Testing large samples of PCM in water calorimeter and PCM used in room applications by night-air cooling

RICKARD BELLANDER

Licentiate Thesis in Building Materials Technology
Gävle, Sweden 2005
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October 2005
We are the ones who will hear, said Phouchg, 'the answer to the great question of Life...!'

'The Universe...!' said Loonquawl.

'And Everything...!' said Phouchg with a slight gesture, 'I think Deep Thought is preparing to speak!'

Shhh,' said Loonquawl. 'I think Deep Thought is preparing to speak!

Though I don't think,' added Deep Thought, 'that you are going to like it.

'Doesn't matter!' said Phouchg. 'We must know it! Now!'

'Now?' inquired Deep Thought.

'Yes! Now...!'

'All right,' said the computer and settled into silence again. The two men fidgeted. The tension was unbearable.

'You're really not going to like it,' observed Deep Thought.

'Tell us!'

'All right,' said Deep Thought. 'The Answer to the Great Question...'

'Yes...!'

'Of Life, the Universe and Everything...' said Deep Thought.

'Yes...!'

'Is...?' said Deep Thought, and paused

'Yes...!'

'Is...?'

'Yes...!!...?'

'Forty-two,' said Deep Thought, with infinite majesty and calm

'Forty-two!' yelled Loonquawl. 'Is that all you've got to show for seven and a half million years' work?

'I checked it very thoroughly,' said the computer, 'and that quite definitely is the answer. I think the problem, to be quite honest with you, is that you never actually known what the question is. '"

Douglas Adams,
The Hitchhiker's Guide to the Galaxy

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Abstract

The latent-heat-storage capacity in Phase-Change Materials can be used for storing or releasing energy within a small temperature interval. Upon the phase transition taking place in a narrow temperature span, the material takes up or releases more energy compared to sensible heat storage. For an ideal phase-change material, the transition temperature is a single value, but for the most common phase-change materials on the market, used in building applications, the transition temperature is distributed within a temperature range of several degrees.

Integration of phase-change materials in building applications can be effected in several ways, for example by impregnating phase-change materials into porous building materials like concrete, wallboards, bricks or complements of the building structure. Integrating storages filled with phase-change materials makes other implementations, for instance accumulating tanks or envelopes as presented in this thesis, in an air heat exchanger. An appropriate phase-transition temperature of the supposed application is critical to the functionality of the material. For example, in cooling applications, the transition temperature of the material should be a few degrees lower than the requested comfort temperature in the building, and the opposite for heating applications.

In order to assess the thermal properties and the durability of the material, a water-calorimetric equipment was developed and employed in an accelerated testing programme. The heat capacity of the material and in particular possible change in the heat capacity over time, after thermal cycling of the material, were measured. In the thermal cycling of the material from solid to liquid phase, the temperature rise and required energy supply were recorded. The testing programme was undertaken according to control procedures and documents. In order to be able to utilize the heat-storage capacity in the best way, it is necessary to gain knowledge about thermal properties of the material, especially the long-term behaviour of the material and the deterioration rates of the thermal properties.

A semi-full-scale air heat exchanger based on phase-change material was developed and tested under real temperature conditions during the summer of 2004. The test results were used to compare and verify computer simulations made on a similar plant. The air heat exchanger utilises the ambient diurnal temperature swing to charge and discharge the phase-change material. The material tested in the calorimeter and in the air heat exchanger has an estimated phase-change temperature of about 24 °C.

Keywords: phase-change material, PCM, water calorimeter, air heat exchanger, durability, thermal properties, heat capacity.
Sammanfattning

Fasförändringsmaterial, PCM, Phase Change Material, kan bland annat användas till att lagra energi, värme eller kyla inom ett smalt temperaturintervall. Då ett material byter fas, till exempel från fast till flytande alternativt från flytande till gas eller omvänt, krävs en större energimängd, latent heat, jämfört med en temperaturökning/sänkning i ett material som inte inkluderar en fasövergång, specific heat. En liknelse kan göras med smältande is i ett vattenglas. Energilager som utnyttjar fasförändringsmaterialets konstanta fasomvandlingstemperatur kan bland annat användas för uppvärmning eller kylning av bostäder eller kontorslokaler.

Som fasförändringsmaterial i byggnadssammanhang kan både organiska och oorganiska material användas, såsom växer, paraffiner, saltlösningar eller rena saltar. I detta projekt har en saltlösning som till största del består av modifierat Glaubersalt, Na$_2$SO$_4$•10H$_2$O, använts. Saltlösningen har en angiven fasomvandlingstemperatur på 24 °C. Det finns olika metoder för att integrera PCM i byggnadssammanhang. De vanligaste metoderna är genom impregnering av PCM i porösa byggnadsmaterial såsom betong, lättbetong eller tegel alternativt genom att kombinera behållare eller förpackningar fyllda med PCM i olika byggnadssystem.

Forskningsprojektet har varit inriktat på att undersöka materialegenskaperna för ett fasförändringsmaterial, främst med inriktning på långtidsegenskaperna hos materialet och dess förpackningsmaterial. Bland nödbrytningsfaktorerna kan nämnas bland annat fasseparation, kemisk instabilitet, underkylning, volymförändring, oxidation och mekanisk motståndskraft. En av de viktigaste materialegenskaperna är dess specifika värmekapacitet, $c_p$, det vill säga materialets förmåga att lagra värme eller kyla, per massenhet, [J/kg K]. Därför har det även ingått att undersöka materialets värmekapacitet, speciellt om det har skett någon förändring av kapaciteten över tiden då materialet har termiskt cyklats under ett stort antal fasförändringscyklar. Dessa tester har utförts i en vattenkalorimeter som har utvecklats och byggts i laboratoriet vid Högskolan i Gävle. Testerna har genomförts då materialet har uppvärmts och övergått från fast till smält fas, under det att energitågen och temperaturökning i provet har uppmätts/loggats. Den använda försöksutrustningen och utvärdering av resultatet presenteras i denna licentiatavhandling.

Preface

This thesis is based on results from the project C-TIDE (Changeable Thermal Inertia Dry Enclosure), in which the possibility of changing the thermal inertia in lightweight buildings was explored. The project was a co-operative work between Swedish and Italian universities and manufacturing industries and was run under the CRAFT-scheme in the European Fifth Framework Programme, thematic sub programme “Energy and Environment Sustainable Development”.

I would like to thank everyone who has made this work possible, both here in Gävle and at KTH. These include first of all persons that have helped me regularly, but also a lot of people who have helped me with different things during my research work in the past years.

In particular, I would like to thank my supervisors Professor Ove Söderström and Professor Christer Sjöström and also Associate Professor Per Jernberg who all have helped me in different ways during this work. I also wish to direct my gratitude to my colleagues at the KTH Research School in Gävle, especially Göran Hed, for co-operative work in the laboratory and co-writing of the articles presented in this thesis.

Finally, I would like to thank my wife Malin for supporting me in my work and making the journey possible.

Gävle, September 2005
Rickard Bellander


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Introduction

This thesis describes a method to determine heat capacity and the performance over time of Phase-Change Materials, PCMs. An application that utilises PCM for storing and releasing energy in an air heat exchanger is also described. The work is divided into several parts including simulations, experiments on a laboratory scale and by experimental buildings. The laboratory tests are performed as a part of a European founded project aiming to investigate the possibilities of integrating PCM into lightweight buildings/ constructions in order to make them thermally behaving like heavyweight buildings. This work is a co-operation work between Italian and Swedish universities and companies. The main objective for the Italian group is to integrate PCMs in building systems, especially in wall constructions.

This part of the project includes the water-calorimetric measurement that is used to determine the thermal storage capacity on large samples of PCM. It also includes a semi full-scale PCM-based air heat exchanger. The water calorimeter is used to determine the heat capacity and possible change of the thermal storage capacity over time when exposing the material to thermal cycling. Durability tests of the encapsulating material of the PCM are also conducted. The semi full-scale air heat exchanger is tested in the laboratory in order to determine the effectiveness and the thermal capacity of the plant. The test was conducted during summer 2004, under real temperature conditions. Also, the measured values from the air heat exchanger are compared to simulations and calculations for a fictive air heat exchanger. The air heat exchanger utilises cool outdoor night air to charge a battery filled with PCM and at daytime the PCM-battery discharges the coolness to the room. In order to examine the effectiveness of the air heat exchanger and to be able to compare the result from a room without phase-change materials, two rooms were built having identical boundary conditions. The measuring campaign was conducted at the same time for both rooms.

State of the art

Energy storage in sensible heat storages has been used for centuries. Latent-heat storage in building applications has only been used since 1940s (Lane, 1983). The earliest form of latent-heat storages might be the ice stack. To cool diary products and groceries ice blocks were stored in the winter season to be used in iceboxes during summer time. The first attempt to use PCMs in building applications was made in the early twentieth century. Tests and development have been in progress since then. Different materials, both inorganic and organic, have been tested and used. The first ones were salt hydrates, while later experiments have been made on paraffins, fatty acids and waxes. The organic materials have lower thermal heat-storage capacity compared to inorganic materials, but they are cheaper and more chemical stable (Farid et al. 2004). Disadvantages of inorganic materials, especially salt hydrates, are durability problems caused by phase separation, corrosion problems and problems due to super cooling. Salt hydrates are not, due to that fact, always suitable for building applications. For the organic materials, the fire-retardant problems may cause problems in building applications.
Construction Product Directive

In order to harmonise the market for building materials and products and to prevent trade barriers between countries in the European Union, a common platform for product standards has been approved. The Construction Product Directive, 89/106/EEC, CPD, is the European directive for building products concerning all building materials and products used for constructions and in building premises. The European organisations like CEN or EOTA specify the regulated demands on the construction or the material. The specific material or product can be approved according to the directive by a standardisation organisation, for example ISO. Before the product can be approved, according to the directive, the product must meet six major requirements:

1. Mechanical resistance and stability;
2. Safety in case of fire;
3. Hygiene, health and the environment;
4. Safety in use;
5. Protection against noise, and;

All these essential requirements must be met by a whole construction or a part of a construction using normal maintenance during an economical reasonable working life thereof. The definition of economical reasonable working life is: “all essential requirements are fulfilled and all relevant aspects are included, such as risk and consequence, planned partial renewal cost of inspection and maintains, care and repair disposal and environment aspects” (CPD, guidance paper F, 2002). The economical working life is depending on the product, the market and the development in the society. The economical working life of a product is often not the same as the real working life (Aikivuori 1999). A product or a component can be approved for the European market by using either a harmonised standard, European technical approval or a non-harmonised technical standard that is approved by the commission. A technical approval shall include indications for the working life of the product, in relation to the intended use of the product (CPD, Working life and durability. 2002).

Phase-Change Material

Different types of building applications employing PCM have been tested, but most of these are just for experimental purpose. Only a few products are produced for commercial use. The most common way to implement PCM in building materials is impregnating or immersing PCM in porous material or microencapsulating PCM in small shells. Another way is to integrate containers, vessels or envelopes filled with PCM into the building system. Also combinations with PCM in water accumulation tanks have been tested. Different methods and applications for building systems are described by for example (Feldman and Banu, 1991; Hawes et al. 1993; Kissock et al. 1998; Hawlander et al. 2002; Sari and Kaygusuz, 2002).

Impregnating PCM into gypsum wallboards is one application for building materials. Normally the impregnation can be carried out in two ways. One is to immerse the board in a solution of liquid PCM and let the pores become filled. The other way is to mix plastic pellets filled with PCM in the gypsum slurry during the manufacturing process (Feldman and Banu, 1991; (Kissock et al. 1998). So far, no commercial products have reached the building market. There have only been some experimental applications for research and test constructions. Tests have shown that it is possible for wallboards to absorb as much as 50 % of the wallboards weight with PCM, but in practical use, the optimal proportion is 25–30 % of
the wallboard weight (Hawes et al. 1993). Other tests have shown that it is possible to develop and integrate PCM-wallboards for building construction. More developed PCMs having larger thermal storage capacity are required to make the product economical useful (Rudd, 1993). The most examined PCMs for these purposes are paraffins and waxes. A lot of tests and experiments have been carried out on these materials, both practically and by computer simulations, for example by (Neeper, 2000; Peippo et al. 1991; Ip K, 1998; Ng et al. 1998; Velraj et al. 1999; Scalat et al. 1996; Feldman and Banu, 1996). The results of these tests are not in concordance with each other. For example, Scalat et al. show in their report that the temperature swing in a room enveloped by impregnated gypsum, compared to a room having regular gypsum wallboard, is small due to the small volume of phase-change material in the boards. That is not the same result as Feldman et al. report. They claim that, compared to a regular wallboard, the impregnated one has at least eight times higher heat-storing capacity. The large transformation area is one advantage in wallboard applications compared to non-integrated PCM storage applications. To get optimal use of the PCM, for example in wallboards, both melting and solidification are required during the diurnal temperature swing. One disadvantage is that furniture, bookshelves, pictures and so on can disturb the heat transfer between the room and the wallboards. Another disadvantage with paraffin-impregnated wallboards is the fire resistance, due to the fact that paraffins are flammable. A regular gypsum wallboard is fire resistant but an impregnated may be flammable unless it is also impregnated with fire-retardant chemicals. Such an impregnation may change the thermal properties of the PCM and reduce the heat capacity.

Tests have also been performed on autoclaved concrete blocks, both by immersing the blocks in PCM and by adding PCM in the concrete slurry during mixing. Both types have been investigated and the results are promising. The energy-storage capacity of an impregnated concrete block increases over 200 % compared to conventional autoclaved concrete (Hadjieva et al. 2000; Rudd 1993). The disadvantages with concrete blocks are similar as with wallboards.

Another application is the “Cool Deck” that employs forced night ventilation to cool the construction frame of a building and a layer of PCM. At daytime the construction frame and the PCM are used as an “air-conditioner” to cool the inner air. One full-scale experiment is in operation in Stevenage Borough Council’s, UK, (Barnard, 2002), where a false ceiling is used in combination with ventilation ducts and PCM storage. Ventilation fans blow cool night air in a ventilation gap between the concrete frame and a layer of PCM, see figure 1. The cool air cools down the concrete slab and makes the PCM to change phase from liquid to solid. This type of storage utilises both sensible and latent heat. During warm days, the inner air circulates in the ventilation gap and becomes cooled down before distribution in the premises.
Systems of latent heat in floor systems have also been investigated and developed. The natural convection may cause problems for these kinds of systems at the charging process for heating purpose and the discharging process for cooling purpose, if indoor air is used for the charging or discharging processes. The problems can be solved by using systems of pipes and ducts in combination with fans for transportation of the air. Another application of PCM in buildings is to integrate PCM in solar collectors to increase the effectiveness of the assembly.

Another example of PCM applications not concerning buildings and building materials are transportation of medical accessories, which requires a constant temperature independent of electrical supply. Further examples are electrical equipment, like telephone exchanges, that requires constant cooling to maintain the function even in case of power failure (Ulfvengren, 1998), and delivery of fast food. Another application used for drying herbs or other crops is described by (Enibe, 2002) where PCM is applied in combination with solar heating systems. Also, applications to maintain uniform temperature and prevent frost in greenhouses have been investigated, for example by (Kürklü, 1998).

In addition to experimental setups and full-scale attempts, a lot of calculations and simulations have been made on PCM integration in building applications, for example by (Peippo et al. 1991; Kim and Darkwa, 2003; Heim and Clarke, 2004; Ismail and Gonçalves, 1999). Faggembauu et al. describe in two articles a mathematical model for calculating ventilated facades in combination with PCM in Mediterranean climates. (Faggembauu et al. 2003)

One option for using PCM, is to reduce energy consumption on peak hours. Energy is in some regions more expensive during peak load. If there is a possibility to conserve, for example heat from periods of the day when the energy is cheap and consume it during peak load, there might be an economical benefit to store energy in PCM storages. There is also a possibility of using cooling water from industries or waste heat from processes to charge PCM storages and use the energy for example in heating purposes. In building applications, the required phase-change temperature for heating is some degrees higher than the temperature for cooling. That causes problems when both heating and cooling are required, due to, for example, seasonal changes in temperatures. The design and mixture of the PCM become complicated in these cases. The use of two PCMs having different transition temperatures may solve the problem. A disadvantage of such a solution is that the required volume of PCM is doubled for that application to be able to fulfil the thermal demands.
Criteria for building applications

In durability design of PCM products for thermal storage, there are some properties that must be taken into consideration, for example (Carlsson \textit{et al.} 1978, Abhat, 1983):

- Chemical instability
- Phase separation
- Super cooling
- Volumetric change of PCM
- Corrosion on encapsulation material

\textit{Chemical instability}

Thermal cycling is one of the most important test criteria for PCMs, especially for inorganic materials such as salt and salt hydrates due to the reduction of thermal capacity after cycling. For example a test with pure Na$_2$SO$_4$•10H$_2$O, so called Galubersalt, in which the thermal capacity decreases from initially 238 kJ/kg to 63 kJ/kg after 40 transition cycles (Abhat, 1983). The reason is phase separation and incongruent melting of the salt. In a test made by SP (Swedish National Testing and Research Institute, 1981), the phase-change material started as a homogeneous microcrystalline, so-called one-phase system, but after some temperature cycles the material became a two-phase system with a saturated solution and non-hydrated hard salt phase. The phases never mixed due to different densities in the material. Leaving the material in rest and non-cycled for a period or heated to a temperature much above the transition temperature, the phase separation reverses for some PCMs and the material recovers its original properties. However, this does not work on Glaubersalt, which never recovers.

\textit{Phase separation}

A problem with some salt hydrates is decomposition from a higher level of salt hydrate to a lower, such as the decomposition of CaCl$_2$•6H$_2$O to CaCl$_2$•4H$_2$O where the new composition has a lower heat-storage capacity. To prevent phase separation in salt hydrates, it is possible to add some types of thickening agents or suspension media (Abhat, 1983), so called nucleating agents. The added nucleating agents displace a part of the salt hydrate that causes a reduction in the volumetric heat capacity in the storage container. Another method is to add extra water into the salt solution, which dissolves all the solid anhydrous salt. It is also possible to make some chemical modifications of the salts. In thermal cycling of a solution of Glaubersalt, without nucleating agents, it will form 16 % non-hydrate salt for every thermal cycle. This process will persist until no salt solution remains, just solid salt and liquid water. The difference in density between salt and salt solution will counteract mixing of non-hydrate salt and salt solution. The phase-separation problem and the chemical instability are interlinked.

\textit{Super cooling}

A problem that occurs in some PCM, mostly salt hydrates, is called super cooling or sub cooling. The transition between two phases requires that the transition temperature is lower than the crystallisation point of the material to make the change of phase to occur, see figure 2. The values in figure 2 are taken from one day of the test series of the air heat exchanger. Super cooling may cause a problem in some applications, where the transition temperature is lower than the operation temperature of the application. The super-cooling temperature is for some materials more than 10 °C lower than the actual crystallisation temperature. By
introducing nucleating agents into the PCM, there is a possibility of preventing, or
minimising, the super-cooling effect. The nucleating agents have a crystal structure similar to
that of the PCM. Another way to prevent super cooling is to use a “cold finger” which is a
small piece of dry ice (Wettermark et al. 1979). There is also a possibility of using metal
“tinsel” as an initiator.

Figure 2. Super cooling.

Volumetric change of PCM
The volumetric change of PCM during phase transformation may also cause a durability
problem. Either the container material must be flexible or the expansion volume of the PCM
must be included in the container, but the extra volume must not contain oxygen due to the
oxidation problem. Some types of organic PCM have a volume expansion of up to 22 % from
the solid to the liquid phase, which may cause problems and make extra demands on the
container material. Generally, salt hydrates have a small volumetric expansion compared to
organic PCM (Hasnin, 1998).

Corrosion on encapsulation material
Another decomposing process is oxidation of the PCM or corrosion on the container material.
Some paraffin products cause deterioration on plastic containers in the form of cracks or
brittleness of the containers. That may cause leakages from the container. It is also important
that paraffin is stored in an airtight container. Otherwise it will start to oxidise (Carlsson et al.
1978) and most plastic materials are not totally airtight. Both salt and fatty acids may react
with metal containers, especially if they are made of copper or aluminium. The reaction may
appear as pitting corrosion or oxidation over parts of the exposed areas or over the whole
exposed surface. Stainless steel is a better choice for PCM-containers. Even in a short test
period, say two weeks, both corrosion and oxidation on metals may occur. Reaction between
salt hydrates and metals may cause a pH change in the PCM that may be a starting point of
corrosion. That change may lead to reactions between the PCM and the container material in
the form of transformation of the PCM or breaking down of the chemical structure of the
PCM. It can also cause alterations in the thermal properties of the material (Cabeza et al.
2001). Therefore, the PCM should be inert to the material used for encapsulation to prevent
leaking or oxidation products in the container.
**Other criteria**

The economical aspects of the PCM must also be considered like price, service life and disposal costs of the material after use. In order to become common in building applications, it is necessary that the PCM is cheap and available in large quantities. Otherwise the material will just be used for experimental use and in test plants. The phase change of the material has to be reversible only by the temperature swing in the ambient medium, i.e., air or water, and not by adding chemicals or electrical energy to make the process to reversible. In addition, the melting or solidification point of the PCM must be in the supposed in-use temperature. Otherwise, of course the material is useless as a latent-heat storage.

**Design and construction**

*Water calorimeter*

The water-calorimeter equipment is described in paper III. Complementary comments on the calorimeter article will be described below.

Figure 3 shows the complete water calorimeter including regulation equipment. The tempering bath is missing in the picture. The principal sketch in figure 4 shows the including parts and materials and there mutual placing in the water-bath. The cover of the water-bath consists of two layers of polystyrene. One is placed on top of the water-bath and the other one is placed on the water surface to prevent evaporation from the surface.

![Figure 3. Calorimetric equipment including regulation device.](image-url)
Figure 4. Principal layout of a water calorimeter.

Figure 5 shows the water-bath having a PCM sample immersed into the water. The test sample is shown in figure 6 complete with the thermocouple.

Figure 5. Water-calorimeter bath including PCM sample.
Figure 6. Test sample for calorimetric measurement complete with thermocouple.

Figure 7 shows the regulation and log equipment for the water bath. The log unit, the regulation and the switch unit are placed on the top shelf. The regulation equipment for the water circulation is placed on the left side of the computer-screen.

Figure 7. Regulation and log equipment.

Air heat exchanger

The equipment and the experimental set-up of the air heat exchanger unit are not presented in any of the appended articles. During the summer of 2004, a semi-full-scale test plant for an air heat exchanger, including a battery filled with PCM, was tested in real temperature conditions in Gävle, Sweden, see figures 8 and 9. The aim is to determine the effectiveness of the system and verify simulations and calculations for this type of configuration. The air heat exchanger uses cool night air to cool down a battery filled with PCM and used the stored energy to cool down the premises during warm days. The air heat exchanger works independently of the normal ventilation. The prototype of the tested air heat exchanger unit is built from transparent acrylic glass, see figures 10 and 11, to make the unit more visible. The PCM is enclosed in aluminium envelopes, see figure 12. The tested PCM is ClimSel C24 provided by
Climator, Skövde, Sweden. The size of the envelopes was 150 mm × 80 mm × 10 mm with an approximate weight of 130 g each. The PCM envelopes are placed on aluminium shelves, having a size of 480 mm × 480 mm, and stacked in layers, see figure 12. Between the aluminium shelves, there is an air gap, see figure 13. Bottom and top plates consist of one layer of PCM envelopes having a thickness of 10 mm. Shelves in the middle have double layers of PCM envelopes at a total thickness of 20 mm. The total weight of the PCM in the prototype air heat exchanger is 18.5 kg, which corresponds to 2.2 kg/m² floor area.

Figure 8. Principal use of a PCM-based air heat exchanger in a building application.

Figure 9. Principal layout of an air heat exchanger in the experimental room.
Figure 10. Drawing of the PCM air heat exchanger.

Figure 11. Air heat exchanger and ducts in the experimental room.
The duct system is made of ventilation pipes having a diameter of 125 mm combined with two electrically operated dampers, Belimo NM230F, see figure 14. A timer regulates the dampers. A circular ducted fan model CK 125 C is used for external and internal circulation of the air through the air heat exchanger, see figure 14. The fan characteristic and technical data of a CK 125, from Östberg C.A. AB, are showed in figure 15. Technical specifications of the fan are presented in table 1. The airflow in the duct system is calculated from the pressure difference in a calibrated ventilation-tube bend. The pressure difference is measured by an ALNOR micro-manometer 3KDS. During daytime, with internal air circulation in the room, the airflow volume is measured to 225 m$^3$/h or 62.4 l/s. At night with external circulation through the PCM-battery with cool outdoor air, the airflow is measured to 144 m$^3$/h or 40 l/s. The outdoor ventilation grills cause the difference in airflow.
During the summer season 2004, the temperatures and the relative humidity have been recorded for the PCM-battery. The measuring equipment is a Mitec AT40g Universal Recorder, see figure 16, supplemented with Mitec MU-TT106 including a thermocouple type T for measuring the PCM temperature. The temperatures in the PCM-battery are measured
between two PCM-envelopes in the middle shelf, at the leading edge and at the rear edge A MITEC MU-TE100 probe measures the inlet- and outlet-air temperature in the PCM-battery. A MITEC MU-RV103 is used to measure the relative humidity at the inlet before the PCM-battery. In order to determine and examine temperature gradients in the PCM-battery during charge or discharge cycles, the temperatures are measured in two locations. At the leading edge of the PCM-battery and at the rear end of the battery, see figure 17, thermocouples measure the temperature. Temperatures in the in test room, in the reference room and the outdoors temperature are also measured. The relative humidity of the air at the inlet of the PCM-battery is also recorded. In the night case, the relative humidity is the same as the outdoor relative humidity. For the day cases, the humidity is the same as the relative humidity in the room.

Figure 16. Mitec AT40g Universal Recorder.

Figure 17. Picture of the rear end of PCM-battery complete with thermocouples.
Experimental

Water calorimeter

The Thermal Storage Capacity, TSC, is determined by using water-calorimetric equipment and measure the heat supply and the temperature raise in PCM samples. The performance over time is also examined, i.e., if there has been any change in TSC over time when the material has been thermally cycled. Furthermore, the durability of the encapsulating material is also tested. The calorimetric measurement is conducted with constant water temperature in the water-bath and rising temperature in the samples. During the test, the water temperature, the temperature rise in the PCM samples and the energy supply are recorded. By this test setup, the desired heat supply values are measured directly.

The calorimetric tests are conducted in three different temperature ranges. The first is 15 to 45 °C according to the working range of the material as stated by the manufacturer of the PCM. The other two test-temperature ranges are 18–28 °C and 21–27 °C, based on the material and the supposed in-use temperature of the application. The interval 21–27 °C is included to determine the heat capacity in a more narrow temperature interval of the room applications and to encircle the supposed phase-transition temperature of the material.

The experimental set-up of the calorimeter is described in paper III. Complementary comments on the calorimeter article will be given below.

Calibration of the calorimeter was made in order to determine the margin of error and the reliability of the measured results. The first calibration attempts were made by the same test procedure as for the PCM samples. Tempered iron or aluminium alloys were immersed into the calorimeter while the required heat supply for the material was measured. Different masses of metal were tested, from 1.7 kg up to 18.5 kg, in an attempt to get more reliable results. One problem with this setup was to measure the correct temperatures in the whole test sample, i.e., to decide when the temperature in the material was equal to the temperature in the tempering bath and the set temperature of the calorimeter. Another problem was to decide the correct tabulated heat capacity of the materials, particularly of the aluminium alloys. These calibration attempts caused too much spreading in the result to be reliable. Next and the final calibration set-up were made by adding a specific mass of water at the same start temperature that was used for the PCM in the test series. The result of the calibration shows that the measured heat supplied to the PCM is 5% too high compared to tabulated values. The presented results in table 2 are the measured values, i.e., they are not corrected to the margin of error.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tabulated heat capacity [kJ/kg °C]</th>
<th>Measured heat capacity [kJ/kg °C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>0.46–0.54*</td>
<td>0.51</td>
</tr>
<tr>
<td>Aluminium alloy</td>
<td>0.87–0.96*</td>
<td>1.15</td>
</tr>
<tr>
<td>Water</td>
<td>4.18 **</td>
<td>4.40</td>
</tr>
</tbody>
</table>

(* Callister, 2003; **Abel et al. 1997)
Air heat exchanger

A semi-full-scale plant is tested in an experimental room to verify the calculations and simulations of the air heat exchanger paper II. In order to allow comparison of the results from a room with PCM and one without PCM, two similar rooms were built. The test room had the PCM-based air heat exchanger installed under the ceiling and the other one was built as a reference room without PCM. The boundary conditions were the same for both rooms. In the test room, the PCM air heat exchanger was discharged with cool night air from a separate air duct. The air duct was assembled in a loop from outside through the PCM-battery and out again. The cool night air was never mixed with the indoor air while it passed the PCM-battery, and the air heat exchanger worked independently of normal ventilation.

Table fans were placed on the floor to mix the air and maintain uniform temperature in the rooms and prevent temperature tiers in the room. The normal ventilation rate for the rooms is 37 m\(^3\)/h or 0.5 air changes. The inlet for normal ventilation was placed above the windows. Outlet ventilation pipes were placed above the doors in separate ventilation ducts with a fan on the roof. Calibrated ventilation bends on the roof were used to measure the flow rate of the normal ventilation. In figure 18, a drawing of the test room and the reference room is shown. Outside the rooms, the small corridor was used for measurement and regulation equipments. Both rooms were supplied with electrical heaters to simulate heat supply from persons and electrical equipment in the room. The heater was adjusted to 350 W per room, which is equal to 42 W/m\(^2\).

Figure 18. Drawings of the test room and reference room.

The experimental campaign started in April 2004 with a running-in phase to test the timers, heaters and the electrical dampers. In May, tests were started with short temperature cycles. At 1 June, the real campaign started and continued until 1 September, except for a short break in a week in June. During the running-in phase of the equipment, different heat effects and different flow rates of ventilation were tested. Different locations of the measuring probes were also tested. The height of the air gap, between the PCM layers, was also adjusted to
optimise the airflow and minimise the pressure drop. The measuring equipment and the location of the thermocouples was adjusted for optimal use.

The air heat exchanger used the diurnal variation in temperature to charge or discharge the PCM-battery. From 08.00 to 17.00, the fan circulated the indoor air through the PCM-battery. At 17.00, the dampers closed and the outdoor air was circulated through the PCM-battery to cool the PCM. At 08.00, the dampers shifted to internal circulation. During office hour from 08.00 to 17.00, the heaters supplied both rooms to simulate persons and electrical apparatus in an office building. The same timer regulated the dampers and the heaters.

One probe measured the relative humidity of the air that passed the PCM-battery to determine if there was a risk of moisture precipitation on the PCM-envelope surfaces, which may cause corrosion on the aluminium envelopes. According to (Mendoza and Corvo, 2000), there is a significant risk of corrosion on aluminium surfaces caused by distribution of moisture and airborne pollutant agents even if the surface are protected from outdoor exposure, like rain. The corrosion problem is one factor that may affect the durability and the long-time behaviour of the PCM envelopes.

**Results**

*Water calorimeter*

The results from calorimetric measurement are presented in paper III. Complementary facts to these results are presented below. The tested material shows no exact transition temperature. The materials starts to melt at about 22 °C and are totally melted at about 32 °C. During the melting phase, salt crystals are imbedded in liquid solution. According to the temperature curves from the air heat exchanger, the PCM has a transition temperature at about 28,5 °C. Temperatures below 28 °C show no tendency for super cooling but temperatures over 28,5 °C show a super-cooling effect in the material. Figure 19 shows the melting phase of sample 1355 in the temperature range of 15–45 °C. The curve of an ideal PCM should show a horizontal line at the transition temperature. Here, the temperature line shows no exact transition temperature, but there is a melting phase of the material in the temperature range. In figure 20, of sample 1452, the temperature range 18–28 °C are shown and no transition temperature are visible. According to the results from the air heat exchanger, the transition temperature are at about 28 °C and in this test series the stop temperature was set to 28 °C, so the material never reached the transition temperature.
Figure 19. Temperature curves of sample 1355 in the temperature range of 15–45 ºC.

Sample 1355 Nov 2003
15 - 45ºC

Figure 20. Temperature curves of sample 1452 in the temperature range of 18–28 ºC.

Sample 1452 May 2004
18 - 28ºC
### Table 3. Results of the calorimetric tests.

<table>
<thead>
<tr>
<th>Temperature range [ºC]</th>
<th>Average Specific heat [kJ/kgºC]</th>
<th>Max/Min Specific heat [kJ/kgºC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-45</td>
<td>6,5</td>
<td>7,1/6,0</td>
</tr>
<tr>
<td>18-28</td>
<td>9,7</td>
<td>10,7/8,5</td>
</tr>
<tr>
<td>21-27</td>
<td>9,9</td>
<td>12,2/8,7</td>
</tr>
</tbody>
</table>

The difference in heat capacity, presented in table 3 and in paper III, between the samples used in the calorimeter may be explained by the fact that the test samples were from different batches from the manufacturer. In table 4, the results of the calorimetric measurement of the PCM can be compared to other common building materials. The value of the specific heat of the PCM is measured over the temperature interval of 18–28 ºC.

### Table 4. Specific heat of different building materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [kg/m³]</th>
<th>Specific Heat Weight [kJ/kgºC]</th>
<th>Volume [MJ/m³ºC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCM C24 (measured)</td>
<td>1480***</td>
<td>9,9</td>
<td>14,6</td>
</tr>
<tr>
<td>Water (10 ºC)</td>
<td>1000</td>
<td>4,19**</td>
<td>4,19</td>
</tr>
<tr>
<td>Concrete</td>
<td>2300</td>
<td>0,85-1,15*</td>
<td>1,96–2,65</td>
</tr>
<tr>
<td>Aerated concrete</td>
<td>400</td>
<td>1,0**</td>
<td>0,4</td>
</tr>
<tr>
<td>Steel</td>
<td>7800</td>
<td>0,49*</td>
<td>3,82</td>
</tr>
<tr>
<td>Plasterboard (gypsum)</td>
<td>900</td>
<td>1,0*</td>
<td>0,9</td>
</tr>
<tr>
<td>Wood/timber</td>
<td>500</td>
<td>2,9*</td>
<td>1,45</td>
</tr>
</tbody>
</table>

(*Callister, 2003; **Jóhannesson, 1998; ***Climator 2005)

**Air heat exchanger**

The results of the air heat exchanger examination are not presented in any of the appended articles. The results from the measuring campaign in the experimental rooms during summer 2004 show a great variation in temperatures, especially in the test room. At some nights, the temperatures in the test room fell below 15 ºC, and at daytime, the temperature exceeded 35 ºC. The fluctuation in temperature in the test room is too high to be considered as comfortable. Measuring probes for temperature and relative humidity were placed in the test room, in the reference room and on the outside of the facade and at three locations in the PCM-battery. The probes were named and placed as followed:

- In – air temperature at the inlet in front of the PCM-battery
- PCM inlet – temperature in the PCM at the leading edge of the battery
- PCM outlet – temperature in the PCM at the rear edge
- Test room – air temperature in the test room at a height of 1,8 m
- Out – air temperature behind the PCM-battery
- Reference room – air temperature in the reference room at a height of 1,8 m
- Outdoor – outdoor temperature beside the ventilator grill for external air circulation

The curves in the figure 21 show the results of the measured outlet temperature from the air heat exchanger, the test room and the temperature in the reference room, during summer 2004. Temperatures from the reference room and from the test room are presented to compare
the values between the rooms. The rest of the measured values are not presented in the graph due to the indistinct figure. Measured maximum and minimum values from the period are presented in table 5.

![Temperature values of the summer season in Gävle 2004.](image)

**Figure 21.** Temperature values of the summer season in Gävle 2004.

**Table 5.** Measured maximum and minimum temperatures and relative humidity during summer 2004.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>In</th>
<th>PCM inlet</th>
<th>PCM outlet</th>
<th>Test-room</th>
<th>Out</th>
<th>Reference-room</th>
<th>Outdoor</th>
<th>RH [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>8.5</td>
<td>7.1</td>
<td>7.5</td>
<td>13.7</td>
<td>8.3</td>
<td>10.3</td>
<td>6.6</td>
<td>14.5</td>
</tr>
<tr>
<td>Max</td>
<td>37.0</td>
<td>36.7</td>
<td>36.5</td>
<td>35.7</td>
<td>36.7</td>
<td>36.2</td>
<td>34.8</td>
<td>88.5</td>
</tr>
</tbody>
</table>

The curves in figures 22-24 represent temperatures in the PCM-battery during the period 25 June to 1 July 2004. The curves in figure 22 describe the temperature at the leading edge and the rear edge of the PCM-battery. This period is chosen for extra examination due to the measured maximum temperature in the PCM is at about 28 °C. The super-cooling effect is visible if the temperatures exceeds 28.5 °C but not at temperatures below 28 °C. The small temperature differences between the curves indicate a melting front in the PCM-battery during the cooling phase. This effect is caused by the large temperature difference between outdoor air and the PCM-battery. In the heating phase, while the air circulates in the room, the temperature difference is not high enough to create a melting front in the material.
Figure 22. Temperature at the leading edge and the rear edge in the PCM-battery.

Figure 23 describes the measured temperature values of inlet temperature in the air heat exchanger and the temperature in the PCM-battery. Also, the temperature in the test room is showed the graph. The reference room shows higher peak temperatures compared to the test room. The low outdoor temperature causes the low night temperatures in the test room and in the PCM-battery.

Figure 23. Inlet temperature, temperature in PCM-battery and temperature in the test room.
Figure 24 describes the measured temperature in the test room with the PCM-based air-heat exchanger and the reference room without PCM for the period of 25 June to 1 July 2004. The temperature in the reference room increases faster than in the test room, and the temperature peaks are also shorter in the test room as compared to the reference room.

![Figure 24. Temperatures in the test room and reference room.](image)

Also, the durability of the encapsulating material was investigated. Some of the samples that were tested in the water calorimeter were affected by pit-corrosion on the aluminium surface. One sample started to leak PCM and was destroyed by corrosion, see figure 25. For some of the samples, the encapsulating materials were delaminated during the thermal cycling in the water calorimeter. The relative humidity was measured in the PCM-battery to determine if there was a risk for corrosion on the PCM envelopes used in an air heat exchanger. In figure 26, the relative humidity and the outdoor air temperature are presented. The relative humidity was measured at the inlet before the PCM-battery after the dampers. During nighttimes, the relative humidity was the same as the outdoor relative humidity. Measured values from 08.00 to 17.00 represent the relative humidity of circulated indoor air. During the summer 2004, the relative humidity exceeded the critical value of 80 % at several occasions. (Mendoza and Corvo, 2000). When the plant was dismantled, no corrosion was visible on the PCM-envelopes, but the PCM-battery was filled with dust and other particles from the outdoor air.
Discussion

The calorimeter is developed and used to determine material properties of the same size of PCM samples that are supposed to be used in the building applications. The large sample size offers an advantage compared to the common tests made by DSC, Differential Scanning Calorimetry. In DSC, small samples, less than 1 g, are analysed and are used to test, for example, heat-storage capacity. That sample size does not correspond to actual in-use applications. The result from a DSC measurement depends on the test-temperature range, the composition and the structure of the material (He 2004). The accelerated test conducted in the water calorimeter gives quick and easily comparable results between different test series, and the requested heat supply is easy to calculate. The water-calorimetric equipment is cheap to build and consists of readily available components.
The measured maximum temperatures in the test room are a few degrees lower than in the reference room. This indicates that the PCMs have an effect on the indoor temperature, even if the low night temperature also chills the interior of the test room, which may affect the result. The temperature swings more in the test room than in the reference room, which is caused by the low temperatures at nights in the test room. The low night temperatures might cause comfort problems in the mornings in a building application employing this type of thermal storage unit. This type of comfort problems can be avoided by correct dimensioning of the plant. The heat capacity of the material was underestimated, the air heat exchanger became under-sized, the PCM-battery was discharged too fast, and the cooling effect did not last for the whole day. Also the night case showed similar problems. The temperature in the test room became low, almost as low as the outdoor temperature. The durability of the encapsulating material was also examined. The air heat exchanger was dismantled in September 2004 after having been in use during the summer, season from May to the end of August. No visible corrosion attacks were discovered on the aluminium pouches but the exchanger was filled with dust and other airborne particles. This indicates the necessity of ventilation filters for this type of plant, which also cause dimensioning problems with resistance in filters and pressure drops. No moisture was visible on the PCM-envelopes or in the air heat exchanger even if the relative humidity exceeded 80 %. The moisture film could evaporate fast due to the high temperatures and did not cause any corrosion during the short test period.

The use of night-cool to cool down premises during days are widely spread and examined in the world. A lot of different projects and studies have been made and are still in progress that utilises PCM in similar building applications as described in this thesis, for example by (Koschenz and Lehmann 2004). In their article, they describe a PCM-integrated ceiling panel that uses water as a transformation medium instead of air. Also (Yanbing et al. 2003) describe simulations and measured values of a similar application. The principal questions while dimensioning a PCM-based cooling/heating unit are: What is the required heat/cooling demand for the construction? Is it possible to use PCM to meet the needed heating/cooling demand?

Conclusions

The developed water-calorimetric equipment is easy to handle and use. The requested heat capacity of the material is easy to calculate from the measured result. Different temperature ranges can be tested. The conducted accelerated test in the water calorimeter shows no or a small decrease in TSC of the tested PCM. The strain on the encapsulating material does not correspond to the supposed in-use application of the material, but for an application in water, the corrosion and delamination problems must be considered. A drawback of the calorimetric equipment is that the plant is too labour-intensive. Before further use of the equipment, it should be more automatic and be able to be run more continuously. Particularly, the tempering phase and the procedure to reach correct start temperature need to be improved.

Knowledge of material parameters, such as durability, heat capacity and phase-transition temperature, is essential for dimensioning and predicting the service life of PCM-based applications and also for being able to estimate the total cost of the plant. In this case, the thermal properties of the PCM did not correspond to the expectations on the material. The heat capacity was too low and the transition temperature was too high for the cooling purpose. If the material has been used in a heating application of rooms instead, the thermal properties
would be appropriate. The test procedure has focused on the melting phase, i.e., cooling application, and the heat supply and not on the solidification phase. This is one reason why the tested was conducted in the actual temperature range and not the optimal temperatures range of the material, which might be 28 ± 4 °C.

During the dimensioning phase of a PCM-based air heat exchanger, the crucial points are:

- Phase-change temperature of the material
- Heat capacity of the material
- Power of the circulation fan
- Air gap between layers
- Sweep length of PCM layers

The storage capacity, compared to its price must also be considered while dimensioning a plant. The previous points do not regard economical aspects. The phase-transition temperature must be in the working range of the supposed application to be able to utilize the latent heat in the phase change. The required power of the fan is also crucial. The gain of the cooling/heating effect must be higher than the required power of the fan. By a correct dimensioning of the air gap and the length of the PCM-battery, the pressure drop should not be a bottleneck of the needed fan. The pressure drop caused by filters must be considered while dimensioning a PCM-based air heat exchanger.

The conclusion of this test is that accelerated test in water-bath is not a relevant method of estimating the service life or the deterioration environment of the aluminium envelopes used in an air heat exchanger. A better method might be to use moistened air to circulate over the pouches. The corrosion on the pouches was just a side effect that occurred during the calorimetric and chemical-stability tests of the contained PCM. If the corrosion is a severe problem for the air heat exchanger, a possible way to solve the problem might be to use an external electrode, i.e., sacrificial anode (prEN 13509:2002).

**Future work**

Based on the results from the calorimetric measurement and the prototype of the air heat exchanger, a possible future work could be a full-scale test with a PCM-based air heat exchanger installed in a building, like a shopping mall or a classroom, to test the material and the effectiveness under real conditions. The PCM-battery should also be filled with a PCM that corresponds to comfort temperature of the premises, i.e., having an actual transition temperature at 24 °C and not 28 °C. The air heat exchanger should be in-use for more than one season to be able to determine if the TSC changes over time in non-accelerated conditions. If changes occur, would the TSC of the material recover during the non-cycled periods?

An automatization of the calorimetric equipment is a necessary development in a future use of the calorimeter, especially for long time tests. The present design of the equipment requires constant personnel for changing samples and supervision. The water calorimeter can still be used for experimental tests and short test series, but a duplication of the equipment allows simultaneous testing of several samples and in different temperature ranges.

Another follow-up project of the laboratory tests would be a microscopic examination of the used envelopes, to determine possible non-visible corrosion attacks on the aluminium.
surfaces. Also corrosion tests by circulating moistened air, to test the durability of the encapsulating material, will become a future work.

Development of a user-friendly dimensioning tool for calculation and optimization of PCM-based air heat exchangers would be one way to gain a market share for PCM products.

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEN</td>
<td>European Committee for Standardization</td>
</tr>
<tr>
<td>CPD</td>
<td>Construction Product Directive</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EOTA</td>
<td>European Organisation for Technical Approval</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>PCM</td>
<td>Phase-change Material</td>
</tr>
<tr>
<td>SP</td>
<td>Swedish National Testing and Research Institute</td>
</tr>
<tr>
<td>TSC</td>
<td>Thermal Storage Capacity</td>
</tr>
<tr>
<td>i.e.</td>
<td>id est.</td>
</tr>
</tbody>
</table>
References


prEN 13509 final draft.(2002) Cathodic protection measurement techniques. European Standard. prEN13509:2002 E


