Inventory of Phase Change Materials (PCM)
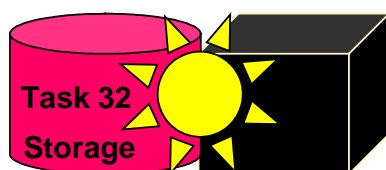
A Report of IEA Solar Heating and Cooling programme - Task 32
"Advanced storage concepts for solar and low energy buildings"

Report C2 of Subtask C

February 2005

Edited by
Wolfgang Streicher

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Task 32 Storage

SHC
SOLAR HEATING & COOLING PROGRAMME
INTERNATIONAL ENERGY AGENCY

Report C2 of Subtask C
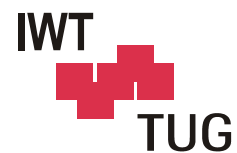# Inventory of Phase Change Materials (PCM)

by

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A technical report of Subtask C

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IEA Solar Heating and Cooling Programme

The *International Energy Agency* (IEA) is an autonomous body within the framework of the Organization for Economic Co-operation and Development (OECD) based in Paris. Established in 1974 after the first "oil shock," the IEA is committed to carrying out a comprehensive program of energy cooperation among its members and the Commission of the European Communities.

The IEA provides a legal framework, through IEA Implementing Agreements such as the *Solar Heating and Cooling Agreement*, for international collaboration in energy technology research and development (R&D) and deployment. This IEA experience has proved that such collaboration contributes significantly to faster technological progress, while reducing costs; to eliminating technological risks and duplication of efforts; and to creating numerous other benefits, such as swifter expansion of the knowledge base and easier harmonization of standards.

The *Solar Heating and Cooling Programme* was one of the first IEA Implementing Agreements to be established. Since 1977, its members have been collaborating to advance active solar and passive solar and their application in buildings and other areas, such as agriculture and industry. Current members are:

Australia	Finland	Portugal
Austria	France	Spain
Belgium	Italy	Sweden
Canada	Mexico	Switzerland
Denmark	Netherlands	United States
European Commission	New Zealand	
Germany	Norway	

A total of 39 Tasks have been initiated, 30 of which have been completed. Each Task is managed by an Operating Agent from one of the participating countries. Overall control of the program rests with an Executive Committee comprised of one representative from each contracting party to the Implementing Agreement. In addition to the Task work, a number of special activities—Memorandum of Understanding with solar thermal trade organizations, statistics collection and analysis, conferences and workshops—have been undertaken.

The Tasks of the IEA Solar Heating and Cooling Programme, both underway and completed are as follows:

Current Tasks:

Task 32   *Advanced Storage Concepts for Solar and Low Energy Buildings*
Task 33   *Solar Heat for Industrial Processes*
Task 34   *Testing and Validation of Building Energy Simulation Tools*
Task 35   *PV/Thermal Solar Systems*
Task 36   *Solar Resource Knowledge Management*
Task 37   *Advanced Housing Renovation with Solar & Conservation*
Task 38   *Solar Assisted Cooling Systems*
Task 39   *Polymeric Materials for Solar Thermal Applications*

Completed Tasks:

Task 1   *Investigation of the Performance of Solar Heating and Cooling Systems*
Task 2   *Coordination of Solar Heating and Cooling R&D*
Task 3   *Performance Testing of Solar Collectors*
Task 4   *Development of an Insolation Handbook and Instrument Package*
Task 5   *Use of Existing Meteorological Information for Solar Energy Application*
Task 6   *Performance of Solar Systems Using Evacuated Collectors*
Task 7   *Central Solar Heating Plants with Seasonal Storage*
Task 8   *Passive and Hybrid Solar Low Energy Buildings*
Task 9   *Solar Radiation and Pyranometry Studies*
Task 10   *Solar Materials R&D*
Task 11   *Passive and Hybrid Solar Commercial Buildings*
Task 12   *Building Energy Analysis and Design Tools for Solar Applications*
Task 13   *Advance Solar Low Energy Buildings*
Task 14   *Advance Active Solar Energy Systems*
Task 16   *Photovoltaics in Buildings*
Task 17   *Measuring and Modeling Spectral Radiation*
Task 18   *Advanced Glazing and Associated Materials for Solar and Building Applications*
Task 19   *Solar Air Systems*
Task 20   *Solar Energy in Building Renovation*
Task 21   *Daylight in Buildings*
Task 23   *Optimization of Solar Energy Use in Large Buildings*
Task 22   *Building Energy Analysis Tools*
Task 24   *Solar Procurement*
Task 25   *Solar Assisted Air Conditioning of Buildings*
Task 26   *Solar Combisystems*
Task 28   *Solar Sustainable Housing*
Task 27   *Performance of Solar Facade Components*
Task 29   *Solar Crop Drying*
Task 31   *Daylighting Buildings in the 21st Century*

Completed Working Groups:
CSHPSS, ISOLDE, Materials in Solar Thermal Collectors, and the Evaluation of Task 13 Houses

To find Solar Heating and Cooling Programme publications and learn more about the Programme visit **www.iea-shc.org** or contact the SHC Executive Secretary, Pamela Murphy, e-mail: pmurphy@MorseAssociatesInc.com

September 2007

What is IEA SHC Task 32
"Advanced Storage Concepts for solar and low energy buildings" ?

The main goal of this Task is to investigate new or advanced solutions for storing heat in systems providing heating or cooling for low energy buildings.

The first objective is to contribute to the development of advanced storage solutions in thermal solar systems for buildings that lead to high solar fraction up to 100% in a typical 45N latitude climate.

The second objective is to propose advanced storage solutions for other heating or cooling technologies than solar, for example systems based on current compression and absorption heat pumps or new heat pumps based on the storage material itself.

Applications that are included in the scope of this task include:

1. new buildings designed for low energy consumption
2. buildings retrofitted for low energy consumption.

The ambition of the Task is not to develop new storage systems independent of a system application. The focus is on the integration of advanced storage concepts in a thermal system for low energy housing. This provides both a framework and a goal to develop new technologies.

The Subtasks are:
Subtask A: Evaluation and Dissemination
Subtask B: Chemical and Sorption
Subtask C: Phase Change Materials
Subtask D: Water tank solutions

Duration
July 2003 - December 2007.
www.iea-shc.org look for Task32

IEA SHC Task 32 Subtask C
"Storage with Phase Change Materials"

This report is part of Subtask C of the Task 32 of the Solar Heating and Cooling Programme of the International Energy Agency dealing with solutions of storage based on phase change materials or "PCMs".

The topic of PCM is not completely new for solar energy storage but the way Task 32 has handled it is new. From material to system and simulation, the process was application oriented: a solar combisystem has a target. Can PCM storage do better than water tanks ?

PCM could also be used to reduce the cycling of boilers in a small volume tank. This new idea was also investigated in Task 32 in a project bringing more insight on the usefulness of PCMs in storing heat and power.

This report screens many Phase Change Materials and analyze the current knowledge of the fundamentals associated with PCM behaviour. It is a deep survey of PCM written by european experts in the field of storage for solar heat. It provides also a large list of references.
This work was a basic work for Task 32 in order to select suitable materials for storing solar heat around 50 to 80C.

The Operating Agent would like to thank the authors of this document for their implication in the search of future storage solutions for solar thermal energy, the key to a solar future for the heating and cooling of our buildings.

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Contents

1 INTRODUCTION

The thermal energy absorbed by a material when changing its phase at a constant temperature is called 'latent heat'. For practical applications, materials that exhibit low volume changes are used, for example, solid-to-liquid and some special solid-to-solid phase change materials are applicable.

The commonly used phase change materials for technical applications are: paraffins (organic), salt hydrates (inorganic) and fatty acids (organic) (See Figure 1). For cooling applications, it is also possible to use ice storage.

Latent heat storage offers a significant advantage if the application needs temperature cycles closely around the melting point, since in those cases the corresponding storage density of water is small. In liquid or solid state the specific heat capacity is lower for most PCM materials compared to water.

Possible Applications in Solar Buildings for PCM are
- Cold storage for solar assisted cooling applications (PCT around 5 -18°C)
- PCM (Micro-Capsules) incorporated in wall material (PCT around 22°C)
- Heating storage for Solar Energy and longer running time of boilers (PCT around 60°C)
- Hot storage for Solar Assisted Air Conditioning (PCT around 80°C)

In all cases, heat must be transferred between the phase change material and the fluid cycle (charging, discharging). Different techniques are used, including:
- Direct contact between phase change material and heat transfer fluid: this needs materials that are chemically stable for long periods of direct contact and the solidification of PCM occur in small particles, securing sufficient heat transfer during subsequent melting.
- Macroscopic-capsules: this is the most frequently used encapsulation method. The most common approach is to use a plastic module, which is chemically neutral with respect to both the phase change material and the heat transfer fluid. The modules typically have a diameter of some centimetres.
- Micro-encapsulation: this is a relatively new technique in which the PCM is encapsulated in a small shell of polymer materials with a diameter of some micrometres (in the moment only for paraffins). A large heat-exchange surface results and the powder- like spheres can be integrated into many construction materials or used as aquaeous pumpable slurry. Plasters incorporating micro-encapsulated PCM are on the market since 2004. PC;-slurries are still under development.

The main advantages of phase change storage in comparison to conventional water storage techniques are:
- Higher thermal energy storage capacity (smaller storages) than sensible energy storage, at least if only small useful temperature differences can be achieved.
- Relatively constant temperature during charging and discharging.
- Burner cycles for the back-up heat generation unit and therefore their CO and HC emissions can be reduced.

The main disadvantages of phase change storage are:

- Higher investment cost, in most cases, compared to water storage.
- In many cases, the peak power during discharge is limited due to limited heat conduction in the solid state of PCM. This is the main limit determining the acceptable size for the storage modules.
- Limited experience with long-term operation (after many thousand cycles).
- Risks of loss of stability of the solution and deterioration of the encapsulation material.

In the following the characteristics of PCM materials are described on more detail.

2 STATE OF THE ART OF PHASE CHANGE MATERIALS

2.1 Classification

In 1983 Abhat [49] gave a useful classification of the substances used for thermal energy storage, shown in Figure 1.

Among the most thorough references related with phase change materials, one can cite Abhat [49], Lane [6,50], Kenisarin [36], Dincer and Rosen [1], Zalba et al. [2], and Farid [4]. These contain a complete review of the types of material which have been used, their classification, characteristics, advantages and disadvantages and the various experimental techniques used to determine the behaviour of these materials in melting and solidification.
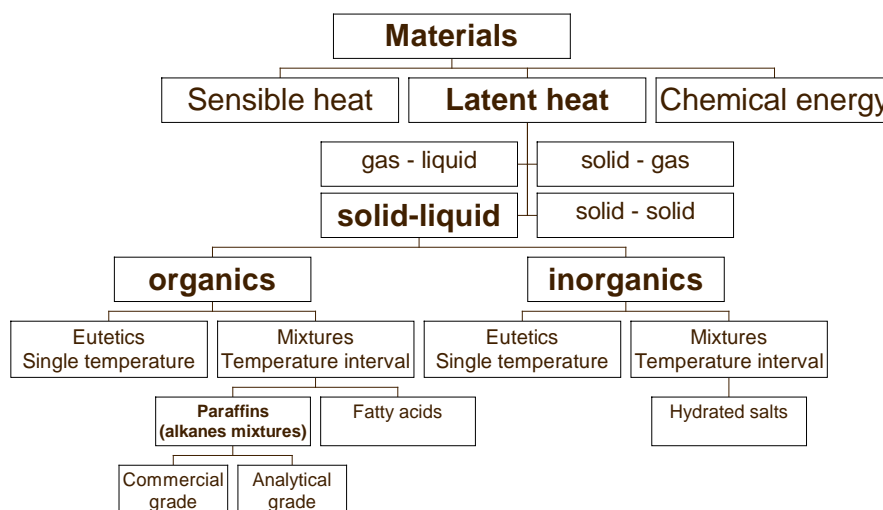

Figure 1: Classification of energy storage materials [49].

2.2 Non-commercial/commercial materials

Many substances have been studied as potential PCMs, but only a few of them are commercialised as so.

Tables 1 to 6 present the different substances, eutectics and mixtures (inorganic, organic and fatty acids), that have been studied by different researchers for their potential use as PCMs. Note that only melting temperatures of 16 to 30ºC have been considered for applications in buildings, and melting temperatures of 45 to 70ºC have been considered for storage tanks. Some of their thermophysical properties are included (melting point, heat of fusion, thermal conductivity and density), although some authors give further information (congruent/incongruent melting, volume change, specific heat, etc.).

Table 7 shows a list of the commercial PCMs available in the market with their thermophysical properties as given by the companies (melting point, heat of fusion and density), and the company that is producing them.

Table 1: Inorganic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
$Na_2CrO_4 \cdot 10\,H_2O$	18 [51]	n.a.	n.a.	n.a.
$KF \cdot 4\,H_2O$	18.5 [3,8,49,52,53]	231 [3,8,49,52]	n.a.	1447 (liquid, 20°C) [49] 1455 (solid, 18°C) [49] 1480 [52]
$Mn(NO_3)_2 \cdot 6\,H_2O$	25.8 [54]	125.9 [54]	n.a.	1738 (liquid, 20°C) [54] 1728 (liquid, 40°C) [54] 1795 (solid, 5°C) [54]
$CaCl_2 \cdot 6\,H_2O$	29 [1,55] 29.2 [53] 29.6 [52] 29.7 [3,8,49] 30 [51] 29-39 [5]	190.8 [1,55] 171 [3,8,49] 174,4 [5] 192 [52]	0.540 (liquid, 38.7°C) [1,55] 0.561 (liquid, 61.2°C) [55] 1.088 (solid, 23°C) [1,55]	1562 (liquid, 32°C) [1,55] 1496 (liquid) [49] 1802 (solid, 24°C) [1,55] 1710 (solid, 25°C) [49] 1634 [5] 1620 [52]
$LiNO_3 \cdot 3\,H_2O$	30 [52]	296 [52]	n.a.	n.a.
$K_3PO_4 \cdot 7\,H_2O$	45 [51]	n.a.	n.a.	n.a.
$Zn(NO_3)_2 \cdot 4\,H_2O$	45.5 [51]	n.a.	n.a.	n.a.
$Ca(NO_3)_2 \cdot 4\,H_2O$	42.7 [53] 47 [51]	n.a.	n.a.	n.a.
$Na_2HPO_4 \cdot 7\,H_2O$	48 [53]	n.a.	n.a.	n.a.
$Na_2S_2O_3 \cdot 5\,H_2O$	48 [49,51-53] 48-49 [5]	201 [49] 209,3 [5] 187 [52]	n.a.	1600 (solid) [49] 1666 [5]
$Zn(NO_3)_2 \cdot 2\,H_2O$	54 [51]	n.a.	n.a.	n.a.
$NaOH \cdot H_2O$	58.0 [53]	n.a.	n.a.	n.a.
$Na(CH_3COO) \cdot 3\,H_2O$	58 [52,56] 58.4 [53,57-63]	264 [57-63] 226 [52]	n.a.	1450 [52]
$Cd(NO_3)_2 \cdot 4\,H_2O$	59.5 [53]	n.a.	n.a.	n.a.
$Fe(NO_3)_2 \cdot 6\,H_2O$	60 [51]	n.a.	n.a.	n.a.
$NaOH$	64.3 [52]	227.6 [52]	n.a.	1690 [52]
$Na_2B_4O_7 \cdot 10\,H_2O$	68.1 [53]	n.a.	n.a.	n.a.
$Na_3PO_4 \cdot 12\,H_2O$	69 [53]	n.a.	n.a.	n.a.
$Na_2P_2O_7 \cdot 10\,H_2O$	70 [52]	184 [52]		n.a.

n.a.: not available or not known at the time of writing

Table 2: Inorganic eutectics with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
51-55% $Cu(NO_3)_3 \cdot 6H_2O$ + 45-49% $LiNO_3 \cdot 3H_2O$	16.5 [36]	250 [36]	n.a.	n.a.
45-52% $LiNO_3 \cdot 3H_2O$ + 48-55% $Zn(NO_3)_2 \cdot 6H_2O$	17.2 [36]	220 [36]	n.a.	n.a.

55-65% LiNO₃·3H₂O + 35-45% Ni(NO₃)₂·6H₂O	24.2 [36]	230 [36]	n.a.	n.a.
66.6% CaCl₂·6 H₂O + 33.3% MgCl₂·6 H₂O	25 [52]	127 [52]	n.a.	1590 [52]
45% Ca(NO₃)₂·6H₂O + 55% Zn(NO₃)₂·6H₂O	25 [36,49]	130 [36,49]	n.a.	1930 [36,49]
48% CaCl₂ + 4.3% NaCl + 0.4% KCl + 47.3% H₂O	26,8 [49,52]	188,0 [52]	n.a.	1640 [52]
67% Ca(NO₃)₂·4 H₂O + 33% Mg(NO₃)₂·6 H₂O	30 [36,49]	136 [36,49]	n.a.	1670 [36]
60% Na(CH₃COO) ·3 H₂O + 40% CO(NH₂)₂	31.5 [36,64] 30 [65]	226 [36,64] 200.5 [65]	n.a.	n.a.
61.5% Mg(NO₃)₂·6 H₂O + 38.5% NH₄NO₃	52 [55]	125.5 [55]	0.494 (liquid, 65.0°C) [55] 0.515 (liquid, 88.0°C) [55] 0.552 (solid, 36.0°C) [55]	1515 (liquid, 65°C) [55] 1596 (solid, 20°C) [55]
58.7% Mg(NO₃)·6 H₂O + 41.3% MgCl₂·6 H₂O	59 [55] 58 [52] 59.1 [36,49]	132.2 [55] 132 [52] 144 [36,49]	0.510 (liquid, 65.0°C) [55] 0.565 (liquid, 85.0°C) [55] 0.678 (solid, 38.0°C) [55] 0.678 (solid, 53.0°C) [55]	1550 (liquid, 50°C) [55] 1630 (solid, 24°C) [55] 1680 (solid) [36,49]
53% Mg(NO₃)₂·6 H₂O + 47% Al(NO₃)₂·9 H₂O	61 [36,49]	148 [36,49]	n.a.	1850 [36]

% in weight

n.a.: not available or not known at the time of writing

Table 3: Non-eutectic mixtures of inorganic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
Mg(NO₃)₂·6 H₂O / Mg(NO₃)₂·2 H₂O	55.5 [51]	n.a.	n.a.	n.a.
80% Mg(NO₃)·6 H₂O + 20% MgCl₂·6 H₂O	60 [66]	150 [66]	n.a.	n.a.

% in weight

n.a.: not available or not known at the time of writing

Table 4: Organic eutectics with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m³)
37.5% urea + 63.5% Acetamide	53 [49]	n.a.	n.a.	n.a.
67.1% naphthalene + 32.9% benzoic acid	67 [55]	123.4 [55]	0.136 (liquid, 78.5°C) [55] 0.130 (liquid, 100°C) [55] 0.282 (solid, 38°C) [55]	n.a.

			0.257 (solid, 52°C) [55]	

% in weight
n.a.: not available or not known at the time of writing

Table 5: Organic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
Dimethyl-sulfoxide (DMS)	16,5 [67]	85.7 [67]	n.a.	1009 (solid and liquid) [67]
Paraffin C_{16}-C_{18}	20-22 [9]	152 [9]	n.a.	n.a.
Polyglycol E600	22 [1,55]	127.2 [1,55]	0.189 (liquid, 38.6°C) [1,55] 0.187 (liquid, 67.0°C) [55]	1126 (liquid, 25°C) [1,55] 1232 (solid, 4°C) [1,55]
Paraffin C_{13}-C_{24}	22-24 [49]	189 [49]	0.21 (solid) [49]	760 (liquid, 70°C) [49] 900 (solid, 20°C) [49]
1-dodecanol	26 [8] 17.5-23.3 [3]	200 [8] 188.8 [3]	n.a.	n.a.
Paraffin C_{18}	28 [49] 27.5 [68] 22.5-26.2 [3]	244 [49] 243.5 [68] 205.1 [3]	0.148 (liquid, 40°C) [68] 0.15 (solid) [49] 0.358 (solid, 25°C) [68]	774 (liquid, 70°C) [49] 814 (solid, 20°C) [49]
Paraffin C_{20}-C_{33}	48-50 [49]	189 [49]	0.21 (solid) [49]	769 (liquid, 70°C) [49] 912 (solid, 20°C) [49]
Paraffin C_{22}-C_{45}	58-60 [49]	189 [49]	0.21 (solid) [49]	795 (liquid, 70°C) [49] 920 (solid, 20°C) [49]
Paraffin wax	64 [1,55]	173.6 [1,55] 266 [52]	0.167 (liquid, 63.5°C) [1,55] 0.346 (solid, 33.6°C) [1,55] 0.339 (solid, 45.7°C) [55]	790 (liquid, 65°C) [1,55] 916 (solid, 24°C) [1,55]
Polyglycol E6000	66 [1,55]	190.0 [1,55]	n.a.	1085 (liquid, 70°C) [1,55] 1212 (solid, 25°C) [1,55]
Paraffin C_{21}-C_{50}	66-68 [49]	189 [49]	0.21 (solid) [49]	830 (liquid, 70°C) [49] 930 (solid, 20°C) [49]

n.a.: not available or not known at the time of writing

Table 6: Fatty acids with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)
Propyl palmiate	10 [8] 16-19 [3]	186 [8]	n.a.	n.a.
Caprylic acid	16 [1,55] 16.3 [49]	148.5 [1,55] 149 [49]	0.149 (liquid, 38.6°C) [1,55] 0.145 (liquid, 67.7°C) [55] 0.148 (liquid, 20°C) [49]	901 (liquid, 30°C) [1,55] 862 (liquid, 80°C) [49] 981 (solid, 13°C) [1,55] 1033 (solid, 10°C) [49]
Capric-lauric acid (65 mol%-35 mol%)	18.0 [69] 17-21 [3]	148 [69] 143 [3]	n.a.	n.a.
Butil stearate	19 [8,36] 18-23 [3]	140 [3,8] 123-200 [70] 200 [36]	n.a.	n.a.
Capric-lauric acid (45%-55%)	21 [8]	143 [8]	n.a.	n.a.
Dimethyl sabacate	21 [36,70]	120-135 [70] 135 [36]	n.a.	n.a.
Octadecyl 3-mencaptopropylate	21 [36]	143 [36]	n.a.	n.a.
34% Mistiric acid + 66% Capric acid	24 [55]	147.7 [55]	0.164 (liquid, 39.1°C) [55] 0.154 (liquid, 61.2°C) [55]	888 (liquid, 25°C) [55] 1018 (solid, 1°C) [55]
Octadecyl thioglycate	26 [36]	90 [36]	n.a.	n.a.
Vinyl stearate	27-29 [70] 27 [36]	122 [36,70]	n.a.	n.a.
Myristic acid	49-51 [71] 54 [49] 58 [55]	204.5 [71] 187 [49] 186.6 [55]	n.a.	861 (liquid, 55°C) [55] 844 (liquid, 80°C) [49] 990 (solid, 24°C) [55]
Palmitic acid	64 [1,55] 61 [72,73] 63 [49]	185.4 [1,55] 203.4 [72,73] 187 [49]	0.162 (liquid, 68.4°C) [1,55] 0.159 (liquid, 80.1°C) [55] 0.165 (liquid, 80°C) [49]	850 (liquid, 65°C) [1,55] 847 (liquid, 80°C) [49] 989 (solid, 24°C) [1,55]
Stearic acid	69 [1,55] 60-61 [73,74] 70 [49]	202.5 [1,55] 186.5 [73,74] 203 [49]	0.172 (liquid, 70°C) [49]	848 (liquid, 70°C) [1,55] 965 (solid, 24°C) [1,55]

% in weight
n.a.: not available or not known at the time of writing

Table 7: Commercial PCMs available in the market

PCM name	Type of product	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (kg/L)	Source
RT20	Paraffin	22	172	0.88	Rubitherm GmbH [75]
ClimSel C 24	n.a.	24	108	1.48	Climator [76]
RT26	Paraffin	25	131	0.88	Rubitherm GmbH [75]
STL27	Salt hydrate	27	213	1.09	Mitsubishi Chemical [77]
AC27	Salt hydrate	27	207	1.47	Cristopia [78]
RT27	Paraffin	28	179	0.87	Rubitherm GmbH [75]
TH29	Salt hydrate	29	188	n.a.	TEAP [79]
STL47	Salt hydrate	47	221	1.34	Mitsubishi Chemical [77]
ClimSel C 48	n.a.	48	227	1.36	Climator [76]
STL52	Salt hydrate	52	201	1,3	Mitsubishi Chemical [77]
RT54	Paraffin	55	179	0,90	Rubitherm GmbH [75]
STL55	Salt hydrate	55	242	1,29	Mitsubishi Chemical [77]
TH58	n.a.	58	226	n.a.	TEAP [79]
ClimSel C 58	n.a.	58	259	1,46	Climator [76]
RT65	Paraffin	64	173	0,91	Rubitherm GmbH [75]
ClimSel C 70	n.a.	70	194	1,7	Climator [76]

n.a.: not available or not known at the time of writing

2.3 Organic/inorganic materials

A comparison of the advantages and disadvantages of organic and inorganic materials is shown in Table 8.

Table 8: Comparison of organic and inorganic materials for heat storage.

Organics	Inorganics
Advantages - No corrosives - Low or none undercooling - Chemical and thermal stability	**Advantages** - Greater phase change enthalpy - Subcooling[1]
Disadvantages - Lower phase change enthalpy - Low thermal conductivity - Inflammability	**Disadvantages** - Subcooling - Corrosion - Phase separation - Phase segregation, lack of thermal stability

[1]Controlled use of subcooling can be used for achievement of partly heat loss free storage solutions for solar combi systems.

Notable among inorganic materials are hydrated salts and their multiple applications in the field of solar energy storage [1,6]. In chapter 1 of Lane [50] there is an extensive review of phase change materials and especially hydrated salts. Chapter 3 of the same work covers the different types of encapsulation and their compatibility with different materials.

A significant number of authors have based their work on organic materials such as alkanes, waxes or paraffins [35,80-85]. Within organic materials, there is a class called MCPAM

(Phase change materials made up of molecular alloys), formed by alkane-based alloys which have the advantage of being thermoadjustable [86], that is, they allow alterations to the phase change temperature through their composition. There is abundant information on this subject in the literature [86-96].

As far as concerns the storage temperature or phase change, the heat transfer in accumulators can be improved choosing the PCM in such a way that its phase change temperature optimises the thermal gradient with respect to the substance with which the heat is being exchanged (Farid [35], Hassan [97], Stub [98]). For example, with paraffins and alkanes it is possible to vary the number of carbon atoms or form different molecular alloys, which allows a practically continuous variation of the phase change temperature within certain ranges.

3 Thermophysical properties

It can be concluded from the information compiled that the main characteristics required of phase change materials are those indicated in Table 9.

Table 9: Important characteristics of energy storage materials.

Thermal properties	Physical properties	Chemical properties	Economic properties
Phase change temperature fitted to application	Low density variation	Stability	Cheap and abundant
High change of enthalpy near temperature of use	High density	No phase separation	
High thermal conductivity in both liquid and solid phases (although not always)	Small or no subcooling[1]	Compatibility with container materials	
		Non toxic, non flammable, non polluting	

[1]Controlled use of subcooling can be used for achievement of partly heat loss free storage solutions for solar combi systems.

3.1 Thermophysical properties determination

Speyer [99] gave a good overview of the thermal analysis methods in general, but also Eckert et al. [100] and should be mentioned. Naumann and Emons [53] and others [19,101] focussed their studies on thermal analysis methods for PCMs.

As is mentioned in Gibbs [104], there is considerable uncertainty about the property values provided by manufacturers (who give values of pure substances) and it is therefore advisable to use DSC (Differential Scanning Calorimetry) to obtain more accurate values.

Yinping [105] reviews the above-mentioned conventional methods of PCM property analysis and points out their limitations, of which the following stand out:

a) Small quantities of sample are analysed (1-10 mg), although some behaviour of the PCMs depends on their quantity.
b) The analysis instrumentation is complex and expensive.
c) Phase change cannot be visually observed.

Analysis techniques used to study phase change are mainly conventional calorimetry, differential scanning calorimetry (DSC) (Figure 2) and differential thermal analysis (DTA). Among studies relating to DSC, it is worth citing Flaherty [102] for characterisation of hydrocarbons and natural waxes, Giavarini [103] for characterisation of petroleum products and Salyer [80] for characterisation of paraffins.
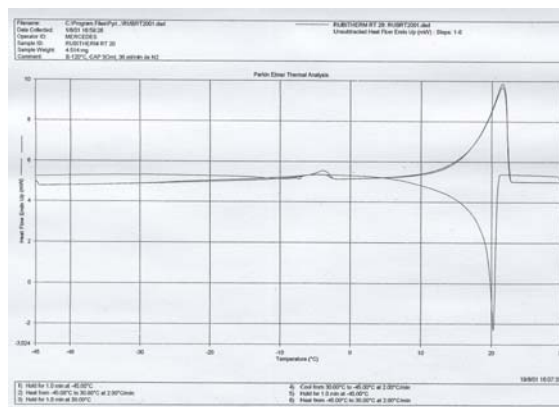

Figure 2: DSC of paraffin RT20

Yinping proposes a simple method for determining phase change temperature, undercooling, enthalpy, specific heat, and thermal conductivity in solid and liquid phases. Temperature – time graphs are drawn and properties evaluated for comparison with the graphs of the other known materials are used (usually pure water) as reference.

Marín et al. [106] developed a further evaluation procedure to determine specific heat and enthalpy as temperature dependent values. The results obtained are presented in the form of enthalpy-temperature curves, and an experimental improvement is proposed (Figures 3 and 4).
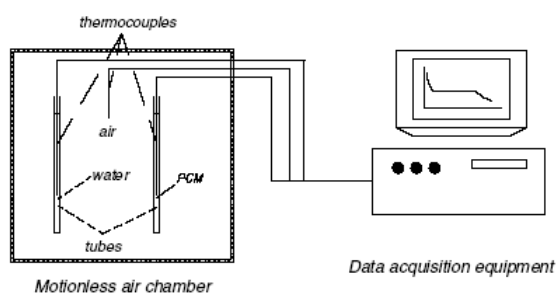

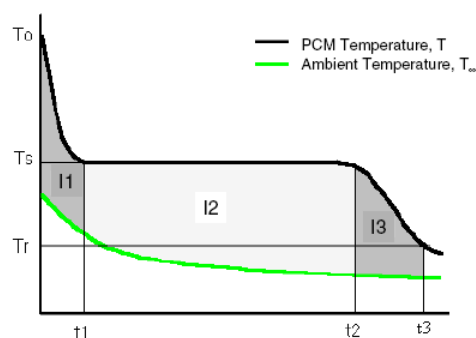Figure 3: Experimental set-up of the T-history method

Figure 4: Temperature–time curves for PCM and ambient air

Another method for determining thermal conductivity in PCM at temperatures around phase change temperature is established in Delaunay [107]. This method is based on analysing one-dimensional conduction in a cylinder. Various alternatives are proposed in the literature for the enhancement of thermal conductivity such as increasing the heat transfer surface, inserting metallic fins (Sadasuke [108]) or adding metallic additives (Bugaje [109]). In Manoo [110] there are some interesting charts relating to variations in conductivity, density and enthalpy against temperature for some paraffins.

3.2 Long term stability

Insufficient long term stability of the storage materials and containers is a problem that has limited widespread use of latent heat stores. This poor stability is due to two factors: poor

stability of the materials properties due to thermal cycling, and/or corrosion between the PCM and the container.

3.2.1 Stability of the PCM-container system

A relevant aspect is the useful life of these systems, and the number of cycles they can withstand without any degrading of their properties (Figures 5 and 6). Hadjieva [81] uses three paraffin mixtures; the lack of effect of the cycles on the properties of paraffin is verified. Other authors, such as Gibbs [104], also confirm that neither the cycles nor contact with metals degrade the thermal behaviour of paraffin and that they therefore have excellent thermal stability.
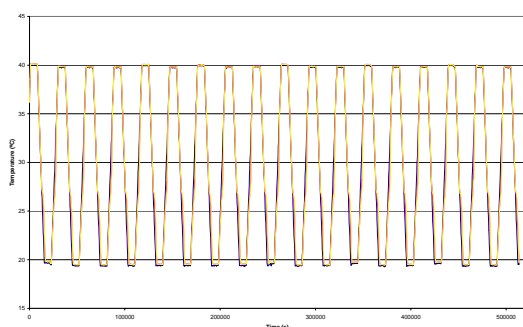

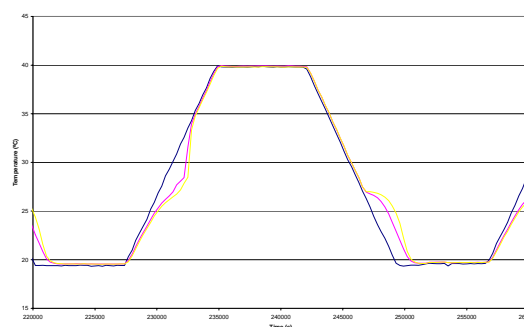Figure 5: Several cycles of a paraffin   Figure 6: One cycle of a paraffin

3.2.2 Corrosion of the materials

Most references on corrosion tests using salt hydrates were performed with diluted salt hydrates, as typically used in the chemical industry, and only a few presented results, usually based on observation over experimental set-ups [111,112]. Porisini [113] tested the corrosion of four commercially available salt hydrates used as PCMs in 1988.

Recently, Cabeza et al. [114-117] studied corrosion resistance of five common metals (aluminium, brass, copper, steel and stainless steel) in contact with molten salt hydrates (zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate, sodium carbonate, potassium hydrogen carbonate, potassium chloride, water, sodium acetate trihydrate, and sodium tiosulphate pentahydrate) in an immersion corrosion test (Figure 7).

Figure 7: Aluminium treated with a salt hydrate. From left to right: before treatment, after treatment, and after treatment in contact with graphite

Some investigations have been concerned with corrosion of molten salts at high temperature. Already in 1980, Heine et al. [118] studied the corrosion performance of six molten salts melting between 235 and 857°C versus four metals used at these temperatures.

3.2.3 Phase segregation and subcooling problems

The high storage density of salt hydrate materials is difficult to maintain and usually decreases with cycling. This is because most hydrated salts melt congruently with the formation of the lower hydrated salt, making the process irreversible and leading to the continuous decline in their storage efficiency (Figure 8).

This problem was studied first in the 70s [119-123] using the extra water principle. The extra water principle is a method that consists in adding extra water to the salt hydrate so that all the anhydrous salt can be dissolved in the water at the melting point, that is, the storage medium is a saturated salt solution at the melting point. The storage medium is stirred softly while it is cooled or heated.

Segregation can be prevented changing the properties of the salt hydrate with the addition of another material that can hinder the heavier phases to sink to the bottom [124]. This can be achieved either with gelling or with thickening materials. Gelling means adding a cross-linked material (e.g. polymer) to the salt to create a three dimensional network that holds the salt hydrate together. Thickening means the addition of a material to the salt hydrate that increases the viscosity and hereby holds the salt hydrate together [6].

Subcooling is another serious problem associated with all hydrated salts. It appears when a salt hydrate starts to solidify at a temperature below its congelating temperature (Fig. 9). Several approximations have been studied to solve this problem. One is the use of hydrated salts in direct contact heat transfer between an immiscible heat transfer fluid and the hydrated salt solution [4]. Another solution is the use of nucleators [6,125].
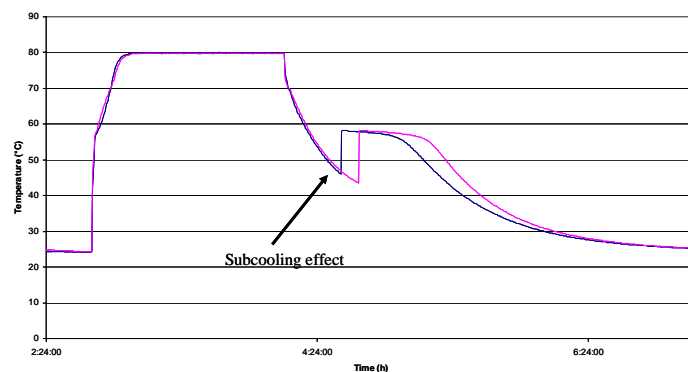

Figure 8: Segregation of a salt hydrate

Figure 9: Subcooling effect of a salt hydrate

3.2.4 Fire retardation of PCM-treated construction materials

An article by Salyer [132] reports on reaction to fire and the possible fire-retardant additives (organic halogenous compounds) that improve the response to fire of the material. This paper covers an important number of applications in the field of heating and cooling, and sets

out a review of materials, advantages, disadvantages and characteristics of a series of PCM substances applicable to thermal storage in buildings. Of the four possible PCM analysed, those with the greatest advantages were of the paraffin type (hydrocarbons; -60 to 80ºC) whose origin can be from the polymerisation of ethylene or as a by-product of petroleum.

Banu et al. [133] conducted flammability tests on energy storing wallboard. Comparison of the test results with similar data for other building materials indicates the possibility of reducing the flammability of energy storing wallboard by incorporation of a flame retardant.

4 Encapsulation of the materials

The encapsulation of the PCM has developed interest in several researchers. Advantages and disadvantages of different geometries of PCM encapsulation with different materials and their compatibility was discussed by Lane [6].

For the use of PCM in buildings applications, an encapsulation of PCM (50-80%) with unsaturated polyester matrix (45-10%), and water (5-10%) was studied by Morikama et al. [8]. In the same area, Inaba [126] and Lee & Choi [10] propose using the storage substance integrated with the building materials without encapsulation ("Shape-stabilised paraffin": 74% paraffin + 26% HDPE [high-density polyethylene]). Structural stability is achieved using high-density polyethylene which retains the paraffin when in liquid phase. Hawes and Feldman [127] have considered the means of PCM incorporation: direct incorporation, immersion and encapsulation. The PCM must be encapsulated so that it does not adversely affect the function of the construction material.

For many applications, PCMs are microencapsulated, and this has been studied by several researchers [18,128,129] and developed by companies like BASF [16,130]. Nevertheless, the potential use of microencapsulated PCMs in various thermal control applications is limited to some extent by their cost. Hawlader et al. [131] have prepared and compared encapsulated paraffin waxes by complex coacervation and spray drying methods, and have shown that microcapsules have high energy storage and release capacity, which depends on core to coating ratio (Figures 10 and 11).

Figure 10: Microencapsulated PCM by copolymerization

Figure 11: Microencapsulated PCM commercialized by BASF

Commercial companies have found different ways of encapsulating their PCMs. For example, Cristopia [78] encapsulates the PCM in nodules (Figure 12). The spherical nodules (balls) are blow moulded from a proprietary blend of polyolefins and filled with PCM. A range of PCMs allow thermal energy to be stored at temperatures between -33°C and +27°C. Rubitherm [75] developed a heat storage granulate in which approx. 35% wt. of a phase change material is bound (Figure 13). This product offer the advantage of maintaining their macroscopic solid form during phase change.
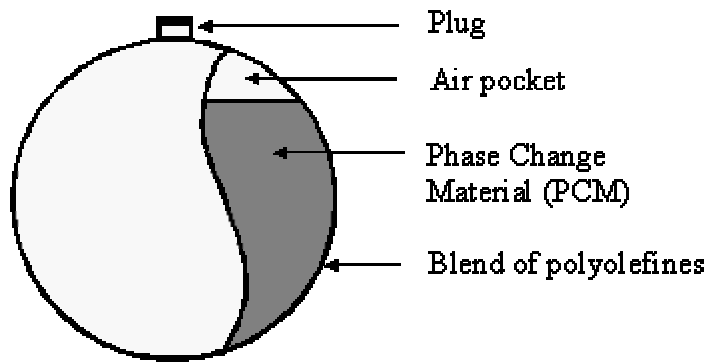
Figure 12: Spherical nodule filled of PCM developed by Cristopia

Figure 13: Granulated developed by Rubitherm

5 Microencapsulated PCM Slurries

5.1 General Considerations about PCM slurries

One major drawback of latent thermal energy storage is the low thermal conductivity of the materials used as PCM. This circumstance makes heat transfer into / out of a thermal energy storage during charging / discharging difficult.

Much work has been performed by enhancing the conductivity of the PCM by embedding structures of material with high thermal conductivity (Velraj et al. [140]; Hamada et al. [159]) or to shorten the heat transport distances inside of the PCM by means of highly dispersed heat exchangers with low distances between fins or pipes (Domañski et al. [160]). Another way is to encapsulate the PCM into containers of different shapes like e.g. plates, cylinders or spheres (Arkar et al.[161]; Bruno, Saman [23], CRISTOPIA "nodule" [78]). These container elements should have a high ratio of surface area to volume, or respectively a large heat transfer area per volume unit and short transport distances in the PCM itself. This results in a container that should be as small as possible.

That's where the topic of microencapsulated PCMs comes up. PCM containers with a diameter of 2-20 µm offer the advantage of excellent surface area/volume ratios and nearly infinitely small transport distances. In addition these microcapsules can be dispersed in a fluid (mostly water) and then be pumped and used as energy transport media, as a so-called PCM slurry (Figure 14).
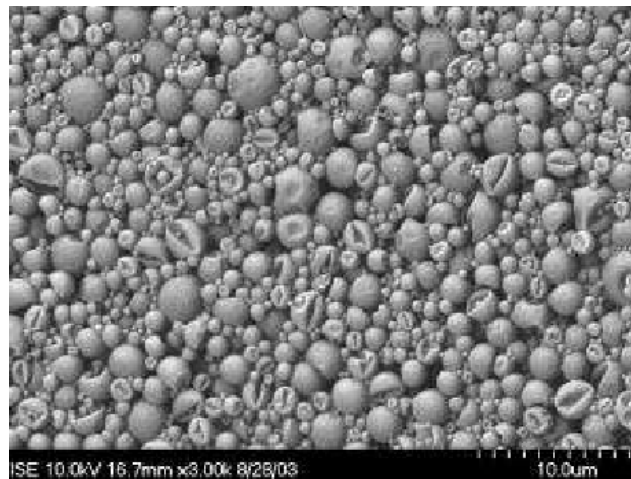

Figure 14: SEM-picture of the dried microcapsules in a PCM slurry (ISE Freiburg)

Concerning calculations, the PCM-slurry can be treated like a homogeneous material (Lumped Capacitance Method). This assumption implies that temperature gradients within the solid are negligible. This is closely approximated if the resistance to conduction within the considered body is small compared with the resistance to heat transfer between the solid and its surroundings. The fulfilment of this condition can be analysed by means of the Biot number, which should have a value of smaller than 0.1 (Incropera, DeWitt [162]). The Biot number is given by the heat transfer coefficient h, the thermal conductivity k and the characteristic length L_c, which in this case can be assumed as the radius of a microcapsule.

$$Bi = \frac{h * L_c}{k} < 0.1$$

If one calculates the Biot number for a PCM microcapsule he will get a value that is far below 0.1. This implies that within a microcapsule no conduction and therefore temperature gradients have to be considered at all. This should solve the problem of the low conductivity of PCM materials.

5.2 Storage capacity and thermodynamic properties

Latent thermal energy storage aims at using the latent heat of fusion of phase change materials. The relatively large amount of latent heat of the phase transition shall give a higher energy storage density compared to the traditional sensible heat storage systems. Unfortunately PCMs have a lower sensible heat capacity than water. Therefore, when a system is operated with high temperature differences, the advantage of the latent heat is reduced due to the lower sensible heat. In such applications water storages are more favourable. Figure 15 shows the specific heat capacity of a PCM slurry with a transition temperature of about 60°C as a function of temperature. The basis of the figure is a T-history measurement (Marin et al., 2002) of a wet slurry probe (50% concentration of microcapsules) during cooling, out of which the graphs for different concentrations were generated. The slurry used in this measurement has a melting temperature range of about 20 K, a latent heat of fusion of about 140 kJ/kg and a sensible heat capacity of about 2.7 kJ/kg.K. Clearly a subcooling part can be seen at 52 °C.
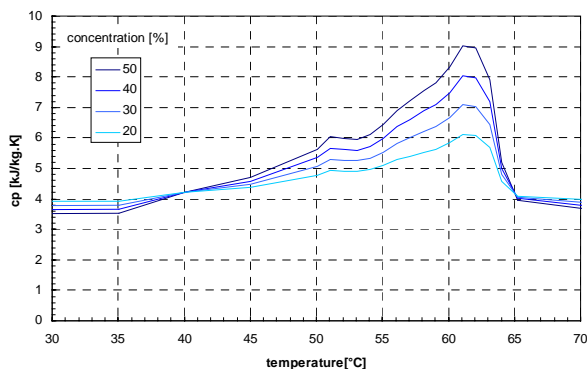

Figure 15: specific heat functions of different concentrations of the 65°C slurry
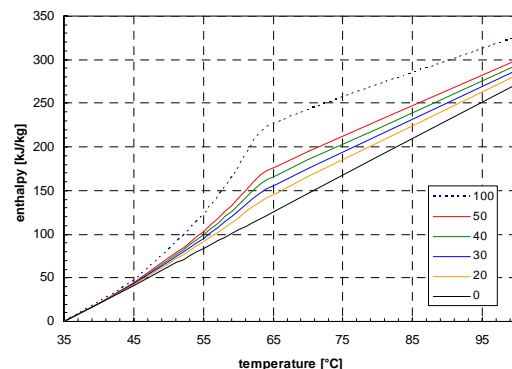

Figure 16: enthalpy functions of different concentrations of the 65°C slurry

In Figure 16 the enthalpies for different concentrations of the slurry are shown, the zero-point of enthalpy was set to 35 °C, where the melting of the PCM sets in.

For high temperature differences of more than 20 K and especially with low concentrations of PCM the storage capacity is not much better than for water. Therefore PCM slurries should potentially be used in systems that are operated with low temperature differences. The concentration of microcapsules should be as high as possible. Figure 17 shows the theoretical storage capacities of different slurry concentrations in different temperature ranges.
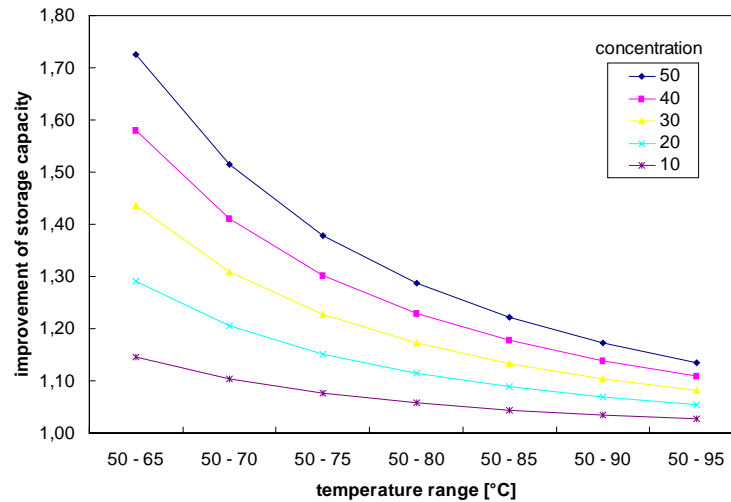
Figure 17: storage capacity enhancement (compared to water) of different concentrations of the 60 °C Slurry in different temperature ranges

The viscosity of PCM slurries is strongly dependent on the concentration of microcapsules and the temperature of the slurry. Figure 18 shows the viscosity as a function of temperature for 3 different concentrations (Egolf [163]. For higher concentrations the viscosity increases strongly. For instance a slurry with a concentration of 50 % and a temperature of 20 °C has a viscosity of 300 mPa.s.
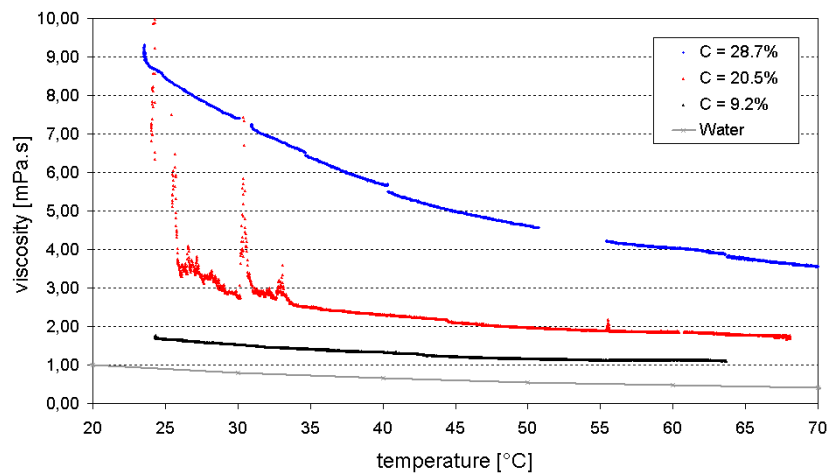

Figure 18: dynamic viscosity of a PCM-slurry as a function of concentration and temperature (measured at EIVD, Switzerland 2004)

6 Conclusions

This reports summarizes the current knowledge on phase change materials that could be suited for storing solar heat in a solar combisystem, where temperatures between 20 and 50 °C are needed and a storage material able to store between 20 and 80C would be best suited.

The report adresses properties of material, types of encapsulation and classification of organic and inorganic materials.

The report shows also some limitations of phase change materials such as the heat exchange power.

Task 32 investigates in other reports the ability for some PCM to be suited to solar combisystems or other heating applications such as reducing the number of cycling of a gas boiler.

7 References

1. I. Dincer, M.A. Rosen, Thermal energy storage. Systems and applications, John Wiley & Sons, Chichester (England) (2002).
2. B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, Applied Thermal Engineering 23 (2003) 251-283.
3. A.M. Khundhair, M.M. Farid, A review on energy conservation in building applications with thermal storage by latent heat using phase change materials, Energy Conversion and Management 45 (2004) 263-275.
4. M.M. Farid, A.M. Khudhair, S.A.K. Razack, A. Al-Hallaj, A review on phase change energy storage: materials and applications, Energy Conversion and Management 45 (2004) 1597-1615.
5. M. Telkes, Thermal storage for solar heating and cooling, Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings, Charlottesville (Virginia, USA), 1975.
6. G.A. Lane, Solar Heat Storage: Latent Heat Material. Volume II: Technology, CRC Press, Florida, 1986.
7. H.G. Barkmann, F.C. Wessling, Use of buildings structural components for thermal storage, Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings, Charlottesville (Virginia, USA) (1975).
8. D.W. Hawes, D. Feldman, D. Banu, Latent heat storage in building materials, Energy and Buildings 20 (1993) 77-86.
9. Y. Morikama, H. Suzuki, F. Okagawa, K. Kanki, A development of building elements using PCM, Proceedings of the International Symposium on Thermal Application of Solar Energy, Hakone (Kanagawa, Japan) (1985).
10. C.H. Lee, H.K. Choi, Crystalline Morphology in High-Density Polyethylene/Paraffin Blend for Thermal Energy Storage, Polymer Composites 19 (6) (1998) 704-708.
11. H. Mehling, R. Krippner, A. Hauer, Research project on PCM in wood-lightweight-concrete, Proceedings of the 2nd Workshop of IEA ECES IA Annex 17, Ljubljana (Slovenia) (2002).
12. T. Haussmann, H.M. Henning, P. Schossig,
Phase Change Materials in wall integrated systems, Proceedings of the 2nd Workshop of IEA ECES IA Annex 17, Ljubljana (Slovenia) (2002).
13. M.M. Shapiro, D. Feldman, D. Hawes, D. Banu, PCM thermal storage in wallboard, Proceedings of the 12th Passive Solar Conference, Portland (Oregon, USA) (1987) 48-58.
14. I.O. Salyer, A.K. Sircar, R.P. Charloff, Advanced phase-change materials for passive solar storage applications, Proceedings of the Solar Building Conference, Silver Spring (Washington D.C., USA) (1985).
15. K. Peippo, P. Kauranen, P.D. Lund, A multicomponent PCM wall optimized for passive solar heating, Energy and Buildings 17 (1991) 259-270.
16. P. Schossig, H.M. Henning, T. Haussman, A. Raicu, Encapsulated Phase-Change Materials integrated into construction materials, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).
17. M. Jaworski, M. Wawreszuk, Thermal behavior of the wall containing PCM capsules, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).
18. J. Marcos, O. Zubillaga, L.F. Cabeza, M. Nogués, J. Roca, P. Alonso, First results on the development of smart microencapsulated organic PCMs to be applied on concrete, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).
19. B. Zalba, Almacenamiento térmico de energía mediante cambio de fase. Procedimiento experimental, Ph.D. Thesis, University of Zaragoza (Spain) (2002).
20. B. Zalba, J.M. Marín, L.F. Cabeza, H. Mehling, Free-cooling in buildings with phase change materials, International Journal of Refrigeration (2004), in press.
21. S.M. Vakilaltojjar, W. Saman, Analysis and modelling of a phase change storage system for air conditioning applications, Applied Thermal Engineering 21 (2001) 249-263.
22. S.M. Vakilaltojjar, W. Saman, Domestic heating and cooling with thermal storage, Proceedings of Terrastock 2000, Stuttgart (Germany) (2000) 381-386.
23. F. Bruno, W. Saman, Testing of a PCM energy storage system for space heating, Proceedings of the World Renewable Energy Congress WII, Cologne (Germany) (2002).
24. N. Barnard, Thermal mass and night ventilation – Utilising "hiden" thermal mass, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).
25. T. Kondo, T. Ibamoto, Research on using the PCM for ceiling board, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).
26. www.unisa.edu.au/sec/PDF's/solar_air_space_heating_system.pdf.
27. S. Takeda, K. Nagano, T. Mochida, T. Nakamura, Development of floor supply air conditioning system with granulated phase change materials, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).

28. M. Zukowski, A numerical model of the air-underfloor heat exchanger, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).

29. Z. Pluta, Numerical analysis of pebble/PCM bed storage systems for solar air heating installations, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).

30. K.A.R. Ismail, J.R. Henríquez, Thermally effective windows with moving phase change material curtains, Applied Thermal Engineering 21 (2001) 1909-1923.

31. K.A.R. Ismail, J.R. Henríquez, Parametric study on composite and PCM glass systems, Energy Conversion & Management 43 (2002) 973-993.

32. O. Merker, V. Hepp, A. Beck, J. Fricke, A new PCM-shading system: a study of the thermal charging and discharging process, Proceedings of Eurosun 2002, Bologna (Italy) (2002).

33. O. Merker, F. Hepp, A. Beck, J. Fricke, A new solar shading system with phase change material (PCM), Proceedings of the World Renewable Energy Congress WII, Cologne (Germany) (2002).

34. E.S. Cassedy, Prospects for Sustainable Energy, Cambridge University Press, 2000.

35. M.M. Farid, Solar Energy Storage with phase change, J. Sol. Energy Res. 4 (1986) 11.

36. M.M. Kenisarin, Short-term storage of solar energy. 1. Low temperature phase-change materials, Applied Solar Energy 29 (2) (1993) 48-65.

37. A.M. Dermott, G.R. Frysinger, Storage assisted air-conditioning using a new low-cost PCM packaging concept, Proc. conference of peak-load pricing and thermal energy storage, Chicago, Illinois, 1979.

38. H. Mehling, L.F. Cabeza, S. Hippeli, S. Hiebler, Improvement of stratified hot water heat stores using a PCM-module, Proceedings of EuroSun 2002, Bologna (Italy) (2002).

39. H. Mehling, L.F. Cabeza, S. Hippeli, S. Hiebler, PCM-module to improve hot water heat stores with stratification, Renewable Energy (2002) in press.

40. M. Esen, A. Durmus, A. Durmus, Geometric design of solar-aided latent heat store depending on various parameters and phase change materials, Solar Energy 62 (1998) 19-28.

41. J.P. Bedecarrats, F. Strub, B. Falcon, J.P. Dumas, Phase-change thermal energy storage using spherical capsules: performance of a test plant, Int. J. Refrig. 19 (1996) 187-196.

42. T. Saitoh, K. Hirose, Spherical capsule-type latent heat thermal energy storage/heat pump system with application to solar system, Proceedings of the International Symposium on Thermal Application of Solar Energy, Hakone (Kanagawa, Japan) (1985).

43. M. Esen, Thermal performance of a solar-aided latent heat store used for space heating by heat pump, Solar Energy 69 (2000) 15–25.

44. M. Sokolov, Y. Keizman, Performance indicators for solar pipes with phase change storage, Solar Energy 47 (1991) 339-346.

45. Y. Rabin, I. Bar-Niv, E. Korin, B. Mikic, Integrated solar collector storage system based on a salt-hydrate phase-change material, Solar Energy 55 (1995) 435-444.

46. S.O. Enibe, Performance of a natural circulation air heating system with phase change material energy storage, Renewable Energy 27 (2002) 69-86.

47. S.O. Enibe, Parametric effects on the performance of a passive solar air heater with storage, Proceedings of the World Renewable Energy Congress WII, Cologne (Germany) (2002).

48. J. Tey, R. Fernández, J. Rosell, M. Ibáñez, Solar collector with integrated storage and transparent insulation cover, Proceedings of Eurosun 2002, Bologna (Italy) (2002).

49. A. Abhat, Low temperature latent heat thermal energy storage: heat storage materials, Solar Energy 30 (1983) 313-332.

50. G.A. Lane, Solar Heat Storage: Latent Heat Material. Volume I: Background and Scientific Principles, CRC Press, Florida, 1983.

51. G. Belton, F. Ajami, Thermochemistry of salt hydrates, Report No. NSF/RANN/SE/GI27976/TR/73/4, Philadelphia (Pennsylvania, USA), 1973.

52. J. Heckenkamp, H. Baumann, Latentwärmespeicher, Sonderdruck aus Nachrichten 11 (1997) 1075-1081.

53. R. Naumann, H.H. Emons, Results of thermal analysis for investigation of salt hydrates as latent heat-storage materials, J. Thermal Analysis 35 (1989) 1009-1031.

54. K. Nagano, T. Mochida, K. Iwata, H. Hiroyoshi, R. Domanski, Thermal performance of $Mn(NO_3)_2 \cdot 6H_2O$ as a new PCM for cooling system, 5th Workshop of the IEA ECES IA Annex 10, Tsu (Japan), 2000.

55. G.A. Lane, Low temperature heat storage with phase change materials, The International Journal of Ambient Energy 1 (1980) 155-168.

56. F. Lindner, Wärmespeicherung mit Salzen und Salzhydraten, Ki Luft- und Kältetechnik 10 (1996) 462-467.

57. T. Wada, R. Yamamoto, Studies on salt hydrate for latent heat storage. I. Crystal nucleation of sodium acetate trihydrate catalysed by tetrasodium pyrophosphate decahydrate, Bul. Chem. Soc. Jpn. 55 (1982) 3603-3606.

58. T. Wada, F. Kimura, Y. Matsuo, Studies on salt hydrate for latent heat storage. IV. Crystallization in the binary system $CH_3CO_2Na-H_2O$, Bul. Chem. Soc. Jpn. 56 (1983) 3827-3829.

59. T. Wada, K. Matsunaga, Y. Matsuo, Studies on salt hydrate for latent heat storage. V. Preheating effect on crystallization of sodium acetate trihydrate from aqueous solution with a small amount of sodium pyrophosphate decahydrate, Bul. Chem. Soc. Jpn. 57 (1984) 557-560.

60. T. Wada, Y. Matsuo, Studies on salt hydrate for latent heat storage. VI. Preheating effect on crystallization of sodium acetate trihydrate from aqueous solution with a small amount of disodium hydrogenphosphate, Bul. Chem. Soc. Jpn. 57 (1984) 561-563.

61. T. Wada, F. Yokotani, Y. Matsuo, Equilibria in the aqueous ternary system containing Na+, CH3CO2-, and P2O74- between 38 and 85°C, Bul. Chem. Soc. Jpn. 57 (1984) 1671-1672.

62. T. Wada, F. Yokotani, Y. Matsuo, Equilibria in the aqueous ternary system containing Na+, CH3CO2-, and HPO42- between 38 and 75°C, Bul. Chem. Soc. Jpn. 57 (1984) 2021-2022.

63. T. Wada, H. Yoneno, Studies on salt hydrate for latent heat storage. VII. The relation between activation process of crystal nucleation catalysts for sodium acetate trihydrate and their deactivation temperatures, Bul. Chem. Soc. Jpn. 58 (1985) 919-925.

64. T. Wada, F. Kimura, R. Yamamoto, Studies on salt hydrate for latent heat storage. II. Eutectic mixture of pseudo-binary system CH3CO2Na·3H2O-CO(NH2)2, Bul. Chem. Soc. Jpn. 56 (1983) 1223-1226.

65. J.H. Li, G.E. Zhang, J.Y. Wang, Investigation of a eutectic mixture of sodium acetate trihydrate and urea as latent heat storage, Solar Energy 47 (6) (1991) 443-445.

66. K. Nagano, K. Ogawa, T. Mochida, K. Simakura, K. Hayashi, H. Ogoshi, Thermal characteristics of magnesium hexahydrate and magnesium chloride hexahydrate mixture as a phase change material for effective utilization of urban waste heat, Proceedings of the 9th International Conference on Thermal Energy Storage – Futurestock'2003, Warsaw (Poland) (2003).

67. M.M. Farid, F.A. Hamad, M. Abu-Arabi, Phase change cool storage using dimethyl-sulfoxide, Energy Convers. Mgmt. 39 (1998) 819-826.

68. K. Sasaguchi, R. Viskanta, Phase change heat transfer during melting and resolidification of melt aroung cylindrical heat source(s)/sink(s), J. En. Resources Techn. 111 (1989) 43-49.

69. M.N.R. Dimaano, T. Watanabe, The capric and lauric acid mixture with chemical additives as latent heat storage materials for cooling application, Energy 27(2002) 869-888.

70. D. Feldman, M.M. Shapiro, D. Banu, Organic phase change materials for thermal energy storage, Solar energy materials 13 (1986) 1-10.

71. A. Sari, K. Kaygusuz, Thermal performance of mystiric acid as a phase change material for energy storage application, Renewable Energy 24 (2001) 303-317.

72. A. Sari, K. Kaygusuz, Thermal performance of palmitic acid as a phase change energy storage material, Energy Convers. Mgmt. 43 (2002) 863-876.

73. A. Sari, K. Kaygusuz, Thermal energy storage system using some fatty acids as latent heat energy storage materials, Energy Sources 23 (2001) 275-285.

74. A. Sari, K. Kaygusuz, Thermal energy storage system using stearic acid as a phase change material, Solar Energy 71 (2001) 365-376.

75. www.rubitherm.de

76. www.climator.com

77. H. Kakiuchi, Mitsubishi Chemical Corporation, private communication (2002).

78. Cristopia (2003), Information from the Cristopia Energy Systems homepage: www.cristopia.com

79. www.teappcm.com

80. I.O. Salyer, A.K. Sircar, R.P. Chartoff, Analysis of Crystalline Paraffinic Hydrocarbons for Thermal Energy Storage by Differential Scanning Calorimetry; Part 1, Pure Hydrocarbons, 15th North American Thermal Analysis Society Conference, Cincinnati, OH, (1986).

81. M. Hadjieva, S. Kanev, J. Argirov, Thermophysical properties of some paraffins applicable to thermal energy storage, Solar Energy Materials and Sollar Cells 27 (1992) 181-187.

82. J.P. Bardon, E. Vrignaud, D. Delaunay, Etude expérimentale de la fusion et de la solidification périodique d'une plaque de paraffine, Rev. Gén. Therm., (212-213) (1979).

83. H.T. EI-Dessouky, W.S. Bouhamra, H.M. Ettouney, M. Akbar, Heat transfer in vertically aligned phase change energy storage systems, Journal of Solar Energy Engineering, Transactions of the ASME 121 (2) (1999) 98-109.

84. S. Himran, A. Suwono, G.A. Mansoori, Characterization of Alkanes and Paraffin Waxes for Application as Phase Change Energy Storage Medium, Energy Sources 16 (1) (1994) 117-128.

85. R.G. Kemink, E.M. Sparrow, Heat transfer coefficients for melting about a vertical cylinder with or without subcooling and for open or closed containment, Int. J. Heat Mass Transfer 24 (10) (1981) 1699-1710.

86. M. Samai, Y. Jarny, D. Delaunay, An optimization method using an adjoint equation to identify solidification front location, Numerical Heat Transfer, Part B 23 (1993) 67-89.

87. M.A. Cuevas-Diarte, T. Calvet-Pallas, J.L. Tamarit, H.A.J. Oonk, D. Mondieig, Y. Haget, Nuevos materiales termoajustables, Mundo Científico June (2000).

88. M.A. Cuevas-Diarte, Y. Haget, D. Mondieig, Nuevos materiales para el almacenamiento de energía térmica: las aleaciones moleculares, El Instalador April (1996) 87.

89. P. Espeau, D. Mondieig, Y. Haget, M.A. Cuevas-Diarte, 'Active' Package for thermal protection of food products, Packaging Technology and Science 10 (1997) 253-260.

90. P. Espeau, L. Roblès, D. Mondieig, Y. Haget, M.A. Cuevas-Diarte, H.A.J. Oonk, Mise au point sur le comportement énergétique et cristallographique des n-alcanes. I. Série de C8H18 à C21H44, J. Chim Phys 93 (1996) 1217-1238.

91. P. Espeau, Syncristallisation dans la famille des alcanes de C8H18 a C17H36. Conception, elaboration et caracterisation de nouveaux materiaux a changement de phases a base d'alliages moleculaires (MCPAM). Application a la protection thermique dans le domaine agro-alimentaire, Thesis at the University of Burdeos I (1995).

92. V. Métivaud, F. Rajabalee, D. Mondieig, Y. Haget, M.A. Cuevas-Diarte, Solid-solid and solid-liquid equilibria in the heneicosane-docosane binary system, Chemistry of materials 11 (1) (1998) 117-122.

93. D. Mondieig, A. Marbeuf, L. Robles, P. Espeau, B. Poirier, Y. Haget, T. Calvet-Pallas, M.A. Cuevas-Diarte, Thermoadjustable molecular alloys for energy storage and thermal protection: fundamental aspects and applications, High Temperatures-High Pressures 29 (1997) 385-388.

94. F. Rajabalee, V. Métivaud, D. Mondieig, Y. Haget, M.A. Cuevas-Diarte, New insights on the crystalline forms in binary systems of n-alkanes: Characterization of the solid ordered phases in the phase diagram tricosane + pentacosane, Journal of Materials Research 14 (6) (1999) 2644-2654.

95. F.A. Rajabalee, Existence et stabilite de sous-familles structurales des cristaux mixtes dans les alcanes normaux (C8H18 à C28H58). Caracterisations cristallographique et thermodynamique. Incidence des desordres de composition, conformation et rotation, Thesis (1998).

96. L. Roblès, D. Mondieig, Y. Haget, M.A. Cuevas-Diarte, Mise au point sur le comportement énergétique et cristallographique des n-alcanes.I I. Série de C22H46 à C27H56, J. Chim. Phys. 95 (1998) 92-111.

97. E.S. Fath Hassan, Heat Exchanger Performance For Latent Heat Thermal Energy Storage System, Energy Convers. Mgmt 31 (2) (1991) 149-155.

98. F. Strub, J.P. Bedecarrats, Numerical Second Law Analysis of a Refrigeration Phase-Change Storage, Int. J. Applied Thermodynamics 2 (3) (1999).

99. R.F. Speyer, Thermal Analysis of Materials, Marcel Dekker, Inc., New York (1994).

100. E.R.G. Eckert, R.J. Goldstein, W.E. Ibele, S.V. Patankar, T.W. Simon, P.J. Strykowski, K.K. Tamma, T.H. Kuehn, A. Bar-Cohen, J.V.R. Heberlein, D.L. Hofeldt, J.H. Davidson, J. Bischof, F. Kulacki, Heat transfer – a review of 1994 literature, Int. J. Heat Trasfer 40 (1997) 3729-3804.

101. H. Inaba, P. Tu, Evaluation of thermophysical characteristics on shape-stabilized paraffin as a solid-liquid phase change material, Heat Mass Transfer 32 (1997) 307-312.

102. B. Flaherty, Characterisation of Waxes by Differential Scanning Calorimetry, J. Appl. Chem. Biotechnol. 21 (1971).

103. C. Giavarini, F. Pochetti, Characterization of petroleum products by DSC analysis, Journal of Thermal Analysis 5 (1973) 83-94.

104. B.M. Gibbs, S.M. Hasnain, DSC Study of Technical Grade Phase Change Heat Storage Materials for Solar Heating Applications, Proceedings of the 1995 ASME/JSME/JSEJ International Solar Energy. Conference. Part 2, (1995).

105. Z. Yinping, J. Yi, J. Yi, A simple method, the T-history method, of determinig the heat of fusion, specific heat and thermal conductivity of phase-change materials, Measurement Science & Technology 10 (1999) 201-205.

106. J.M. Marín, B. Zalba, L.F. Cabeza, H. Mehling, Determination of enthalpy-temperature curves of phase change materials with the T-history method – improvement to temperature dependent properties, Measurement Science & Technology 14 (2003) 184-189.

107. D. Delaunay, P. Carre, Dispositifs de mesure automatique de la conductivité thermique des matériaux à changement de phase, R. Physique Appliquée 17 (1982) 209-215.

108. I. Sadasuke, M. Naokatsu, Heat transfer enhancement by fins in latent heat thermal energy storage devices, Solar Engineering, ASME (1991), 223-228.

109. I.M. Bugaje, Enhancing the thermal response of latent heat storage systems, International Journal of Energy Research 21 (1997) 759-766.

110. A. Manoo, E. Hensel, One-dimensional two-phase moving boundary problem, HTD-Vol. 159, Phase Change Heat Transfer, ASME (1991) 97-102.

111. D. Heine, The chemical compatibility of construction materials with latent heat storage materials, Proceedings of the International Conference on Energy Storage, Brighton, UK (1981).

112. F.S. Pettit, Molten Salts, In: Corrosion Test Standards, ASTM, 380.

113. F.C. Porisini, Salt hydrates used for latent heat storage: corrosion of metals and reliability of thermal performance, Solar Energy 41 (1988) 193-197.

114. L.F. Cabeza, J. Illa, J. Roca, F. Badia, H. Mehling, S. Hiebler, F. Ziegler, Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36°C temperature range, Materials and Corrosion 52 (2001) 140-146.

115. L.F. Cabeza, J. Illa, J. Roca, F. Badia, H. Mehling, S. Hiebler, F. Ziegler, Middle term immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36°C temperature range, Materials and Corrosion 52 (2001) 748-754.

116. L.F. Cabeza, F. Badia, J. Illa, J. Roca, H. Mehling, F. Ziegler, Corrosion experiments on salt hydrates used as phase change materials in cold storage, IEA ECES IA Annex 17 Kick-off Workshop, Lleida (Spain) (2001).

117. L.F. Cabeza, H. Mehling, S. Hiebler, Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58°C temperature range, Materials and Corrosion 53 (2002) 902-907.

118. D. Heine, F. Heess, Chemische uns physikalische Eigenschaften von Latentwärmespeichermaterialien für Solarkraftwerke, Proceedings of the 3rd International Solarforum, Hamburg (Germany), 1980.

119. S. Furbo, S. Svensen, Report on heat storage in a solar heating system using salt hydrates, Thermal Insulation Laboratory, Technical University of Denmark, 1977.

120. S. Furbo, Investigation of heat storages with salt hydrate as storage medium based on the extra water principle, Thermal Insulation Laboratory, Technical University of Denmark, 1978.

121. S. Furbo, Heat storage with an incongruently melting salt hydrate as storage medium based on the extra water principle, in "Thermal Storage of Solar Energy", C. den Ouden (ed.), 135-145.

122. S. Furbo, Heat storage with an incongruently melting salt hydrate as storage medium based on the extra water principle, Energiministeriets varmelagerprojekt Rapport nr. 8, 1980.

123. S. Furbo, Heat storage units using salt hydrate, Sunworld 6 (1982) 134-139.

124. L.F. Cabeza, G. Svensson, S. Hiebler, H. Mehling, Thermal performance of sodium acetate trihydrate thickened with different materials as phase change energy storage material, Applied Thermal Engineering 23 (2003) 1697–1704.

125. R. Grausch, Neue PCM-Materialien und Keimbildner, Proceedings of the ZAE-Symposium 2004 – Wärme- und Kältespeicherung mit Phasenwechselnmaterialien, Garching (Germany), 2004.

126. H. Inaba, P. Tu, Evaluation of termophysical characteristics on shape-stabilized paraffin as a solid-liquid phase change material, Heat and Mass Transfer 32 (1997) 307-312.

127. D.W. Hawes, F. Feldman, Absorption of phase change materials in concrete, Solar Energy Mater Solar Cells 27 (1992) 91-101.

128. R.C. Brown, J.D. Rasberry, S.P. Overmann, Microencapsulated phase-change materials as heat transfer media in gas-fluidized beds, Powder Technology 98 (3) (1998) 217-222.

129. M.N.A. Hawlader, M.S. Uddin, M.M. Khin, Microencapsulated PCM thermal-energy storage syste, Applied Energy 74 (2003) 195-202.

130. E. Jahns, Microencapsulated phase change materials, Proceedings of the 4th IEA ECES IEA Annex 10 Workshop, Benediktbeuern (Germany), 1999.

131. M.N. Hawlader, M.S. Uddin, M.M. Khin, Microencapsulated phase change materials, Proceedings of the 9th APCChE Congress and CHEMECA 2002, Christchurch (New Zealand), 2002.

132. I.O. Salyer, A.K. Sircar, Phase Change Materials For Heating and Cooling Of Residential Buildings and Other Applications, Proceedings of the 25th Intersociety Energy Conversion Engineering Conference-IECEC'90 (1990).

133. D. Banu, D. Feldman, F. Haghighat, J. Paris, D. Hawes, Energy-storing wallboard: flammability tests, J Mater Civ Eng 10 (1998) 98-105.

134. A. Abhat, S. Aboul-Enein, N. Malatidis, Heat of fusion storage systems for solar heating applications, in: C. Den Quden (Ed.), Thermal Storage of Solar Energy, Martinus Nijhoff, 1981.

135. V.H. Morcos, Investigation of a latent heat thermal energy storage system, Solar Wind Technol. 7 (2/3) (1990) 197–202.

136. I. Sadasuke, M. Naokatsu, Heat transfer enhancement by fins in latent heat thermal energy storage devices, Solar Eng., ASME (1991) 223–228.

137. M. Costa, D. Buddhi, A. Oliva, Numerical Simulation of a latent heat thermal energy storage system with enhanced heat conduction, Energy Convers. Mgmt. 39 (3/4) (1998) 319–330.

138. P.V. Padmanabhan, M.V. Krishna Murthy, Outward phase change in a cylindrical annulus with axial fins on the inner tube, Int. J. Heat Mass Transfer 29 (1986) 1855–1868.

139. R. Velraj, R.V. Seeniraj, B. Hafner, C. Faber, K. Schwarzer, Experimental analysis and numerical modelling of inward solidification on a finned vertical tube for a latent heat storage unit, Solar Energy 60 (1997) 281–290.

140. R. Velraj, R.V. Seeniraj, B. Hafner, C. Faber, K. Schwarzer, Heat transfer enhancement in a latent heat storage system, Solar Energy 65 (1999) 171–180.

141. K.A.R. Ismail, C.L.F. Alves, M.S. Modesto, Numerical and experimental study on the solidification of PCM around a vertical axially finned isothermal cylinder, Appl. Thermal Eng. 21 (2001) 53–77.

142. U. Stritih, Heat transfer enhancement in latent heat thermal storage system for buildings, Energy and Buildings 35 (2003) 1097–1104.

143. R. Siegel, Solidification of low conductivity material containing dispersed high conductivity particles, Int. Heat Mass Transfer 20 (1977) 1087–1089.

144. M. Kamimoto, Y. Abe, S. Sawata, T. Tani, T. Ozawa, Latent heat storage unit using form-stable high density polyehylene for solar thermal applications, Proceedings of the International Symposium on Thermal Application of Solar Energy, Hakone (Kanagawa, Japan) (1985).

145. C.J. Hoogendoorn, G.C.J. Bart, Performance and modelling of latent heat stores, Solar Energy 48 (1992) 53–58.

146. M.A. Khan, P.K. Rohatgi, Numerical solution to a moving boundary problem in a composite medium, Numer. Heat Transfer 25 (1994) 209–221.

147. X. Tong, J. Khan, M.R. Amin, Enhancement of heat transfer by inserting a metal matrix into a phase change material, Numer. Heat Transfer, Part A 30 (1996) 125–141.

148. X. Tong, J.A. Khan, M.R. Amin, Enhancement of heat transfer by inserting a metal matrix into a phase change material, Numer. Heat Transfer, Part A 30 (1996) 125–141.

149. C.A. Bauer, R.A. Wirtz, Thermal characteristics of a compact, passive thermal energy storage device, Proceedings of the 2000 ASME IMECE, Orlando (Florida, USA), 2000.

150. P. Satzger, B. Exka, F. Ziegler, Matrix-heat-exchanger for a latent-heat cold-storage, Proceedings of Megastock_98, Sapporo (Japan), 1998.

151. H. Mehling, S. Hiebler, F. Ziegler, Latent heat storage using a PCM-graphite composite material: advantages and potential applications, Proceedings of the 4th Workshop of IEA ECES IA Annex 10, Bendiktbeuern (Germany), 1999.

152. H. Mehling, S. Hiebler, F. Ziegler, Latent heat storage using a PCM-graphite composite material, Proceedings of Terrastock 2000—8th International Conference on Thermal Energy Storage, Stuttgart (Germany) (2000), pp. 375–380.

153. L.F. Cabeza, H. Mehling, S. Hiebler, F. Ziegler, Heat transfer enhancement in water when used as PCM in thermal energy storage, Appl. Thermal Eng. 22 (2002) 1141–1151.

154. X. Py, R. Olives, S. Mauran, Paraffin/porous-graphite-matrix composite as a high and constant power thermal storage material, Int. J. Heat Mass Transfer 44 (2001) 2727–2737.

155. J. Fukai, Y. Morozumi, Y. Hamada, O. Miyatake, Transient response of thermal energy storage unit using carbon fibers as thermal conductivity promoter, Proceedings of the 3rd European Thermal Sciences Conference, Pisa (Italy), 2000.

156. J. Fukai, M. Kanou, Y. Kodama, O. Miyatake, Thermal conductivity enhancement of energy storage media using carbon fibers, Energy Convers. Mgmt. 41 (2000) 1543–1556.

157. J. Fukai, Y. Hamada, Y. Morozumi, O. Miyatake, Effect of carbon-fiber brushes on conductive heat transfer in phase change materials, Int. J. Heat Mass Transfer 45 (2002) 4781–4792.

158. M. Xiao, B. Feng, K. Gong, Thermal performance of a high conductive shape-stabilized thermal storage material, Solar Energy Materials. Solar Cells 69 (2001) 293–296.

159. Hamada Y., Fukai J., Morozumi Y. and Miyatake O., (2002), Performance Test of Practical-Scale Thermal Energy Storage Units Using Paraffin/Carbon-Fiber Composites, Department of Chemical Engineering, Kyushu University Japan.

160. Domañski R., Banaszek J., Rebow M., (2000), Complex analysis of spiral PCM thermal energy storage unit performance, Institute of Heat Engineering, Warsaw University of Technology, POLAND.

161. Arkar C., Kavcic M., Medved S., (2003), Increasing Building's Ventilation Efficiency Using Solar Roof and PCM Heat Storage, University of Ljubljana, SLOVENIA.

162. Incropera F.P., DeWitt D., (2002), Fundamentals of Heat and Mass Transfer

163. Egolf P., (2004), Physical Properties, Fluid Dynamics and Thermodynamics of PCMS, Presentation at the final meeting of the european project PAMELA in Brüssels