

## 2 Solid-liquid phase change materials

In this chapter, basic know-how on phase change materials is summarized. The chapter starts with a description of the basic requirements on a material to use it as phase change material. Then different material classes are discussed with respect to their most important properties, advantages, and disadvantages. Then examples for materials from each material class are given. Usually, a material is not able to fulfill all the requirements. Therefore, for several common material problems solutions are given. The chapter ends with a set of examples showing the currently available range of commercial products.

### 2.1 Physical, technical, and economic requirements

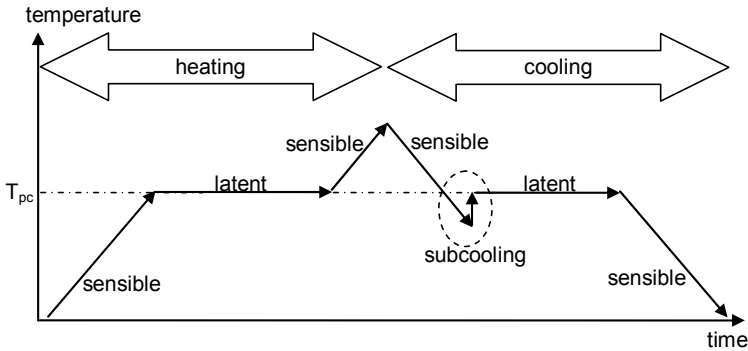
A suitable phase change temperature and a large melting enthalpy are two obvious requirements on a phase change material. They have to be fulfilled in order to store and release heat at all. However, there are more requirements for most, but not all applications. These requirements can be grouped into physical, technical, and economic requirements.

- Physical requirements, regarding the storage and release of heat:
  - Suitable phase change temperature  $T_{pc} \Rightarrow$  to assure storage and release of heat in an application with given temperatures for heat source and heat sink.
  - Large phase change enthalpy  $\Delta_{pc}h \Rightarrow$  to achieve high storage density compared to sensible heat storage.
  - Reproducible phase change, also called *cycling stability*  $\Rightarrow$  to use the storage material as many times for storage and release of heat as required by an application.

The number of cycles varies from only one, when the PCM is used for heat protection in the case of a fire, to several thousand cycles when used for heating or cooling of buildings. One of the main problems of cycling stability is phase separation. When a PCM consists of several components, phases with different compositions can form upon cycling. *Phase separation* is the effect that phases with different composition are separated from each other macroscopically. The phases with a composition different from the correct initial composition optimized for heat storage then show a significantly lower capacity to store heat.

- Little subcooling  $\Rightarrow$  to assure that melting and solidification can proceed in a narrow temperature range.

*Subcooling* (also called *supercooling*) is the effect that a temperature significantly below the melting temperature has to be reached, until a material begins to solidify and release heat (fig.2.1). If that temperature is not reached, the PCM will not solidify at all and thus only store sensible heat.



**Fig. 2.1.** Schematic temperature change during heating (melting) and cooling (solidification) of a PCM with subcooling.

- Good thermal conductivity  $\Rightarrow$  to be able to store or release the latent heat in a given volume of the storage material in a short time, that is with sufficient heating or cooling power.

If a good thermal conductivity is necessary strongly depends on the application and the design of the storage.

- Technical requirements, regarding the construction of a storage:
  - Low vapor pressure  $\Rightarrow$  to reduce requirements of mechanical stability and tightness on a vessel containing the PCM
  - Small volume change  $\Rightarrow$  to reduce requirements of mechanical stability on a vessel containing the PCM
  - Chemical stability of the PCM  $\Rightarrow$  to assure long lifetime of the PCM if it is exposed to higher temperatures, radiation, gases, ...
  - Compatibility of the PCM with other materials  $\Rightarrow$  to assure long lifetime of the vessel that contains the PCM, and of the surrounding materials in the case of leakage of the PCM

This includes destructive effects as for example the corrosivity of the PCM with respect to other materials, but also other effects that significantly reduce or stop important functions of another material.

- Safety constraints  $\Rightarrow$  the construction of a storage can be restricted by laws that require the use of non-toxic, non-flammable materials. Other environmental and safety consideration can apply additionally.

- Economic requirements, regarding the development of a marketable product:
  - Low price  $\Rightarrow$  to be competitive with other options for heat and cold storage, and to be competitive with methods of heat and cold supply without storage at all
  - Good recyclability  $\Rightarrow$  for environmental and economic reasons

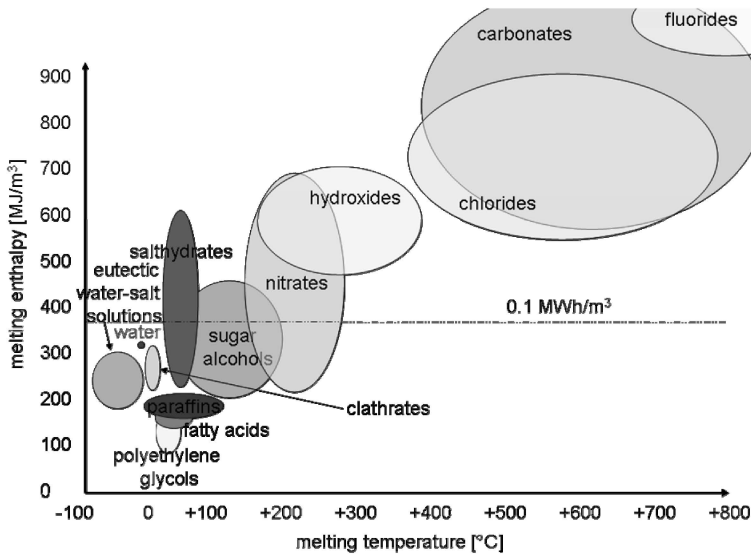
Lane et al. 1983 gives a detailed discussion of these selection criteria and examples of how to select candidate materials. A first selection of a material is usually done with respect to the physical requirements phase change temperature, enthalpy, cycling stability, and subcooling. The classes of the materials to choose from, as well as lists of examples for different classes with data on phase change temperature and enthalpy, are discussed in the following section.

Usually, a material is not able to fulfill all the requirements mentioned above. For example, the thermal conductivity of a PCM is usually small, inorganic PCM often show subcooling, and compatibility with the container material is not always given. Therefore, different strategies have been developed to cope with these problems. These strategies are discussed in section 2.3. Section 2.4 then concludes with the commercial examples.

## 2.2 Classes of materials

### 2.2.1 Overview

Because the two most important criteria, the melting temperature and the melting enthalpy, depend on molecular effects, it is not surprising that materials within a material class behave similar. Fig.2.2 shows the typical range of melting enthalpy and melting temperature of common material classes used as PCM.



**Fig. 2.2.** Classes of materials that can be used as PCM and their typical range of melting temperature and melting enthalpy (picture: ZAE Bayern).

By far the best-known PCM is water. It 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 temperatures below 0 °C, usually water-salt solutions with a eutectic composition are used. Several material classes cover the temperature range from 0 °C to about 130 °C. Paraffins, fatty acids, and sugar alcohols are organic materials. Salt hydrates are salts with a large and defined amount of crystal water. Clathrates are crystalline structures in which molecules of one type are enclosed in the crystal lattice of another. When the enclosed molecule is from a gas and the surrounding crystal structure is water, the clathrate is also called a gas hydrate. They cover a temperature range from about 0 °C to 30 °C. At temperatures above 150 °C, different salts and their mixtures can be applied.

A close look at fig.2.2 indicates that the energy density is roughly proportional to the melting temperature in K. This can be understood from thermodynamics according to the theory of Richards (tab.1.2). The theory of Richards shows that the melting enthalpy per volume is proportional to the melting temperature, the number of bonds per molecule, and the density divided by the molar mass that relates to the packing density of the molecules or atoms (Lindner 1984).

### 2.2.2 Detailed discussion

Probably thousands of single materials and mixtures of two or more materials have been investigated for their use as PCM in the past decades. Because the scope of this book is to give an introduction, important and typical examples are discussed here; no attempt is made to give a large or even complete list of materials. For more comprehensive lists of materials the reader should look at the early publications of Steiner et al. 1980, Abhat 1983, Lane 1983 and 1986, Schröder 1985, and more recent publications like Kakiuchi et al. 1998, Hiebler and Mehling 2001, Zalba et al. 2003, Sharma et al. 2004, Farid et al. 2004, and Kenisarin and Mahkamov 2007.

Inorganic materials cover a wide temperature range. Compared to organic materials, inorganic materials usually have similar melting enthalpies per mass, but higher ones per volume due to their high density (fig.2.2). Their main disadvantage is material compatibility with metals, since severe corrosion can be developed in some PCM-metal combinations.

*Eutectic water-salt solutions* have melting temperatures below 0 °C, because the addition of the salt reduces the melting temperature, and usually good storage density. Tab.2.1 shows a selection of typical examples.

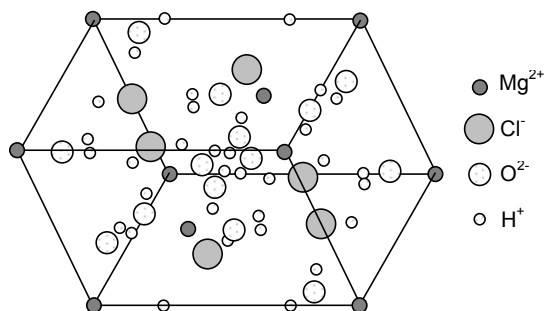
**Table 2.1.** Examples of eutectic water-salt solutions that have been investigated as PCM (Schröder 1985).

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
Al(NO <sub>3</sub> ) <sub>3</sub> (30.5 wt.%) / H <sub>2</sub> O	-30.6	131	-	1283 (liquid)
			-	1251 (solid)
NaCl (22.4 wt.%) / H <sub>2</sub> O	-21.2	222	-	1165 (liquid)
			-	1108 (solid)
KCl (19.5 wt.%) / H <sub>2</sub> O	-10.7	283	-	1126 (liquid)
			-	1105 (solid)
H <sub>2</sub> O	0	333	0.6 (liquid, 20 °C)	998 (liquid, 20°C)
			2.2 (solid)	917 (solid, 0 °C)

Water-salt solutions consist of two components, water and salt, which means phase separation could be a problem. To prevent phase separation, and to achieve a good cycling stability, eutectic compositions are used. *Eutectic compositions* are mixtures of two or more constituents, which solidify simultaneously out of the liquid at a minimum freezing point. Therefore, none of the phases can sink down due to a different density. Further on, eutectic compositions show a melting temperature and good storage density. A more detailed discussion on phase separation and how to get rid of it follows in section 2.3.1. The thermal conductivity of eutectic

water-salt solutions is similar to that of water and they can subcool like water by several K or more. The vapor pressure at temperatures as low as their melting temperature is quite small, however like water they can show considerable volume change in the order of 5 to 10 vol.% during melting and solidification. Water can cause severe damage upon freezing and melting for example like cracking stones in winter. Water-salt solutions are chemically very stable, but can cause corrosion to other materials like metals. Compared to water, the addition of a salt usually makes the problem worse. Most of the salt solutions are rather safe, but should not leak in larger amounts. They are usually cheap, often less than 1 €/kg, and therefore the basis for many commercial PCM used in large-scale applications.

The temperature range between 5 °C and 130 °C is covered by salt hydrates. *Salt hydrates* consist of a salt and water in a discrete mixing ratio. It is usually an integral number of water molecules per ion pair of the salt, where a stable crystal structure forms. The bonds are usually ion-dipole bonds or hydrogen bonds. The water molecules are located and oriented in the structure in a well-defined manner. In some structures, the water is more closely oriented to the anion, in others to the cation of the salt.



**Fig. 2.3.** Molecular structure of the salt hydrate  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

An example, magnesium chloride hexahydrate  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , is shown in fig.2.3. The lattice consists of two parts:  $\text{Cl}^-$  ions, and 6 water molecules oriented octahedral around a magnesium ion  $\text{Mg}^{2+}$  and bound by ion-dipole bonds. Because of the stable crystal structure of salt hydrates, the melting temperature is higher than for water. Tab.2.2 shows a selection of typical examples that are the basis for many commercial PCM. Where several data for the same property are given in the following tables, these data reflect the typical variation of literature data. In some examples, a range is given for the melting temperature, rather than a single value. The different reasons why a material shows a melting range are explained in section 2.3.1.

**Table 2.2.** Examples of salt hydrates that have been investigated as PCM

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
LiClO <sub>3</sub> ·3H <sub>2</sub> O	8	155	-	1530 (liquid) 1720 (solid)
KF·3H <sub>2</sub> O	18.5	231	-	1447 (liquid, 20 °C) 1455 (solid, 18 °C)
CaCl <sub>2</sub> ·6H <sub>2</sub> O	29, 30	171, 190	0.540 (liquid, 39 °C) 1.088 (solid, 23 °C)	1562 (liquid, 32 °C) 1710 (solid, 25 °C)
LiNO <sub>3</sub> ·3H <sub>2</sub> O	30	296	-	-
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	32	254	-	-
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	35-44	280	0.554 0.476 (liquid) 0.514 (solid)	1485 (solid) 1442 (liquid) 1522 (solid)
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	48-55	187, 209	-	1670 (liquid) 1750 (solid)
Na(CH <sub>3</sub> COO)·3H <sub>2</sub> O	58	226, 264	-	1280 (liquid) 1450 (solid)
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	78	265, 280	0.653 (liquid, 86 °C) 1.255 (solid, 23 °C)	1937 (liquid, 84 °C) 2180 (solid)
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	89, 90	149, 163	0.490 (liquid, 95 °C) 0.669 (solid, 56 °C)	1550 (liquid, 94 °C) 1636 (solid, 25 °C)
MgCl <sub>2</sub> ·6H <sub>2</sub> O	117	165, 169	0.570 (liquid, 120 °C) 0.704 (solid, 110 °C)	1450 (liquid, 120 °C) 1569 (solid, 20 °C)

Salt hydrates often have comparatively high storage density with respect to mass, but even more with respect to volume due to their high density. Because salt hydrates consist of several components, at least one salt and water, they can potentially separate into different phases and thus show problems with cycling stability. In fact, phase separation is a common problem with salt hydrates. Their thermal conductivity is similar to that of water and eutectic water-salt solutions. Most salt hydrates subcool, some of them by as much as 80 K. Their vapor pressure is somewhat lower than for water, as the salt usually reduces the vapor pressure. Salt hydrates melting close to or above 100 °C however show already considerable vapor pressure when melting. The volume change of salt hydrates is up to 10 vol.%. In most, but not all cases, salt hydrates are chemically very stable. However, many

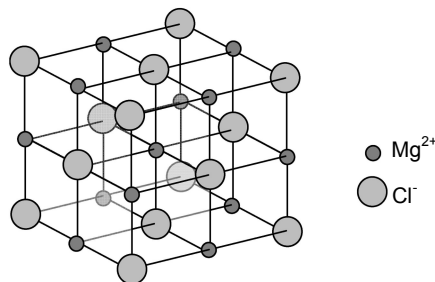
of them are potentially corrosive to metals. Regarding the safety of salt hydrates there is a high variation, so the respective data sheets have to be checked. The price of salt hydrates is usually low, in the order of 1 to 3 €/kg unless bought in a pure form.

Above 150 °C, different *salts* can be used as PCM. Tab.2.3 shows a selection of typical examples.

**Table 2.3.** Examples of salts that have been investigated as PCM

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
LiNO <sub>3</sub>	254	360	0.58 (liquid)	1780 (liquid)
			1.37 (solid)	2140 (solid)
NaNO <sub>3</sub>	307	172	0.51 (liquid)	1900 (liquid)
			0.59 (solid)	2260 (solid)
KNO <sub>3</sub>	333	266	0.50 (liquid)	1890 (liquid)
			-	1900 (solid)
MgCl <sub>2</sub>	714	452	-	2140
			-	-
NaCl	800	492	-	2160
			-	-
Na <sub>2</sub> CO <sub>3</sub>	854	276	-	2533
			-	-
KF	857	452	-	2370
			-	-
K <sub>2</sub> CO <sub>3</sub>	897	236	-	2290
			-	-

Because the melting enthalpy rises roughly proportional to the melting temperature given in K, salts with high melting temperatures often show a very high melting enthalpy. Fig.2.4 shows an example of a salt: MgCl<sub>2</sub>. A salt always consists of two components, so theoretically phase separation is a potential problem. However, unless the rare case that two different salt compositions exist, phase separation is not possible.



**Fig. 2.4.** Crystal structure of the salt MgCl<sub>2</sub>.



The thermal conductivity of salts can be quite good. Subcooling, as far as data are available, is not more than a few K, and their vapor pressure is very low. The volume change from solid to liquid can be up to 10 vol.%. Many of the salts are chemically stable; however, carbonates and nitrates can decompose under unsuitable conditions. Regarding the compatibility to other materials, salts can be corrosive to metals. Their safety differs strongly between different salts. The same holds for their price.

In order to get materials with different melting temperature or improved properties, *mixtures of inorganic materials* have been tested. For example, small amounts of NaCl and KCl are added to  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to achieve a better melting behavior without significant change of the melting temperature (Lane 1986). In another example, the combination of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  results in a much lower melting temperature of the mixture compared to the base materials of the mixture. For example, Nagano et al. 2000 systematically investigated the lowering of the melting temperature of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  by the addition of other materials. Neuschütz 1999 presented an eutectic mixture of  $\text{LiNO}_3/\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ . Tab.2.4 shows some examples of mixtures (salt – salt hydrate, salt hydrate – salt hydrate, salt – salt) that are based on materials from tab.2.2 and tab.2.3.

**Table 2.4.** Examples of inorganic mixtures that have been investigated as PCM

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
4.3 % NaCl + 0.4 % KCl + 48 % $\text{CaCl}_2$ + 47.3 % $\text{H}_2\text{O}$	27	188	-	1530 (liquid) 1640 (solid)
58.7 % $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 58, 59 + 41.3 % $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$		132	0.510 (liquid, 65 °C) 0.678 (solid, 53 °C)	1550 (liquid, 50 °C) 1630 (solid, 24 °C)
67 % $\text{KNO}_3$	133	170	-	-
+ 33 % $\text{LiNO}_3$			-	-
54 % $\text{KNO}_3$	222	100	-	1950 (liquid)
+ 46 % $\text{NaNO}_3$			-	2050 (solid)

The search for mixtures of different materials is usually done experimentally. That means, first mixtures with different compositions are prepared, and then their melting temperature and enthalpy are determined. If positive results are achieved with one or several of the compositions, the composition is optimized in a second set of experiments. This procedure involves a lot of work and is very time consuming. A way to reduce the experimental effort is to calculate the liquidus curves

of salt hydrates and multi-component systems (Voigt 1993). Then, only few experiments have to be performed, but such calculations are up to experts in the field.

Besides the material classes of inorganic materials, there are also organic materials used as PCM like paraffins, fatty acids and sugar alcohols. These material classes cover the temperature range between 0 °C and about 200 °C. Due to the covalent bonds in organic materials, most of them are not stable to higher temperatures. In most cases, the density of organic PCM is less than  $10^3 \text{ kg/m}^3$ , and thus smaller than the density of most inorganic materials like water and salt hydrates. The result is that, with the exception of sugar alcohols, organic materials usually have smaller melting enthalpies per volume than inorganic materials.

The most commonly used organic PCM are paraffins. *Paraffin* is a technical name for an alkane, but often it is specifically used for linear alkanes with the general formula  $\text{C}_n\text{H}_{2n+2}$ , as shown in fig.2.5.

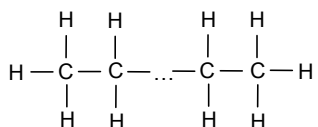


Fig. 2.5. Chemical structure of linear alkanes.

Little information is available on their crystal structure. The picture in fig.2.6 shows the crystal structure of n-hexane. It is based on data published by Boese et al. 1999.

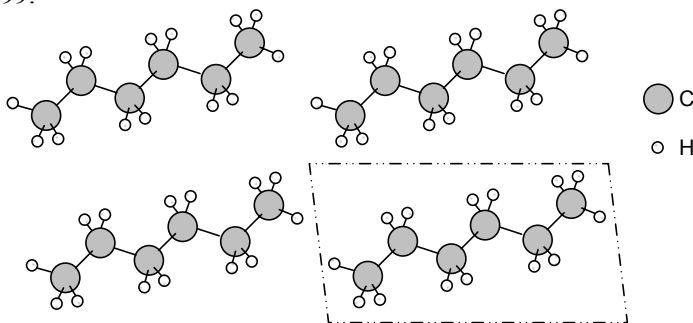


Fig. 2.6. Crystal structure of n-hexane.

Paraffins show good storage density with respect to mass, and melt and solidify congruently with little or no subcooling. Their thermal conductivity is however comparatively low. Regarding the stability of a container, their vapor pressure is usually not significant. Their volume increase upon melting is in the order of 10 vol.%; this is similar to that of many inorganic materials, but less critical as paraffins are softer and therefore build up smaller forces upon expansion. Paraffins are insoluble in water as they are water repellent. They do not react with most

common chemical reagents; in fact, the name “paraffin” originates in the Latin and means that they are little reactive. At elevated temperatures, paraffin bonds can crack and the resulting short chain molecules evaporate. Paraffins are combustible and people often conclude that paraffins burn easily. The fact that candles do not burn as a whole shows that this is not correct. The compatibility of paraffins with metals is very good; with plastics however, paraffins can cause softening of the plastic. Paraffins have very few safety constraints. Tab.2.5 shows examples of paraffins. It indicates that with rising number of C atoms in  $C_nH_{2n+2}$  the melting temperature increases. The limit is Polyethylene with thousands of C atoms. At very low numbers of C atoms, methane  $C_1H_4$ , ethane  $C_2H_6$ , and propane  $C_3H_8$  are gasses at ambient conditions. Tetradecane is the smallest n-alkane that melts above  $0^\circ\text{C}$ .

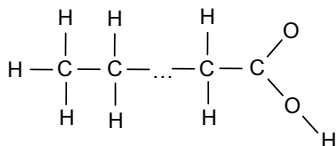
**Table 2.5.** Examples of paraffins that have been investigated as PCM.

Material	Melting temperature ( $^\circ\text{C}$ )	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density ( $\text{kg/m}^3$ )
n-Tetradecane	6	230	-	760 (liquid, $20^\circ\text{C}$ )
$C_{14}H_{30}$			0.21 (solid)	-
n-Pentadecane	10	212	-	770 (liquid, $20^\circ\text{C}$ )
$C_{15}H_{32}$			-	-
n-Hexadecane	18	210, 238	-	760 (liquid, $20^\circ\text{C}$ )
$C_{16}H_{34}$			0.21 (solid)	-
n-Heptadecane	19	240	-	776 (liquid, $20^\circ\text{C}$ )
$C_{17}H_{36}$			-	-
n-Octadecane	28	200, 245	0.148 (liquid, $40^\circ\text{C}$ )	774 (liquid, $70^\circ\text{C}$ )
$C_{18}H_{38}$			0.358 (solid, $25^\circ\text{C}$ )	814 (solid, $20^\circ\text{C}$ )
n-Eicosane	38	283	-	779
$C_{20}H_{42}$			-	-
n-Triacontane	66	-	-	775
$C_{30}H_{62}$			-	-
n-Tetracontane	82	-	-	-
$C_{40}H_{82}$			-	-
n-Pentacontane	95	-	-	779
$C_{50}H_{102}$			-	-
Polyethylene	110-135	200	-	-
$C_nH_{2n+2}$ n up to 100000			-	870-940 (solid, $20^\circ\text{C}$ )

Pure alkanes are rather expensive. Commercial paraffin is usually obtained from petroleum distillation and contains a number of different hydrocarbons. These mixtures show a melting range and a lower heat of fusion than the pure alkanes.

Alkanes of different chain length are also mixed intentionally, especially to get PCM with different melting temperatures. He et al. 1998 and He et al. 1999 for example investigated binary mixtures of tetra-, penta-, and hexadecane, to adjust the melting temperature. Further data on mixtures of paraffins are listed in Kenisarin and Mahkamov 2007.

A *fatty acid* is characterized by the formula  $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ . In contrast to a paraffin, one end of the molecule ends with a  $-\text{COOH}$  instead of a  $-\text{CH}_3$  group (fig.2.7).



**Fig. 2.7.** Chemical structure of fatty acids.

Tab.2.6 lists some of the most common saturated fatty acids. Their melting enthalpy is similar to that of paraffins, and their melting temperature increases with the length of the molecule. Fatty acids are stable upon cycling; because they consist of only one component there cannot be phase separation. Like paraffins, fatty acids also show little or no subcooling and have a low thermal conductivity.

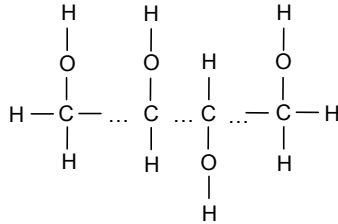
**Table 2.6.** Examples of fatty acids that have been investigated as PCM.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
Caprylic acid	16	149	0.149 (liquid, 38 °C)	901 (liquid, 30 °C)
$\text{CH}_3(\text{CH}_2)_6\text{COOH}$			-	981 (solid, 13 °C)
Capric acid	32	153	0.149 (liquid, 40 °C)	886 (liquid, 40 °C),
$\text{CH}_3(\text{CH}_2)_8\text{COOH}$			-	1004 (solid, 24 °C)
Lauric acid	42-44	178	0.147 (liquid, 50 °C)	870 (liquid, 50 °C),
$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$			-	1007 (solid, 24 °C)
Myristic acid	58	186, 204	-	861 (liquid, 55 °C),
$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$			0.17 (solid)	990 (solid, 24 °C)
Palmitic acid	61, 64	185, 203	-	850 (liquid, 65 °C)
$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$			-	989 (solid, 24 °C)

A difference to paraffins can be expected in the compatibility of fatty acids to metals as experiments by Sari and Kaygusuz 2003 show; this is due to the acid character.

Different fatty acids can also be mixed to design PCM with different melting temperatures than the pure fatty acids. Data on such mixtures can be found in Nikolić et al. 2003, Tunçbilek et al. 2005, and Kenisarin and Mahkamov 2007.

*Sugar alcohols* are a hydrogenated form of a carbohydrate. The general chemical structure is  $\text{HOCH}_2[\text{CH}(\text{OH})]_n\text{CH}_2\text{OH}$ , as fig.2.8 shows. Different forms are obtained depending on the orientation of the OH groups.



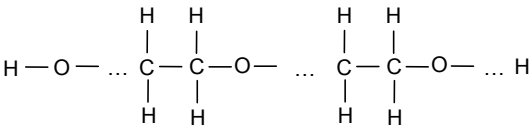
**Fig. 2.8.** Chemical structure of sugar alcohols.

Sugar alcohols are a rather new material class, therefore little general information is available. As tab.2.7 shows, they have melting temperatures in the 90 °C to 200 °C range, and their mass specific melting enthalpies are comparatively high in most cases. In addition, their density is also high, which results in very high volume specific melting enthalpies. In contrast to many other organic materials, sugar alcohols however show some subcooling. According to Kakiuchi et al 1998, sugar alcohols are safe; erythritol and xylitol are used to replace sugar as sweetener.

**Table 2.7.** Examples of sugar alcohols that have been investigated as PCM.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
Xylitol	94	263	-	-
C <sub>5</sub> H <sub>7</sub> (OH) <sub>5</sub>			-	1500 (solid, 20 °C)
D-Sorbitol	97	185	-	-
C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub>			-	1520 (solid, 20 °C)
Erythritol	120	340	0.326 (liquid, 140 °C), 0.733 (solid, 140 °C), 20 °C)	1300 (liquid, 140 °C), 1480 (solid, 20 °C)
C <sub>4</sub> H <sub>6</sub> (OH) <sub>4</sub>				
D-Mannitol	167	316	-	-
C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub>			-	1520 (solid, 20 °C)
Galactitol	188	351	-	-
C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub>			-	1520 (solid, 20 °C)

*Polyethylen glycol*, or short *PEG*, is a polymer with the general formula  $\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$ . It is produced from ethylenglycol  $\text{C}_2\text{H}_4(\text{OH})_2$ . The base unit of a linear PEG chain are monomers of  $-\text{CH}_2-\text{CH}_2-\text{O}-$ , as shown in fig.2.9.



**Fig. 2.9.** Chemical structure of polyethylene glycols.

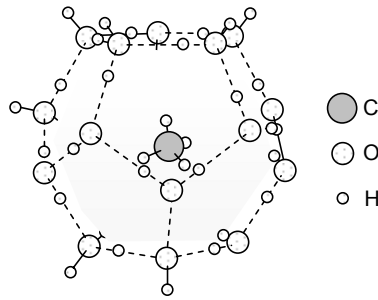
The monomers have a molecular weight of 44 g/mole. Polyethylene glycols are available in a molecular weight range from about 200 to 35000; this corresponds to 5 monomers to about 800 monomers. Tab.2.8 lists some properties of PEGs.

**Table 2.8.** Examples of PEGs and some of their properties.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
Diethylene glycol C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>	-10 to -7	-	- -	1120 (liquid, 20 °C), -
Triethylene glycol C <sub>6</sub> H <sub>14</sub> O <sub>4</sub>	-7	-	- -	1120 (liquid, 20 °C), -
PEG400	8	100	0.19 (liquid, 38 °C), -	1125 (liquid, 25 °C), 1228 (solid, 3 °C)
PEG600	17 - 22	127	0.19 (liquid, 38 °C), -	1126 (liquid, 25 °C), 1232 (solid, 4 °C)
PEG1000	35 - 40	-	- -	- -
PEG3000	52 - 56	-	- -	- -
PEG6000	55 - 60, 66	190	- -	1085 (liquid, 70 °C), 1212 (solid, 25 °C)
PEG10000	55 - 60	-	- -	- -

The various PEG types available have no precisely defined molar mass, but a certain molar mass distribution. PEGs with an average molecular weight between 200 and 400 are liquids at room temperature; PEG 600 melts at 17 – 22 °C. The melting temperature of all PEGs with a molecular weight exceeding 4000 g/mol is around 58 – 65 °C.

A class of materials that is not generally organic or inorganic is the clathrates. *Clathrates* are crystalline structures where molecules of one type are enclosed in the crystal lattice of another. Clathrates do not have a stoichiometric composition; instead, there is an ideal composition when all free lattice positions are occupied. When the crystal lattice is formed by water, the clathrate is called a clathrate hydrate and the crystal structure of the solid clathrate hydrate is a modification of the crystal structure of ice. The molecules of the added substance are enclosed within free spaces in the crystal lattice of the ice and thereby stabilize it and raise the melting temperature. When the enclosed molecules are from a gas and the surrounding crystal lattice is water, the clathrate is called a gas hydrate. Gas hydrates have melting temperatures in the range from 0 °C to 30 °C, with the enclosed molecules being noble gases, chlorofluorocarbons, or straight chain hydrocarbons. The best-known gas hydrate is methane hydrate. Fig.2.10 shows its structure.



**Fig. 2.10.** Structure of methane hydrate: the methane molecule is located at the center of a cage of 20 water molecules

The gas molecules in a gas hydrate usually dissolve only at higher pressures in water and thus gas hydrates are often not stable at ambient pressure. This makes them difficult to use as PCM. Several exceptions however exist where the solubility in water is good and stability at ambient pressure is given. Other examples use special unpolar liquids or organic salts instead of gases. Tab.2.9 shows a few examples of clathrates.

**Table 2.9.** Examples of clathrates that have been investigated as PCM.

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
tetrahydrofuran THF C <sub>4</sub> H <sub>8</sub> O	5	280	-	-
+ H <sub>2</sub> O			-	970 (solid)
tetrabutyl ammoniumbromide [(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> NBr	12	193	-	-
+ H <sub>2</sub> O 40:60 wt.% (type A)			-	-

(Continued)

**Table 2.9.** (Continued)

Material	Melting temperature (°C)	Melting enthalpy (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m <sup>3</sup> )
tetrabutyl ammoniumbromide	10	199	-	-
[(CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> NBr + H <sub>2</sub> O 38:62 wt.% (type B)			-	-

Tetrabutylammonium bromide for example forms two different hydrates (Oyama et al. 2005), one with 26 water molecules per salt molecule (type A) and one with 38 (type B). Xiao et al. 2006 published further information on this hydrate. Like salt hydrates, clathrate hydrates may melt congruently or incongruently and tend to subcool. Further on, slow formation can be a problem.

As described until now, usually materials within the same material class are mixed. In the last few years, also mixtures of organic and inorganic materials have been investigated. However, at present not many results have been published. Therefore, this topic is not treated in this introductory text.

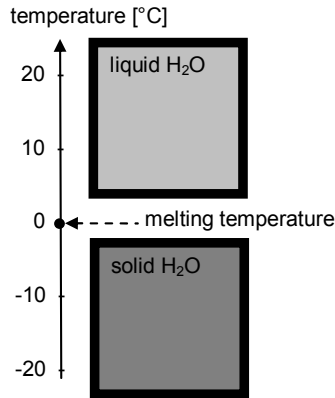
### 2.3 Typical material problems and possible solutions

Usually, a candidate material for a PCM does not fulfill all the requirements listed in section 2.1. Nevertheless, it is often still possible to use such a material if some of the strategies developed to solve or avoid potential problems are applied. Some of these strategies are now discussed.

#### 2.3.1 Phase separation solved by mixing, gelling, or thickening

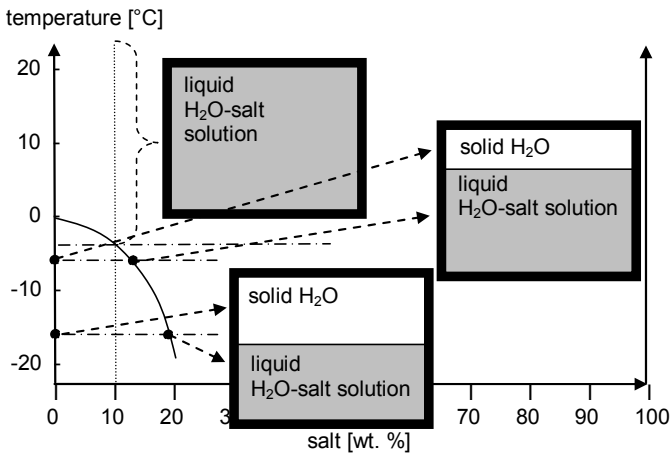
What is phase separation? When a pure substance with only one component, like water, is heated above its melting temperature and thereby melted, it will have the same homogeneous composition in the liquid as before in the solid (fig.2.11). When the material is solidified again by cooling it below the melting temperature, the solid will again be of the same homogeneous composition throughout and the same phase change enthalpy and melting temperature is observed at any place. Such a material is said to melt *congruently*.





**Fig. 2.11.** Schematic phase diagram of water  $H_2O$ , a single component substance.

When a substance consists of two or more components, the phase diagram has to be extended. Fig.2.12 shows an example for a water-salt solution. For the second component, the salt, a new axis is added that gives the weight fraction of the components. In the case of two components, usually only one value is given; here it is the amount of salt in the salt solution. The second value, here for water, can be calculated as both fractions have to add up to 100 wt.%.



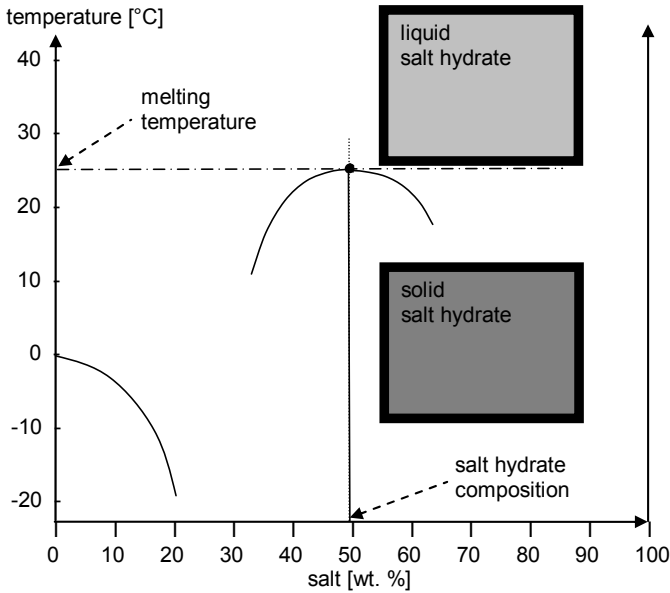
**Fig. 2.12.** Extension of the phase diagram when a second component, here a salt, is added to water.

The two-component system now behaves very different. A salt-water solution with a composition of 10 wt.% salt and 90 wt.% of water, marked by the vertical dotted line in fig.2.12, is a homogeneous liquid above  $-4^\circ\text{C}$ . When cooled below  $-4^\circ\text{C}$ , water freezes out of the solution and consequently the remaining solution

has higher salt concentration. This means the substance separates into two different phases, one with only water, and a second one with a higher salt concentration than initially. Due to gravitation, the phase with higher density will sink to the bottom and the one with lower density to the top. This phenomenon is called *phase separation* or *decomposition*, because the original composition is changed. When the temperature is reduced further, more water freezes out, and the salt concentration in the remaining liquid increases, as shown in fig.2.12. For different initial compositions, the temperature where water starts to freeze out is also different: the higher the salt concentration, the lower the temperature where water starts to freeze out of the solution.

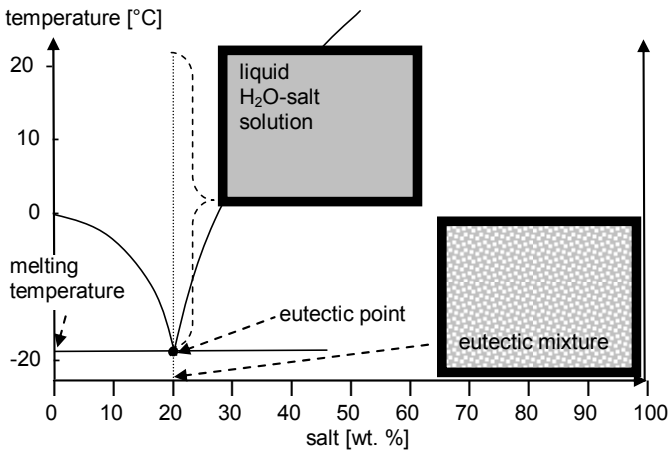
The line that separates the parts of the phase diagrams where there is only a homogeneous liquid from others is called liquidus line. Fig.2.12 only shows a small fraction of the liquidus line for compositions with low salt concentration. For high salt concentrations, the liquidus line must rise with increasing salt concentration again. The reason is that the melting temperature of a salt is higher than for water and with the addition of small amounts of water to the salt the salt will melt at a lower temperature. Pure water and pure salt have locally high melting temperatures and high phase change enthalpies. If salt is added in a small amount to water, or if water is added in a small amount to salt, the liquidus line moves to lower temperatures and the enthalpy difference between two temperatures is also reduced.

Another energetically stable mixture are salt hydrates, which consist of a salt and water in a discrete mixing ratio  $\text{salt} \cdot n\text{H}_2\text{O}$ . Fig.2.13 shows the phase diagram for a salt hydrate with congruent melting. The composition in the example is 50 wt.% salt and 50 wt.% water. If the homogeneous liquid with this composition is cooled, a single solid phase is formed from the liquid: the salt hydrate. This is the same as for pure water or for the pure salt, and again, there is no phase separation.



**Fig. 2.13.** Phase diagram for a salt hydrate, which shows congruent melting.

The liquidus lines from the water with added salt, and from the salt hydrate with less water, have to meet somewhere. This could be at an eutectic point; the respective composition is called eutectic composition. Fig. 2.14 shows this case.

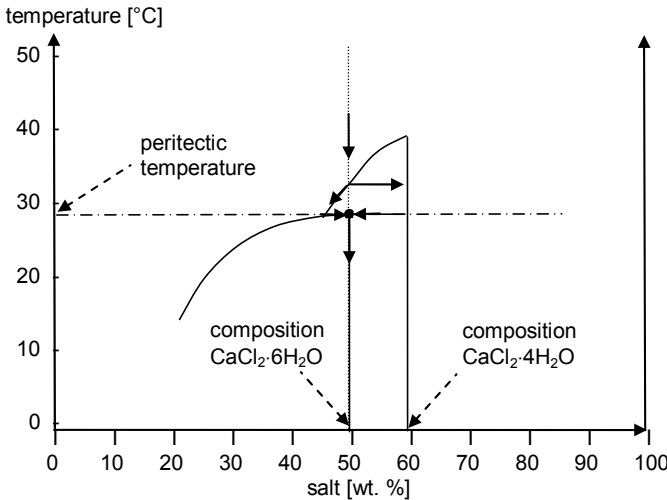


**Fig. 2.14.** Phase diagram for an eutectic composition, which shows congruent melting.

*Eutectic mixtures* are mixtures of two or more constituents, which solidify simultaneously out of the liquid at a minimum freezing point, also called *eutectic*

*point.* At the eutectic point, the liquid reacts to a solid that is composed of two or more solid phases with different composition; however, the overall composition is still the same as in the liquid! Therefore, eutectic compositions do not show phase separation. This is the reason why the salt-water solutions used as PCM (fig.2.2, tab.2.1) all have an eutectic composition. Strictly speaking, eutectic compositions are not under all circumstances congruent melting. If there is subcooling, the different solid phases will not be formed simultaneously out of the liquid, and phase separation can occur. However, this is usually not the case (Lane 1983).

After discussing the most important cases for congruent melting, it is time to discuss those where melting is not congruent. The most commonly used salt hydrates cannot be described by the phase diagram shown in fig.2.13. Often, compositions of salt- $n\text{H}_2\text{O}$  with different  $n$  exist, and the associated liquidus lines overlap. This can lead to a complex phase diagram and different melting behavior. An example is  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , which is said to melt semi congruent. According to the schematic phase diagram shown in fig.2.15,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  has a composition of about 50 wt.% of  $\text{CaCl}_2$  and 50 wt.% of water. The cool down of a liquid of this composition is indicated by arrows. When the liquid is cooled, solid  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  does not form directly. Instead, a solid and a liquid are formed first. The solid has the composition of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and the liquid consequently has a higher water content than  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The reason for this behavior is that the liquidus curve of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  intersects the one of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  at a lower salt concentration.



**Fig. 2.15.** Schematic phase diagram of  $\text{CaCl}_2\text{-H}_2\text{O}$ , which shows semi congruent melting.

When a temperature of about 28 °C is reached, the solid  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and the liquid salt solution react at a fixed temperature to a single solid phase:  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . This transformation of a solid and a liquid to a solid is called a *peritectic transformation*, in contrast to eutectic transformations where a liquid transforms to two

or more solid phases. The corresponding temperature is called *peritectic temperature*. When solid  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  is heated again above the peritectic temperature of about  $28^\circ\text{C}$ , first solid  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and liquid salt solution is formed. When a temperature a few Kelvin above the peritectic temperature is reached, a homogeneous liquid can form again. The problem of peritectic transformations is that in the intermediate step phases with different densities show up. Here, these phases are solid  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  with less water, which sinks down, and a solution with less  $\text{CaCl}_2$ . Only when the temperature is above the liquidus curve long enough, solid  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  can dissolve and a homogeneous liquid is formed. If cooling is done slowly, the different phases can build up and separate again. If cooling however is fast enough, or if macroscopic separation of the two phases is avoided by some other means, solid  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  can be formed again from the liquid and the phase change enthalpy is released completely. Such a melting behavior that is not congruent and not incongruent melting is called *semi congruent melting*.

The problem with phase separation is that it can severely reduce the storage density. Because locally the right concentration of the molecules to form the PCM is not given anymore, the PCM cannot solidify throughout. This means the latent heat of solidification can usually not be released completely, sometimes only to a small fraction. To retrieve the latent heat stored in the initial material, the correct concentration of the chemical components is required throughout the whole sample. Only then, the PCM can solidify completely.

An example where phase separation is worse than in  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  is the salt hydrate  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , also called Glaubersalt. Glaubersalt is composed of  $\text{Na}_2\text{SO}_4$  and 10 molecules of  $\text{H}_2\text{O}$ , that is equal to about 43 wt.% of  $\text{Na}_2\text{SO}_4$  (fig.2.16). When solid  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is heated up, the composition follows the vertical line in the phase diagram at 43 wt.%. When the peritectic point of  $32^\circ\text{C}$  is reached, again two phases are formed:  $\text{Na}_2\text{SO}_4$  and a liquid, which contains only about 32 wt.%  $\text{Na}_2\text{SO}_4$ . The two phases have very different densities and the pure  $\text{Na}_2\text{SO}_4$ , the one with the higher density, sinks down. Up to this point, the behavior is similar to the one of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . When the temperature is raised further, the concentration of  $\text{Na}_2\text{SO}_4$  in the liquid however decreases further because in contrast to the case of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  the solubility of  $\text{Na}_2\text{SO}_4$  decreases with rising temperature. This means it is not possible to get a homogeneous liquid with the original composition by raising the temperature. When the temperature is lowered again below  $32^\circ\text{C}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  will form again from the already diluted solution and sink down with an even more diluted solution remaining.

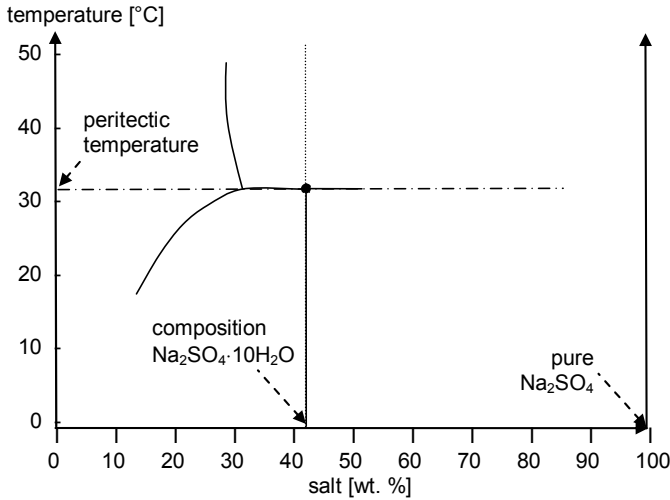


Fig. 2.16. Schematic phase diagram of  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ , which shows incongruent melting.

From equilibrium thermodynamics,  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$  is still the most stable phase below the melting temperature. However, to dissolve  $\text{Na}_2\text{SO}_4$  by molecular diffusion in the solution will take a very long time because it is separated from the solution by a layer of  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ .

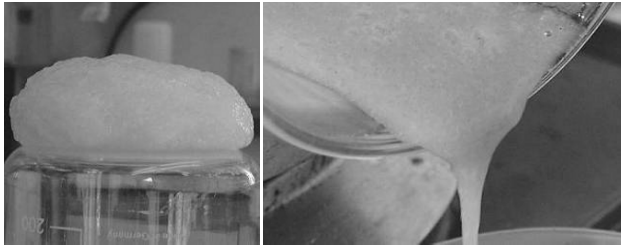
Depending on how severe phase separation occurs and how difficult it is to get rid of it, the melting behavior of a PCM showing phase separation is described as *semi congruent melting* or as *incongruent melting*, in contrast to congruent melting if no phase separation occurs. The use of these words however does not follow an exact definition and therefore only roughly indicates how a material will perform. In this discussion, it is also important to keep in mind that phase diagrams are supposed to show data in thermodynamic equilibrium. This means two things: first that the temperature is the same throughout the bulk of the sample, and second, that dynamic processes like molecular diffusion and reactions have come to a halt. This also includes the effect of subcooling. Because data in phase diagrams are taken from measurements, this ideal case can only be approached (section 3.2.2). Therefore, phase diagrams can be helpful to understand how a sample will perform, but there is no guarantee that they show all effects. Depending on the heating and cooling rate, the degree of phase separation in semi congruent and incongruent melting PCM will be different. This explains that often for the same material different literature sources give different melting behavior.

The question is now: if a candidate material for a PCM has a potential for phase separation, how is it possible to get rid of that problem? If phase separation has occurred, of course *artificial mixing* can be used. This is a well-known approach to dissolve sugar in coffee, or salt in water. Applied to PCM, the PCM is allowed to separate on macroscopic distances, but instead of waiting for diffusion to

homogenize the PCM, the faster process of mixing is used. This approach has been used successfully with many salt hydrates. Its main disadvantage is the necessary equipment. Because artificial mixing is not a solution on the material level but on the level of the storage concept, this approach is discussed in chapter 5.

An easy approach on the level of the material is to add additional water to the salt hydrate. For example instead of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  with about 50 wt.% of  $\text{CaCl}_2$  a more diluted mixture with less than 45 wt.% can be used. The phase diagram in fig.2.15 shows, that upon heating the formation of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  is now avoided, because the intersection of the two liquidus lines is passed on the left side. Further on, the additional water will make the homogenization of the liquid phase by diffusion of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  faster. The drawbacks of this method are that due to the addition of water, the overall storage density is reduced, and that the melting range becomes broader.

A second way to reduce the problem of phase separation on the material level is by using diffusion processes for homogenization. Diffusion is however only efficient on small scales, because the speed of diffusion processes goes with the square of the distance. Therefore, this approach can work only if the PCM separates only on small distances. One way to limit the distance that the phases can separate to the scale of several mm is to use shallow containers for the PCM. But often this is not sufficient. To reduce the distance that the phases can separate down to a microscopic scale, *gelling* can be used. In gelling, a three dimensional network is formed within the bulk of the PCM. This network holds the different phases of the PCM together on a microscopic scale. The gel can be formed by a polymer, for example. Fig.2.17 shows water gelled with a cellulose derivative. The same effect as with gelling can be achieved if the PCM is infiltrated into a micro porous material.



**Fig. 2.17.** Water gelled with a cellulose derivative, left, and thickened salt hydrate, right (pictures: ZAE Bayern).

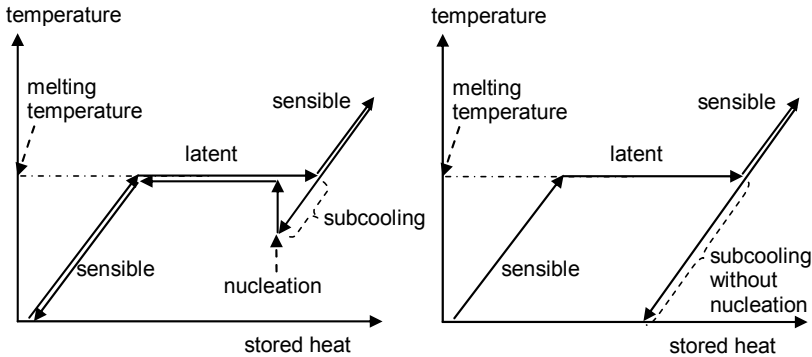
Another way to reduce the distance that the phases can separate is by *thickening* the PCM. Thickening means the addition of a material to the PCM to increase its viscosity. Due to the high viscosity, different phases cannot separate far until finally the whole PCM is solid. Fig.2.17 shows a thickened salt hydrate. There is a third way to reduce phase separation on the material level; it is probably the best but also most complicated one. This way is changing the phase diagram of the PCM itself by the addition of other materials until congruent melting results. If

achieved, the PCM can be used without any restrictions. However if and how the melting behavior can be changed advantageously is a topic for experts in the field.

For readers interested in more details, the following literature can be recommended. A very good introduction into phase diagrams can be found in Atkins et al. 2002. Phase equilibriums, phase diagrams and how they are determined, and the dynamics of the formation of different phases, is described in Lane 1983. The discussion also includes an in depth description of supersaturation and subcooling, nucleation and crystallization, and nucleators. Thickening and gelling are described in Lane 1986. Farid et al. 2004 give examples of thickeners for several important PCM.

### 2.3.2 Subcooling and methods to reduce it

Many PCM do not solidify immediately upon cooling below the melting temperature, but start crystallization only after a temperature well below the melting temperature is reached. This effect is called *subcooling* or supercooling (fig.2.1). For example, liquid water can be cooled to temperatures well below 0 °C; if highly pure and in small quantities even below -15 °C. Fig.2.18 shows the effect of subcooling on heat storage.



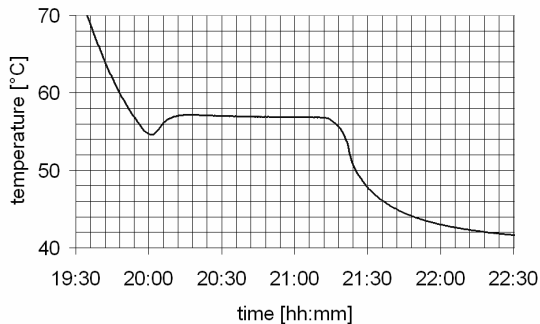
**Fig. 2.18.** Effect of subcooling on heat storage. Left: with little subcooling and nucleation, right: severe subcooling without nucleation.

During the supply of heat, there is no difference whether a PCM shows subcooling or not. During extraction of heat however, the latent heat is not released when the melting temperature is reached due to subcooling. The effect of subcooling makes it necessary to reduce the temperature well below the phase change temperature to start crystallization and to release the latent heat stored in the material. If nucleation does not happen at all, the latent heat is not released at all and the material



only stores sensible heat. In technical applications of PCM, subcooling therefore can be a serious problem.

When water is subcooled to  $-8\text{ }^{\circ}\text{C}$  and crystallization starts, the latent heat of crystallization is released. At that temperature of  $-8\text{ }^{\circ}\text{C}$ ,  $8\text{ K} \cdot 4\text{ kJ/kg}\cdot\text{K} = 32\text{ kJ/kg}$  of sensible heat were lost due to subcooling, much less than the latent heat of  $333\text{ kJ/kg}$  which is released during crystallization. If the heat released upon solidification is larger than the sensible heat lost due to subcooling, the temperature rises to the melting temperature and stays there until the phase change is completed. This case is shown at the right in fig.2.18. If the loss of sensible heat during subcooling is however larger than the latent heat released upon crystallization, or if the rate of heat loss to the ambient is larger than the rate of heat release during crystallization, it is possible that the temperature will not rise to the melting temperature again. This means that subcooling can cause surprising effects when performing a dynamic experiment. Fig.2.19 shows the effect of subcooling on a cool down experiment with  $\text{NaOAc}\cdot 3\text{H}_2\text{O}$ . After the crystallization has started at a temperature of about  $55\text{ }^{\circ}\text{C}$ , the temperature rises sharply until the melting temperature of about  $57\text{ }^{\circ}\text{C}$  is reached. When the melting temperature is reached at a location, no more phase change enthalpy is released and the temperature rise is stopped. From the location where the first crystallization occurs, the phase front moves until the boundaries of the sample are reached and phase change takes place throughout. This usually leads to a longer or shorter plateau in the temperature at the melting temperature. The length of this plateau depends on the rate of heat loss at the boundaries of the sample to the environment. In fig.2.19, the plateau is about 1 hour long before the temperature goes down to the temperature of the environment, which is  $40\text{ }^{\circ}\text{C}$ .



**Fig. 2.19.** Cooling of  $\text{NaOAc}\cdot 3\text{H}_2\text{O}$  at an ambient temperature of  $40\text{ }^{\circ}\text{C}$  with about  $2\text{ K}$  subcooling (picture: ZAE Bayern).

What is the reason for subcooling, or better why does a material not solidify right away when cooled below the melting temperature? Solidification means that the amount of solid phase grows because the liquid phase at the interface with the solid phase solidifies. However, this has to start at some point and the starting can

be a problem. At the very beginning, there is no or only a small solid particle, also called nucleus. For the nucleus to grow by solidifying liquid phase on its surface, the system has to release heat to get to its energetic minimum. There is however a competition between the surface energy, which is proportional to the surface area and therefore to  $r^2$  ( $r$  is the radius of the nucleus), and the heat released by changing the phase, which is proportional to the volume and therefore to  $r^3$ . At small radius, it is possible that the heat released by crystallization is smaller than the surface energy gained. That means there is an energetic barrier; only when a nucleus of sufficiently large radius is present solidification starts. For this, in some cases temperatures significantly lower than the melting temperature are necessary. Based on this, nucleation is divided into two cases:

- *Homogeneous nucleation* means nucleation solely started by the PCM itself.

Homogeneous nucleation includes nucleation by low enough temperatures and a second possibility, that particles of the solid PCM are added to the subcooled PCM. The latter one is sometimes also called *secondary nucleation*.

- *Heterogeneous nucleation* means nucleation not by the PCM itself.

Origins of heterogeneous nucleation can be special additives intentionally added to the PCM, but also impurities, or cracks at the wall of the vessel that contain solid PCM.

The most common approach to get rid of subcooling on the level of the PCM is to add special additives, also called *nucleator*, to the PCM to cause heterogeneous nucleation. Nucleators have been developed for most well investigated PCM, and reduce subcooling typically to a few K (fig.2.19). Most nucleators are materials with a similar crystal structure as the solid PCM to allow the solid phase of the PCM to grow on their surface, but a higher melting temperature to avoid deactivation when the PCM is melted. The problem with this method is that usually a similar crystal structure also means a similar melting temperature. Therefore, many nucleators are only stable up to a temperature 10 K to 20 K above the melting temperature of the PCM. There are also other nucleators where the mechanism is completely unknown. The fact that there is still no reliable theoretical approach makes the search for a new nucleator time consuming. Examples of nucleators for some of the most important PCM are given in Farid et al. 2004 and in Lane 1983. Lane 1983 also gives an in depth description of nucleation, crystallization, and nucleators. Other sources of general information on nucleation, not specialized on PCM, are the books by Kashchiev 2000, Kurz and Fisher 1992, Mutaftschiev 1993, Pimpinelli and Villain 1998, and Herlach 2004.

The difficulty of finding a nucleator can be circumvented if the PCM is locally cooled to a sufficiently low temperature to always have some solid phase left that acts as homogeneous nucleator. The necessary local cooling can be done by a Peltier element or by the *cold finger* technique. The cold finger technique uses a cold spot in the containment, caused for example by an intentionally bad insulation,

to always have some solid PCM. It is therefore only useful when the melting temperature of the PCM is higher than the temperature of the ambient.

Until recently, it was a common theory that the metal clip used in pocket heaters causes nucleation by a shock wave. The shock wave emitted when the metal clip is bent was thought to locally cause a high pressure in the PCM and thereby start nucleation. Rogerson and Cardoso 2003a-c however proved that this theory was wrong. They could show that surface effects stabilize solid PCM particles in small cracks of the metal clip in a way that the melting temperature of these PCM particles is much higher than the melting temperature of the bulk PCM. When the metal clip is bent, these solid PCM particles are ejected into the bulk of the PCM and initiate homogeneous nucleation. Nevertheless the option to start solidification using the high pressure associated with shock waves is very attractive and currently investigated in the project LWSNet supported by the German Federal Ministry of Education and Research (BMBF) under the funding code 03SF0307A (<http://www.lwsnet.info/objective.htm>). First experimental results published by Günther et al. 2007 have shown the general feasibility to nucleate salt hydrates by high pressures. In these experiments, static pressures of several kbar were used. The necessary equipment to produce sufficiently high static pressures is however prohibitive in PCM applications. If dynamic pressures in pressure waves, which can be produced with less effort, also cause nucleation will be investigated in future experiments.

### ***2.3.3 Encapsulation to prevent leakage and improve heat transfer***

In most cases, except for some applications of water-ice, the PCM needs to be encapsulated. The two main reasons are to hold the liquid phase of the PCM, and to avoid contact of the PCM with the environment, which might harm the environment or change the composition of the PCM. Further on, the surface of the encapsulation acts as heat transfer surface. In some cases, the encapsulation also serves as a construction element, which means it adds mechanical stability. Encapsulations are usually classified by their size into macro- and microencapsulation.

*Macroencapsulation* means filling the PCM in a macroscopic containment that fit amounts from several ml up to several liters. These are often containers and bags made of metal or plastic. Macroencapsulation is very common because such containers or bags are available in a large variety already from other applications. In that case, macroencapsulation is mainly done to hold the liquid PCM and to prevent changes in its composition due to contact with the environment. If the container is rigid enough, the encapsulation can also add mechanical stability to a system.

*Microencapsulation* is the encapsulation of solid or liquid particles of 1  $\mu\text{m}$  to 1000  $\mu\text{m}$  diameter with a solid shell. Physical processes used in microencapsulation are spray drying, centrifugal and fluidized bed processes, or coating processes

e.g. in rolling cylinders. Chemical processes used are in-situ encapsulations like complex coacervation with gelatine, interfacial polycondensation to get a polyamide or polyurethane shell, precipitation due to polycondensation of amino resins, and others. The in-situ processes have the ability to yield microcapsules with the best quality in terms of diffusion-tightness of the wall. Such microcapsules are nowadays widely used in carbonless copy paper (Jahns 1999). Besides the containment of the liquid phase, other advantages of microencapsulation regarding PCM are the improvement of heat transfer to the surrounding because of the large surface to volume ratio of the capsules, and the improvement in cycling stability since phase separation is restricted to microscopic distances. Further on, it is also possible to integrate microencapsulated PCM into other materials. A potential drawback of microencapsulation is however that the chance of subcooling increases. Currently, microencapsulation on a commercial scale is applied only to PCM that are not soluble in water. The reason is the used process technology. Besides that, to microencapsulate salt hydrates there is an additional problem: the tightness of the shell material to the small water molecules has to be sufficient to prevent changes of the composition of the salt hydrate. Two chemical processes for micro encapsulation are now described in more detail.

In *simple and complex coacervation* many products can be used as wall materials. For example, urea-formaldehyde resin, melamine-formaldehyde resin,  $\beta$ -naphthol-formaldehyde resin and gelatine-gum Arabic (this last one for complex coacervation) have been used. The first step of microencapsulation by coacervation is to disperse the core material (PCM) in an aqueous gelatine solution at a temperature range of 40 – 60 °C, at which the solution of the wall material is liquid. In complex coacervation, gum Arabic is added to the gelatine at this point. The process is followed by adjusting the pH and concentration of polymer so that a liquid complex coacervate is formed (usually pH 4 to 4.5). When the liquid coacervate is formed, the system is cooled to room temperature. The final step is hardening and isolation of the microcapsules. Hardening can be done using formaldehyde, which crosslinks the wall material by reacting with amino groups located on the chain. After that, the pH should be raised to 9 - 11 by NaOH solution. Then the capsules are cooled approximately down to 5 – 10 °C and maintained at this temperature for 2 to 4 h. Then the capsules are filtered and dried (Özonur et al. 2006, Jahns 1999).

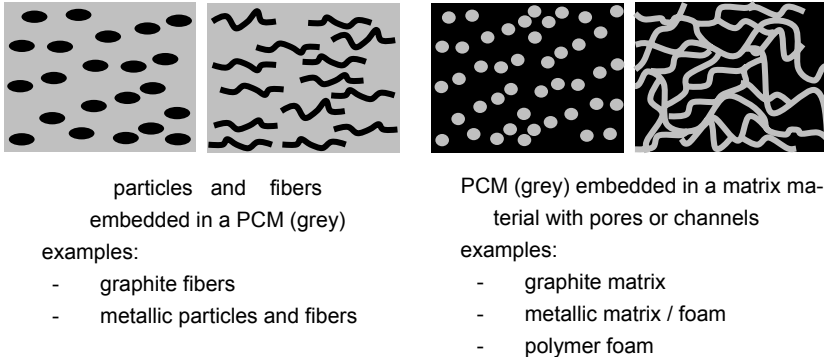
*Polymerization* is a technique usually performed using urea and formaldehyde, in an oil-in-water emulsion. First, at about 20 °C to 24 °C, deionized water and an aqueous solution of ethylene maleic anhydride (EMA) copolymer are mixed in a vessel with a controlled temperature. While mixing, urea, ammonium chloride, and resorcinol are dissolved in the solution. The pH is raised from about 2.60 to 3.50 by drop-wise addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl). A slow stream of PCM is then added to form an emulsion and allow stabilizing for 10 min. After stabilization, an aqueous solution of formaldehyde is added. The emulsion is heated to the target temperature of 55 °C and stays there for 4 h under continuous mixing. Once cooled to ambient temperature, the suspension

of microcapsules is separated under vacuum with a coarse-fritted filter. The microcapsules are rinsed with deionized water and air dried for 24 – 48 h. A sieve can be used to separate the microcapsules (Brown et al 2003).

A good and easy to understand overview on techniques used for micro-encapsulation is available at the website of Microtek Laboratories at <http://www.microteklabs.com>.

### 2.3.4 Mechanical stability and thermal conductivity improved by composite materials

A PCM can be combined with other materials to form a composite material with additional or modified properties. A composite can be formed in different ways, shown in fig.2.20: by embedding another material into the PCM or by embedding the PCM into a matrix of another material.



**Fig. 2.20.** Possibilities to form a composite material, and some examples.

To maintain material properties, the order of magnitude of the structures in the composite should be microscopic, or at least below the scale of mm. Otherwise, the properties of the composite will depend on the sample size and the composite therefore cannot be called a material anymore (section 3.1).

#### 2.3.4.1 Mechanical stability

Composites of a PCM and another material as a mechanically stable structure are often called shape-stabilized PCM (ss-PCM). Independent of the phase of the PCM, solid or liquid, the shape is maintained by the supporting structure. An example is shape-stabilized paraffin, which can be produced by incorporating paraffin on a microscopic level into a supporting structure, for example high-density

polyethylene (HDPE). Inaba and Tu 1997 describe the preparation of samples with about 75 wt.% of paraffin and report that there is no leakage of the paraffin out of the HDPE structure. Recently, Yinping et al. 2006 have published data with even 80 wt.% and other physical properties of the composite. They also report that no containment is needed. Compared to the encapsulation techniques described before, these new materials could be cut into arbitrary shapes without leakage. This is a significant advantage in many applications, however at the cost of using much more HDPE than if just as a wall material for a macroencapsulation. Farid et al. 2004 also report on the composite between HDPE and paraffin in their review paper. Further on, they mention a development published by Royon et al 1997, who have developed a new material where water as a PCM is integrated into a three dimensional network of polyacrylamide during the polymerization process.

Another approach to improve the mechanical stability by forming a composite material is the impregnation of mechanically stable, porous materials with the PCM. For example, ceramic granules and tiles have been infiltrated with salts as PCM to get storage modules for temperatures of several hundred °C. Another example is the impregnation of wood fiberboards with paraffin.

It is also possible to combine both approaches. The company Rubitherm Technologies GmbH developed several materials that consist of three components: a mechanically very stable and highly porous structure, whose pores are filled with a paraffin as PCM, and a polymer structure to keep the paraffin within the pores. As mechanically stable and highly porous structure ceramic or silica powders and wood fiberboards are used.

#### **2.3.4.2 Thermal conductivity**

All non-metallic liquids, including PCM have a low thermal conductivity (tab.2.1 to tab.2.8). Since PCM store large amounts of heat or cold in a small volume, and because it is necessary to transfer this heat to the outside of the storage to use it, the low thermal conductivity can be a problem. In the liquid phase, convection can significantly enhance heat transfer, however often this is not sufficient. In the solid phase, there is no convection. When fast heat transfer is necessary, one possibility to increase the thermal conductivity of the PCM is to add materials with larger thermal conductivity. This can be done at a macroscopic scale, for example by adding metallic pieces (Velraj et al. 1999, Cabeza et al. 2002, and Hafner and Schwarzer 1999), or on a sub mm scale as mentioned before with composite materials. However, adding anything to the PCM will reduce or eliminate convection in the liquid phase; therefore, it is necessary to find out which option is better. One approach under investigation to increase the thermal conductivity is to put the PCM into metallic foams. In recent years, the technology to produce metal foams of different porosity and structure has advanced considerably. Hackeschmidt et al. 2007 have prepared and tested combinations of water and a paraffin as PCM with aluminum foams of different porosity. The results show that with a relative

density of 6 %, that means with 94 % porosity, a thermal conductivity of about 6 W/mK can be achieved. Other experiments are described by Hong and Herling 2006. The use of graphite and its potential to increase the thermal conductivity when paraffins or salt hydrates are used as PCM is described in Mehling et al. 1999, Mehling et al. 2000, Py et al. 2001, and Mills et al. 2006. Recently, the approach to use graphite is also investigated for salts as high temperature PCM (Bauer et al 2006, do Couto Aktay et al. 2005). For PCM-graphite composites with up to 85 vol.% of PCM thermal conductivities of 2 to 30 W/m<sup>2</sup>K have been reported.

Besides the approach on the level of the storage material, the problem of heat transfer can also be approached on the level of the storage concept. This is discussed in chapter 5.

## 2.4 Commercial PCM, PCM composite materials, and encapsulated PCM

The availability of commercial PCM, PCM composite materials and encapsulated PCM is crucial to the development and commercialization of PCM applications. The reason is that from a customers point of view, only commercial PCM, PCM composite materials and encapsulated PCM have defined properties, a warranty, a fixed price, and can be delivered in a given time. From a supplier point of view, the size of the potential market of a PCM, PCM composite, or encapsulated PCM is also important. Both views determine what is commercially available. Commercial PCM and PCM composite materials have to fulfill harder requirements in their development than encapsulated materials (Mehling 2001). Often a potential material cannot be sold as pure PCM because handling of the pure material is critical, for example with respect to its water content. In an encapsulated form, such materials nevertheless can be sold as product. Looking at large systems, the situation can be the opposite: a PCM that shows phase separation might not be useful as encapsulated PCM, however when artificially mixed in a large tank it can be used. Then however, the applicability only to large systems strongly restricts the market for such a PCM unless the system uses large amounts of the PCM or the application is widespread.

The availability of commercial PCM, PCM composite materials, and encapsulated PCM allows companies with no or little knowledge on PCM to use this technology in their own products. Encapsulated PCM can be commercialized by one company specialized on PCM technology, and many other companies can then integrate the encapsulated PCM in their products, without knowing much about PCM technology. A good example is ice packs, which are used by many consumers to keep food cold.

Usually, it is necessary that the main properties of the PCM products are well documented. For this reason, a standard to control product quality has been developed

by the ZAE Bayern and the FhG-ISE recently. Since spring 2007, the quality label shown in fig.2.21 will indicate that a PCM product has been tested according this standard.



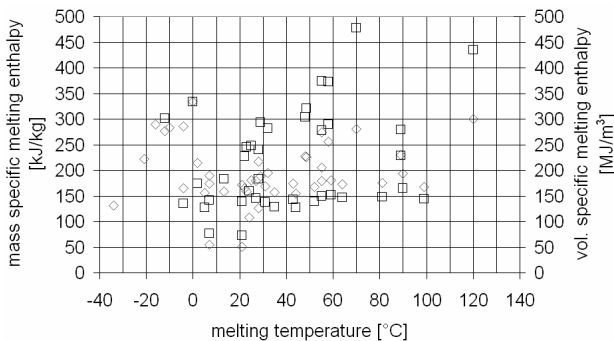
**Fig. 2.21.** Quality label for PCM (picture: Gütegemeinschaft PCM e.V.)

More information on the standard and the label can be found at <http://www.pcm-ral.de/>. Similar activities to develop standards have recently been started in China and in India.

The number of commercial PCM, PCM composite materials, and encapsulated PCM is growing from year to year. Therefore, it is not possible to give a complete description of all available commercial products here. The following sections discuss typical examples to give an overview on what is available; for many examples similar products are available from several companies. Detailed and up to date information is available at the respective websites of the companies listed in the reference section at the end of this chapter.

### 2.4.1 PCM

Currently, more than 50 PCM are commercially available. Fig.2.22 shows an overview of the phase change temperature and enthalpy per volume and mass of these commercial PCM.



**Fig. 2.22.** Phase change temperature and enthalpy per volume (□) and mass (◇) of commercial PCM (picture: ZAE Bayern)



Most commercial PCM are based on materials from the material classes of the salt hydrates, paraffins, and eutectic water-salt solutions. They are however not identical with these materials. In the case of salt hydrates, often the composition is changed, a nucleator is added, the material is gelled or thickened, or the PCM is a mixture of different base materials. With paraffins, commercial grade paraffins usually contain a mixture of different alkanes because pure alkanes are expensive. Commercial PCM cover the temperature range from  $-40\text{ }^{\circ}\text{C}$  to  $+120\text{ }^{\circ}\text{C}$ . Even though many materials have been investigated for higher temperatures, none of them is available commercially because there has been no market yet.

The price of commercial PCM is typically in the range from 0.5 €/kg to 10 €/kg, which has a large influence on the economics of PCM applications. For a rough estimate an energy price of 0.05 €/kWh for heat can be assumed. This means that 3600 kJ cost 0.05 €. Taking an average storage density of a PCM of 180 kJ/kg (fig.2.22), 20 kg of PCM are necessary to store 3600 kJ (=1 kWh), an amount of heat that has a value of 0.05 €. 20 kg of PCM however cost at least  $20\text{ kg} \cdot 0.5\text{ €/kg} = 10\text{ €}$ . To store heat with a value that equalizes the cost of the necessary investment for the PCM, a number of  $10\text{ €} / 0.05\text{ €} = 200$  storage cycles are necessary. Additional investment cost for the storage container and heat exchanger, as well as the stored heat which is also never completely free, have not even been taken into account. Seasonal storage using PCM is therefore far from being economic at current prices for fossil fuels. To be competitive in energy systems, one should try to charge and discharge a storage daily, or in even shorter periods. There are however exceptions. For example if an application has no connection to the energy grid, e.g. in the cargo bay of an airplane, the common energy price is not applicable and the economic situation can be much better. The examples in chapter 7 and 8 reflect this situation.

### ***2.4.2 PCM composite materials***

A composite material is a material that is composed of several different materials, usually to improve a property of a material or to combine properties of different materials. In the case of PCM, a PCM composite material is produced to improve at least one of the PCM properties or to improve the heat storage capacity of another material. There are different ways to form a composite: by embedding PCM in a matrix of another material, or by embedding another material into the PCM (section 2.3.4). The following section gives some examples of composite materials developed to improve different properties of PCM.

### 2.4.2.1 PCM composite materials to improve handling and applicability

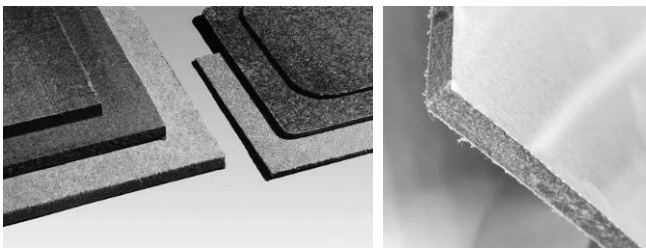
A set of different composite materials with paraffin as PCM, mainly to improve handling and integration into a product, has been developed and commercialized by the company Rubitherm Technologies GmbH. The compound PK (fig.2.23) is a shape stabilized PCM and consists of a paraffin as PCM in a polymer structure.



**Fig. 2.23.** Composites developed and commercialized by Rubitherm Technologies GmbH. From left to right: compound PK, powder PX, and granulate GR (pictures: Rubitherm Technologies GmbH).

The powder PX and granulate GR have an additional mechanically stable structure. The powder RUBITHERM® PX is based on a silica powder as matrix material, which contains up to 60 % PCM and still flows as the pure powder. It is used to fill complicated or flexible shapes, for example in comfort and medical applications as the hot cushion shown in fig.8.9. The granulate RUBITHERM® GR is based on a porous clay mineral and contains about 35 % of PCM. The granulate can be used to fill complex shapes, like the powder, but it is also mechanically very stable. It can even be used in a floor heating system (fig.9.54).

Fig.2.24 shows examples of composites that come as boards or plates. The fiberboard RUBITHERM® FB contains about 65 % of PCM and is used for example for plates to keep Pizza or other food warm. Here the shape as a plate is important.

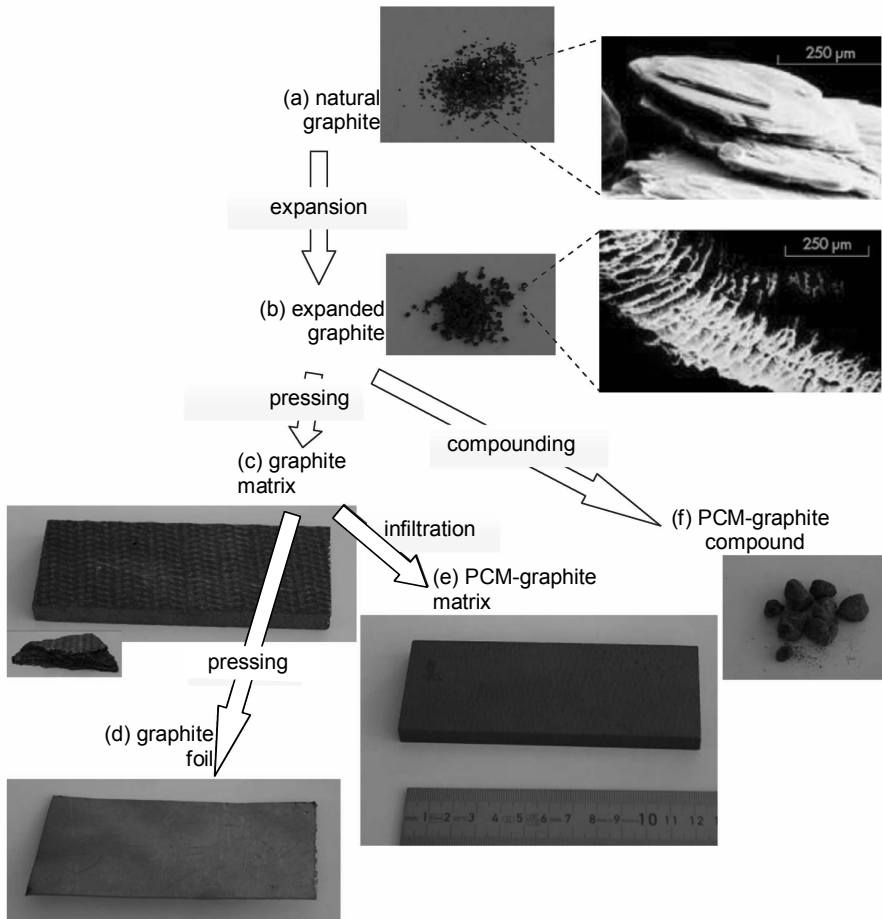


**Fig. 2.24.** Composites that come as boards or plates. Left: fiberboard FB (picture: Rubitherm Technologies GmbH) and right: DuPont™ Energain® panels (picture: DuPont)

DuPont recently announced the commercialization of a composite to be used as building material. DuPont™ Energain® panels contain a copolymer and paraffin compound, with about 60 wt.% of paraffin. Section 9.2.1.4 contains more data on the composite and its application.

#### **2.4.2.2 PCM-graphite composites to increase the thermal conductivity**

If the thermal conductivity of a material is not large enough, it is a common strategy to form a composite with a highly conducting material. In many applications, metal or graphite is used as additive in the form of powders or fibers. Besides the high thermal conductivity of graphite, its stability to high temperatures and corrosive environments is a big advantage compared to metals. This is especially the case when applied in combination with salts, salt hydrates, water, or water-salt solutions. The idea to use a graphite matrix as thermally conducting structure was developed and patented by the ZAE Bayern, and first published by Satzger et al. 1997. Since then, a number of publications (Mehling et al. 1999, Mehling et al. 2000, Py et al. 2001, Mills et al. 2006) have presented the approach as well as experimental results. PCM-graphite composites in two different forms, a matrix and a compound material, are available commercially nowadays under the brand name ECOPHIT™ from SGL TECHNOLOGIES GmbH. A short information sheet is available at [http://www.sglcarbon.com/sgl\\_t/expanded/pdf/Ecophit\\_LC\\_GC\\_d.pdf](http://www.sglcarbon.com/sgl_t/expanded/pdf/Ecophit_LC_GC_d.pdf).

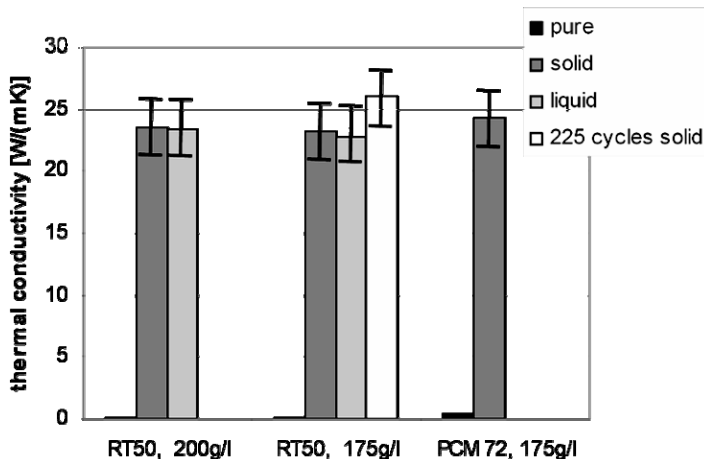


**Fig. 2.25.** Processing of graphite from natural graphite to different products. All pictures have the same scale (microscopic images of expanded graphite: SGL TECHNOLOGIES GmbH).

Fig.2.25 shows the processing from natural graphite to different products. The first processing step starts with natural graphite (a) with a density of about  $2200 \text{ kg/m}^3$ . After a chemical treatment, the following thermal treatment of the natural graphite starts a chemical reaction, which produces gases. These gases lead to an expansion of the graphite structure as the microscopic image in fig.2.25 shows. The particles of the expanded graphite (b) have a highly porous structure and dimensions in the order of one to several mm. This gives them a bulk density of about  $3 \text{ kg/m}^3$ , less than 0.2% of the density of natural graphite. In other words, 99.8% of the volume is pores.

### PCM-graphite matrix

In a standard production process, graphite seals for applications at high temperatures or in corrosive environments are produced. For this, the expanded graphite is compressed in several steps to graphite foil (d). During compression, the density increases by a factor of about 700 from about  $3 \text{ kg/m}^3$  for the expanded graphite, to a density close to the one of pure graphite of  $2.2 \text{ kg/m}^3$ . This is why these foils can be used as seals. In an intermediate step of the compression, the graphite has the shape of about 10 mm thick plates (c). These plates still have about 90 vol.% porosity, but yet good mechanical stability and a thermal conductivity of about 20 to 25 W/mK parallel and 5 to 8 W/mK perpendicular to the plate surface. Compared to this, organic PCM typically have a thermal conductivity of 0.2 W/mK or less; inorganic PCM typically have 1.0 W/mK or less. Because of their high porosity and mechanical stability, the prepressed plates are called a graphite matrix. In one process to produce PCM-graphite composite materials, this matrix is used as thermally conductive matrix. The PCM is infiltrated into the graphite matrix until about 80 to 85 vol.% of PCM are reached. Fig.2.25 shows the PCM-graphite matrix (e). Fig.2.26 shows a comparison of the thermal conductivity of pure PCM and PCM-graphite matrix for two different PCM. The PCM are a paraffin RT50 and a salt hydrate PCM 72 produced by Merck / Germany. Compared to the pure PCM with a thermal conductivity of 0.2 to 0.5 W/mK, the thermal conductivity of the PCM-graphite matrix is higher by a factor of 50 to 100. This is almost independent of the phase of the PCM, solid or liquid. A comparison where the PCM was solid after production and after cycling shows no reduction of the thermal conductivity. The graphite densities have been 200 g/liter and 175 g/liter.



**Fig. 2.26.** Thermal conductivity of pure PCM, and of PCM-graphite matrix. For the PCM-graphite matrix, values are shown for the PCM being solid or liquid, for different graphite densities, and after 225 cycles (picture: ZAE Bayern).

It is possible to produce the PCM-graphite matrix with many organic and inorganic PCM, however some PCM are difficult to infiltrate into the graphite matrix. Besides this restriction, there is a second disadvantage of the approach with the graphite matrix: there are limitations in producing the graphite matrix with respect to shape and size. Thicknesses larger than 10 mm are difficult to achieve due to the current production process. Therefore, the company SGL TECHNOLOGIES GmbH has developed a second PCM-graphite composite with a different production process.

### PCM-graphite compound

In this process, the PCM is mixed with expanded graphite in a compounding process, instead of forming a pre-pressed graphite matrix that is then infiltrated with PCM. The result of the production process is a compound in granular form (f). The advantages of the compound are that it can be produced with any PCM, and that it can be brought into any shape e.g. by injection molding. To do this, the granules are heated above the melting temperature of the PCM; the compound then behaves like a viscous liquid that can be filled into containments of even complex shapes. The compound has a similar volumetric composition as the PCM-graphite matrix, which is about 10 vol.% graphite, 80 vol.% PCM and 10 vol.% air. The thermal conductivity however is lower; about 4 to 5 W/m-K in all directions. The reason for the lower thermal conductivity is that due to the loose contact between the graphite particles in the compound, the graphite particles do not form a connected network as when the graphite is pre-pressed in the case of the graphite matrix. Nevertheless, compared to the pure PCM, the thermal conductivity is still higher by a factor of 5 to 20.

It is often assumed that the thermal conductivity can be calculated similar to the density or the enthalpy of a composite from the volume or mass fractions. However, this is wrong. The fact that PCM-graphite compound and PCM-graphite matrix have very different thermal conductivity, despite having similar graphite content, indicates that the thermal conductivity is not only a function of the volume or mass fractions of the components. To calculate the thermal conductivity the shape, distribution, and orientation of the different components in a composite material must be taken into account.

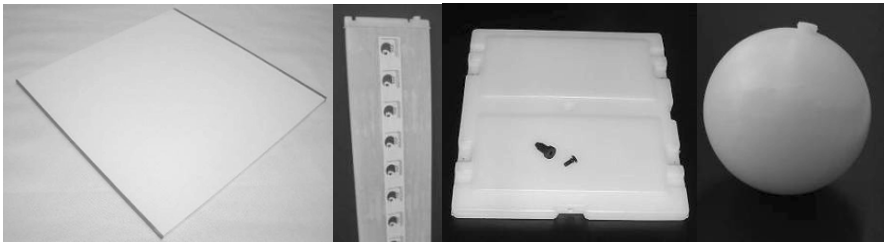
### ***2.4.3 Encapsulated PCM***

Encapsulations are classified according to their size as macro- and microencapsulation, as explained in section 2.3.3. Macroencapsulation is by far the most widely used type of encapsulation, however also microencapsulated PCM are produced on an industrial scale nowadays. When encapsulating PCM, it is necessary to take

into account several aspects. First, the material of the container wall must be compatible with the PCM. Then, taking into account the selected wall material, the container wall has to be sufficiently thick to assure the necessary diffusion tightness. Finally, the encapsulation must be designed in a way that it is able to cope with the mechanical stress on the container walls caused by the volume change of the PCM.

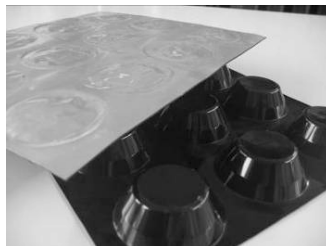
### 2.4.3.1 Examples of macroencapsulation

To encapsulate salt hydrates, usually plastic containers are selected because of material compatibility. Plastics are not corroded by salt hydrates; however, attention has to be paid to the water tightness of the material of the capsule wall. This is to make sure that the water content in the capsule and thus the composition of the salt hydrate does not change with time. Plastic encapsulations can also be used for organic PCM, but the combination of PCM and encapsulation material has to be chosen very carefully because organic materials may soften plastics. Fig.2.27 shows several examples of macro encapsulation in plastic containers from different companies. Many companies produce a selection of different encapsulations. Because plastic containers can nowadays be produced easily in a high variety of shapes, there are few restrictions on the geometry of the encapsulation.



**Fig. 2.27.** Macroencapsulation in plastic containers. From left to right: bar double panels from Dörken (picture Dörken), panel from PCP (picture: PCP), flat container from Kissmann, and balls from Cristopia, also called nodules.

Another form of macroencapsulation shows fig.2.28. Here, plastic sheets form small containments for the PCM that are sealed with a plastic foil. Such encapsulations called capsule stripes or dimple sheets are useful to cover large surfaces and can be manufactured on a fully automated production line.



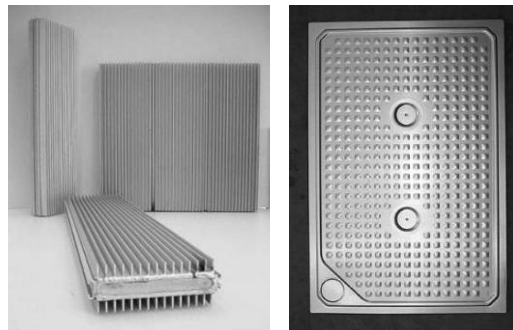
**Fig. 2.28.** Macroencapsulation in capsule stripes as produced by PCP and Dörken for inorganic PCM (picture: ZAE Bayern).

It is of course also possible to use only foils as a wall material, the resulting product is PCM encapsulated in bags. Fig.2.29 shows two examples. To ensure tightness of the bag regarding water, usually plastic foils combined with a metallic layer are used.



**Fig. 2.29.** Macroencapsulation in bags; left, produced by Climator (picture: Climator), and right, produced by Dörken (picture: Dörken).

If good heat transfer is important, the low thermal conductivity of container walls made of plastic can be a problem. An option is to choose containers with metal walls. Metal walls also have the advantage of higher mechanical stability if a sufficient wall thickness is chosen. It is however necessary to select a suitable metal which is not corroded by the PCM. This selection should also take into account that depending on the metal different options and restrictions for shaping, welding, etc exist. Fig.2.30 shows two examples of metal containers used to encapsulate PCM.



**Fig. 2.30.** Macroencapsulation in metal containers: left, aluminum profiles with fins for improved heat transfer from Climator (picture: Climator), and right, coated aluminum plate from Rubitherm Technologies GmbH (picture: Rubitherm Technologies GmbH).

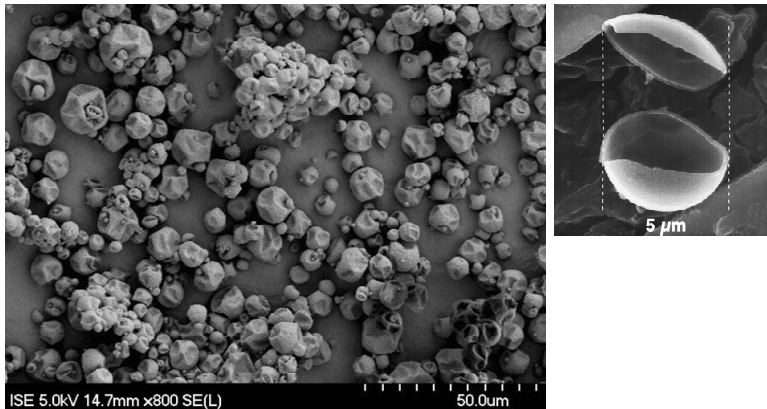
On the left is a ClimSel™ Thermal Battery: a hollow aluminum profile with cooling fins that is filled with PCM. The batteries can be connected to each other, as



shown in the background. On the right is a coated aluminum plate filled with PCM, which is manufactured by Rubitherm Technologies GmbH.

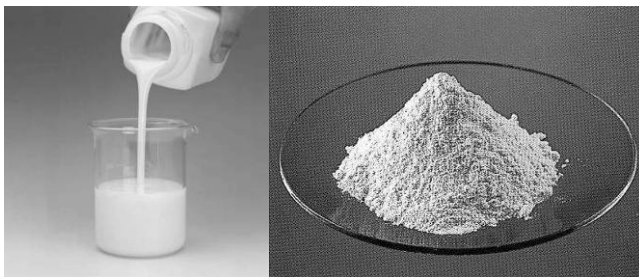
### 2.4.3.2 Examples of microencapsulation

Because of the reasons discussed in section 2.3.3, microencapsulation of PCM is technically feasible today only for organic materials. Commercial products seem to use exclusively paraffins. Fig.2.31 shows commercial microencapsulated paraffin, with a typical capsule diameter in the 2-20  $\mu\text{m}$  range, produced by the company BASF.



**Fig. 2.31.** Electron microscope image of many capsules (picture: FhG-ISE) and an opened microcapsule (picture: BASF).

The microencapsulated PCM is available as fluid dispersion or as dried powder (fig.2.32).



**Fig. 2.32.** Microencapsulated paraffin produced by BASF, on the left as fluid dispersion, and on the right as dry powder (pictures: BASF).

The microcapsules are sold under the brand name Micronal<sup>®</sup> as Micronal<sup>®</sup> DS 5000 (fluid dispersion) and 5001X (dried powder) with a melting temperature of

26 °C, and as Micronal® DS 5007 (fluid dispersion) 5008X (dried powder) with a melting temperature of 23 °C (<http://www.micronal.de>).

Another source for a commercial product is the company Microtek in the USA, which sells microencapsulated PCM with a wide range of melting temperatures.

## 2.5 References

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