diameter, is a recently developed new form of encapsulation for PCM. It can currently only be applied to water repelling PCM. Micro encapsulation serves the same purpose as mentioned above for macro encapsulation, but additionally

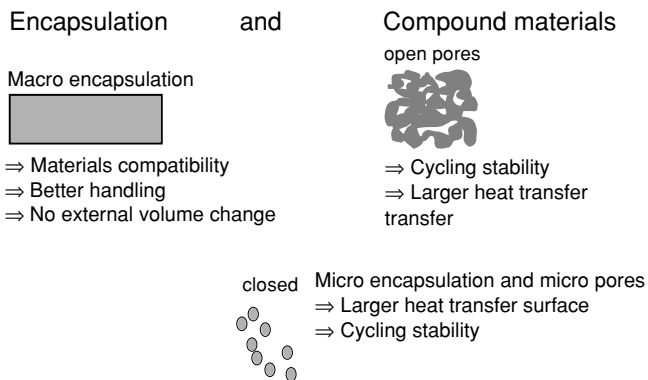


Figure 109. Encapsulation and composite materials and some of their positive effects

- improves heat transfer to the surrounding through its large surface to volume ratio.
- improves cycling stability since phase separation is restricted to microscopic distances.

Composite materials are materials consisting of a PCM and at least one other material. The other material serves to improve at least one of the PCM properties. In most cases this is handling of the PCM, but compounds can also

- improve the cycling stability, again by microscopic structures that reduce phase separation.
- improve heat transfer, through the addition of materials with large thermal conductivity as for example graphite.

17.4.5. COMPATIBILITY WITH OTHER MATERIALS

The compatibility of PCM with other materials is important with respect to lifetime of the encapsulation (or vessel) that contains the PCM, and the potential damage to the close environment of the encapsulation within the system, in case of leakage of the encapsulation.

Common problems in materials compatibility with PCM are:

- corrosion of metals in contact with inorganic PCM.
- stability loss of plastics in contact with organic PCM.
- migration of liquid or gas through plastics that affect the performance of a contained organic or inorganic PCM and outside environment.

To avoid compatibility problems, compatibility tests under conditions typical for the planned application are performed. From their results suitable material combinations are selected. Figure 110 shows a compatibility test for metals in contact with inorganic PCM. Test tubes containing both materials (center) are kept in a controlled environment for a fixed time (left) and later effects on the metal are analyzed (right).

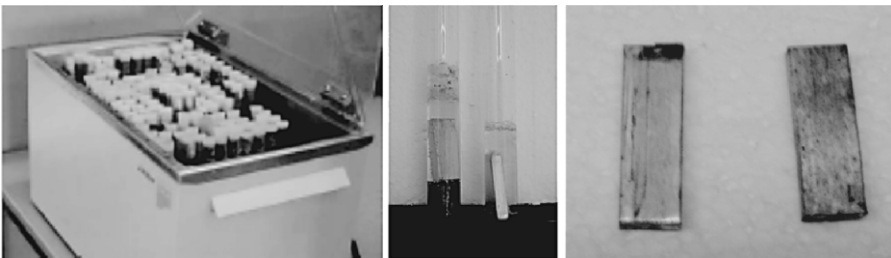


Figure 110. Compatibility test for metal-inorganic PCM combinations

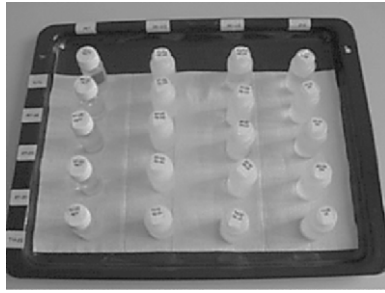


Figure 111. Compatibility test for plastic-inorganic PCM and plastic-organic PCM combinations

Figure 111 shows a similar setup to test plastics in contact with organic and inorganic PCM materials.

17.5. State of the Art

17.5.1. PCM ON THE MARKET

At the moment more than 50 PCM are commercially available from the following companies:

- RUBITHERM GmbH in Germany (<http://www.rubitherm.de/>).
- Dörken GmbH & Co. KG in Germany (<http://www.doerken.de/bvf/de/produkte/pcm/produkte/cool25.php>).
- Climator AB in Sweden (<http://www.climator.com/>).
- TEAP in Australia (<http://www.teappcm.com/>).
- CRISTOPIA Energy Systems in France (<http://www.cristopia.com/>).
- Mitsubishi Chemical in Japan.

Their price varies in the 0.5–10 €/kg range. This means for being competitive in an energy system, daily loading and unloading should be targeted. Figure 112 shows an overview of commercial PCM with respect to melting temperature and melting enthalpy per volume and mass.

17.5.2. ENCAPSULATIONS ON THE MARKET

Encapsulations can be divided into two groups (page 219), depending on their size: macro and micro encapsulation.

17.5.2.1. Examples of Macro Encapsulation

Macro encapsulation in plastic containers is widely used, usually for inorganic PCM. Examples of macro encapsulation are shown in Figure 113 (plastic

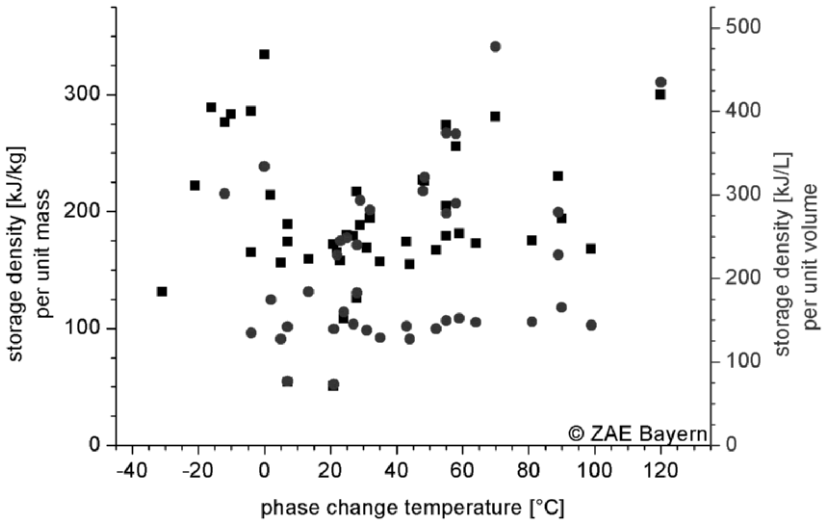


Figure 112. Overview of melting points and storage densities of commercial PCM. (●) in kJ/L, (■) in kJ/kg

containers), Figure 114 (bags), Figure 115 (capsule stripes) and Figure 116 metal containers.

17.5.2.2. Examples of Micro Encapsulation

Micro encapsulated PCM are available from BASF (http://www.basf.com/corporate/080204_micronal.htm) (Figure 117).

BASF encapsulates different paraffins with a special process and sells the micro capsules under the brand name Micronal[®] as fluid dispersion or as dried powder (Figure 118).

17.5.2.3. PCM Compounds on the Market

The market for PCM compounds is currently dominated by the companies Rubitherm and SGL, both from Germany.

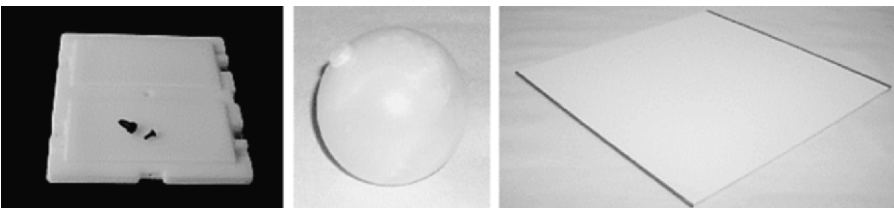


Figure 113. From left to right: Flat container (Kissmann/Germany), spheres and bar double plates (Dörken/Germany)



Figure 114. Macro encapsulation in bags (left from Climator/Sweden; right from Dörken/Germany)

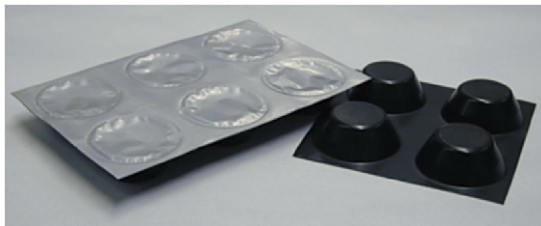


Figure 115. Macro encapsulation in capsule stripes as produced by TEAP/Australia and Dörken/Germany for inorganic PCM.

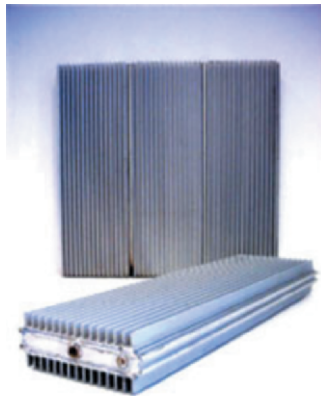


Figure 116. Macro encapsulation in aluminum profiles with fins for improved heat transfer (Climator/Sweden)

17.5.2.4. *PCM Composite Materials to Improve Handling and Applicability*
 Rubitherm produces a set of different composite materials, mainly to improve handling and applicability. Some composites, which are based on different granulates and fiber boards are shown in Figure 119.

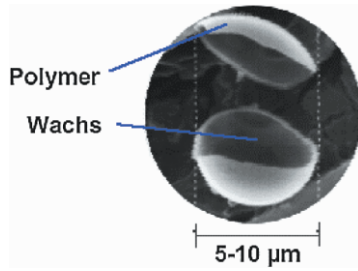


Figure 117. Microscope image of an opened micro capsule (picture: BASF/Germany)

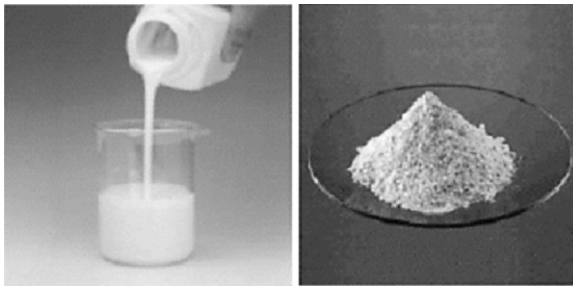


Figure 118. Micro encapsulation of paraffin produced by BASF/Germany as fluid dispersion (left) and dry powder (right) (pictures: BASF/Germany)

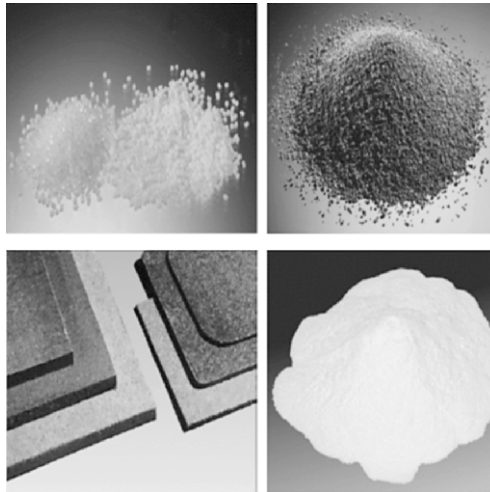


Figure 119. PCM composite materials produced by Rubitherm: compound (PK), granulate (GR), fiber board (FB) and powder (PX)

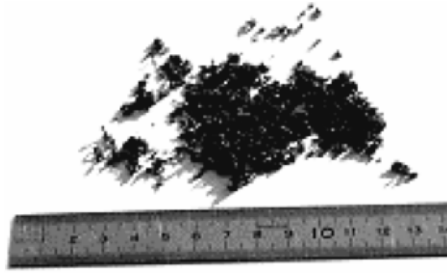


Figure 120. Expanded graphite which is the basic heat transfer structure for PCM-graphite composites

17.5.2.5. PCM-Graphite Composites to Increase the Thermal Conductivity

The use of graphite particles and fibers to enhance the thermal conductivity of PCM has been proposed about 10 years ago. Since then, numerous publications have experimentally proved the concept. Besides the high thermal conductivity of graphite its stability to high temperatures and corrosive environments is a big advantage to other materials. SGL in Germany sells different PCM composites with graphite (http://www.sglcarbon.com/sgl_t/expanded/markets/energy/heat_storage_d.html). SGL uses expanded graphite (Figure 120) on a large scale for producing graphite sheets which are then processed e.g. for high temperature seals. To form a PCM-graphite composite, the expanded graphite is used in two different ways.

PCM-Graphite Matrix

The PCM-graphite matrix is produced in two steps:

- In a first step the expanded graphite is pressed in a continuous process to form about 1 cm thick plates (Figure 121 left). These plates form a graphite

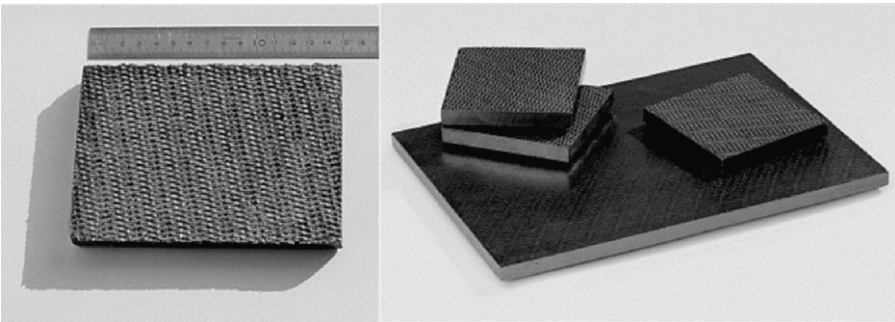


Figure 121. Left: prepressed expanded graphite forms a graphite matrix with thermal conductivity of about 25 W/m K and porosity of 90 vol.%. Right: PCM-graphite matrix after infiltration of PCM with about 85 vol.%

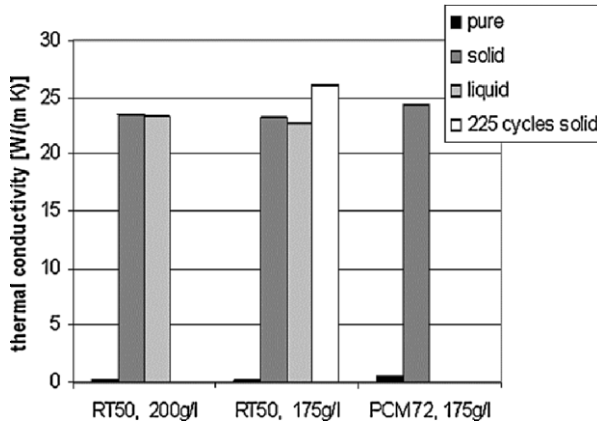


Figure 122. Thermal conductivity of pure PCM, PCM-graphite matrix in the solid and liquid state after production and in the solid state after cycling for different PCM and graphite densities

matrix with about 90 vol.% porosity, good mechanical stability and thermal conductivity of about 20–25 W/m K in plate and 5–8 W/m K perpendicular to the plate surface.

- In a second step, the PCM is infiltrated into this graphite matrix until about 80–85 vol.% PCM are reached.

Figure 122 shows the thermal conductivity of pure PCM, PCM-graphite matrix in the solid and liquid state after production and in the solid state after cycling for different PCM and graphite densities. Compared to the pure PCM with a thermal conductivity of 0.2–0.5 W/m K, the thermal conductivity is enhanced by a factor of 50–100.

The PCM-graphite matrix can be produced with many organic and inorganic PCM, but with some important exceptions. Furtheron, limitations in producing the graphite-matrix with respect to shape and size exist. SGL has therefore developed a second method to produce PCM-graphite composites.



Figure 123. PCM-graphite compound produced from mixing PCM with expanded graphite

PCM-Graphite Compound

In this method the PCM is mixed with expanded graphite in a compounding process. The result is a compound in granular form (Figure 123).

The compound can be produced with any arbitrary PCM and can also be brought into any arbitrary form e.g. by injection molding. The final result has a similar volumetric composition as the PCM-graphite matrix, which is 10 vol. % graphite, 80 vol. % PCM and 10 vol. % air. The thermal conductivity however is only about 4–5 W/m K due to the loose contact between the graphite particles in the compound. Nevertheless, compared to the pure PCM, the thermal conductivity is still enhanced by a factor of 5–20.

References

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