Phase Change Materials (PCMs) - Treated Natural Stone for Thermal Energy Storage in Buildings: Influence of PCM Melting Temperature

Romero-Sánchez, M.D.

AIDICO, Technological Institute of Construction, Camí de Castella, 4, 03660 Novelda, Alicante,

Spain

(email: md.romero@aidico.es)

Rodes, J.M.

AIDICO, Technological Institute of Construction, Camí de Castella, 4, 03660 Novelda, Alicante,

Spain

Guillem-López, C.

AIDICO, Technological Institute of Construction, Camí de Castella, 4, 03660 Novelda, Alicante,

Spain

López-Buendía, A.M.

AIDICO, Technological Institute of Construction, Camí de Castella, 4, 03660 Novelda, Alicante,

Spain

Abstract

The treatment of natural stone with Phase Change Materials (PCMs) provides innovative products with thermal energy storage properties. This allows the storage and release of thermal energy during day/night cycles, contributing to reduce energy demands in buildings, and consequently to CO2 emission reduction. Additionally, health and human comfort indoors can be improved by the reduction of temperature fluctuations between day/night. The objective is to increase energy savings potentials and energy storage capacity of natural stone by improving its thermal properties by means of latent heat storage materials (PCMS). Therefore, PCM treated natural stone can be used as construction materials able to store thermal energy having materials with higher thermal inertia. Energy consumption in buildings (cooling/heating systems) is decreased and negative effects and damages for the environment are reduced. The effectiveness of the treatment with PCM as thermal energy storage system for natural stone has been investigated. A PCM with a melting temperature close to that recommended for human comfort has been used for the natural stone treatment. Different experimental techniques have been used for the characterization of the PCM and for the characterization of the PCM-treated natural stone. Results have shown that these new products based on natural stone have ability to store energy. Temperature fluctuations in the place of use are minimized and the temperature peaks maximum-minimum between day-night are reduced. Moreover, because outdoor temperature changes from summer to winter and in order to have thermal energy storage properties for the full year, the treatment of natural stone with PCMs with different melting temperatures has been carried out.

It has also been demonstrated that the introduction of PCMs with different melting temperatures provides materials with energy storage capacity for different climatic conditions (summer or winter times). In this way, by changing the PCM melting temperature, new stone products can be designed for different climate conditions of different regions and for special exposure conditions. The new products are appropriate for indoor or outdoor applications (tiles, plates and slabs used for cladding, roofing, flooring, systems for ceilings, walls and floors) where energy consumption is crucial for the energy performance of buildings.

Keywords: natural stone, phase change material, thermal energy storage, energy efficiency

1. Introduction

The worldwide economical and technological development requires higher energy demands and higher comfort expectations (heating and cooling systems). However, energy sources are limited and related to harmful gases, which are responsible for climate changes, global warming and environmental problems. PCMs are proposed as a solution to reduce energy demands from buildings by the addition of PCMs to construction materials as concrete, gypsum or plasterboard panels [1, 2].

Several chemical compounds have been found to be useful as latent heat storage materials: paraffin wax, fatty acids, hydrated salts, etc.

The use of PCMs as thermal storage systems for buildings has been of interest since first application in the 1940s. PCMs store latent heat as the ambient temperature rises up to the melting point (PCM changes from solid to liquid state). As the temperature cools down, the PCM return to solid phase and the latent heat is released. This absorption and release of heat takes place at a constant temperature, which is ideal to smooth temperature fluctuations.

The thermal energy storage property of PCMs is based on its capability of latent heat storage, because large amounts of energy can be stored in a small volume of PCM. Therefore, the material containing PCMs can absorb and release heat more effectively than conventional building materials [3]. However, for an effective use of the PCMs for an extended period of the year it is important the selection of the melting point.

Some references have been found about the use of PCMs to improve thermal properties of concrete or gypsum. Some authours [4] have studied the thermal performance of PCMs in different types of concrete blocks. Thermal storage in concrete containing PCMs was increased more than 200%.

Salyer et al [5] have developed different methods of PCM incorporation to building blocks: by imbibing the PCM into porous materials, PCM absorption into silica or incorporation of PCMs to polymeric carriers.

Several applications have been found for PCMs as energy storage systems and coming from a variety of sources. PCMs are currently used for co-generation facilities, air conditioning systems, low

temperature solar thermal applications [6], solar collectors, as insulation materials used in clothing, sport clothes [7] or bedding articles [8], cool thermal storage for vegetable cooling [9].

The use of PCMs for the treatment of natural stone in order to improve its thermal properties is due to several reasons:

1) Energy savings in heating/cooling systems; 2) Enhancement of thermal comfort inside the building (reduction of temperature differences between day and night and different rooms inside the building, health and human comfort); 3) Storage of the heat from outdoors; 4) Avoid excessive heat from outdoors.

Directive 2002/91/EC on the energy performance of buildings indicates that the measures to improve the energy savings of buildings should take into account climatic and local conditions as well as indoor climate environment.

Outdoor temperature changes from summer to winter. In this paper, in order to have thermal energy storage properties for the full year, the treatment of natural stone with PCMs with different melting temperatures has been carried out. The influence of the melting temperature of PCMs incorporated to natural stone materials has been analyzed. The choice of the suitable transition temperature for a given application is a fundamental aspect for an optimum effectiveness of the PCMs, as stated by F. Agyenim et al. [10].

It has been demonstrated that the introduction of PCMs with different melting temperatures provides materials with energy storage capacity for different climatic conditions (summer or winter times). In this way, by changing the PCM melting temperature, new stone products can be designed for different climate conditions of different regions and for special exposure conditions.

The new products are appropriate for indoor or outdoor applications (tiles, plates and slabs used for cladding, roofing, flooring, systems for ceilings, walls and floors) where energy consumption is crucial for the energy performance of buildings.

2. Materials and experimental techniques

Bateig azul has been selected as natural stone in order to study the thermal storage properties of natural stone materials after PCM treatment. This material is extracted in Novelda-Alicante-Spain. It is blue and composed of calcite and quartz, with medium porosity size.

Two PCMs have been used for the treatment of Bateig azul with different melting temperature: 1) Micronal DS 5000X (provided by BASF) has been selected as the phase change material. It is a water-based solution with following characteristics: viscosity equal to 30-100 mPa·s, solid content of 43% and meeting temperature ca. 26°C and 2) Rubitherm RT6. Melting temperature = 8°C, heat storage capacity=175 kJ/kg, density liquid at 15°C=0.77 kg/l. For the treatment, Bateig azul has been immersed in these solutions to be impregnated with the PCMs.

Different experimental techniques have been used for the characterization of Bateig azul without and with PCM treatment.

<u>-Scanning Electron Microscopy (SEM)</u>. The presence of PCM in the pores of Bateig azul has been observed, distribution and shape. Hitachi S-3000 N.

<u>-Porosimetry</u>. Porosity of Bateig azul before and after PCM treatment has been evaluated (Hg porosimeter, Micromeritcs Autopore IV).

<u>-Differential Scanning Calorimetry (DSC).</u> Thermal behaviour of PCMs, melting temperature, entalphy, decomposition, etc can be evaluated with DSC (Star^e SW 8.10, Mettler Toledo).

3. Results and discussion

Some papers in literature indicate that PCMs can be effectively used for the thermal energy storage when incorporated to construction materials such as concrete or gypsum in order to reduce energy demands and to increase human comfort indoors. Therefore, melting temperature of the PCMs used is closed to that of human comfort, ca. 25°C.

To demonstrate the effectiveness of PCM incorporated to natural stone, a number of pilot stations made out of concrete and Bateig azul (with and without PCMs) as natural stone for the façade have been built and placed outdoors (Figure 1). Bateig azul has been impregnated with PCM with melting temperature of 26°C.

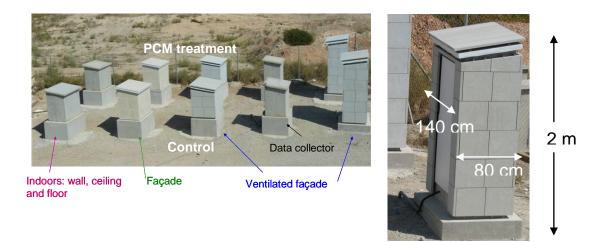


Figure 1. Photographs of pilot stations. Control (without PCMs) and PCM-treated natural stone pilot station.

The objective is to analyze the effect of the PCM-treated natural stones in different parts of the pilot station: south wall, east wall, ceiling, temperature in the air gap, in contact with the concrete or the natural stone, etc. In all cases, sensors have been placed in the control and the "PCM" stations in the

same positions. Variations of temperature in different points of the pilot stations have been monitored every 10 min for several day-night cycles during the summer period in Alicante. Figure 2 shows the monitored temperatures for 1 cycle.

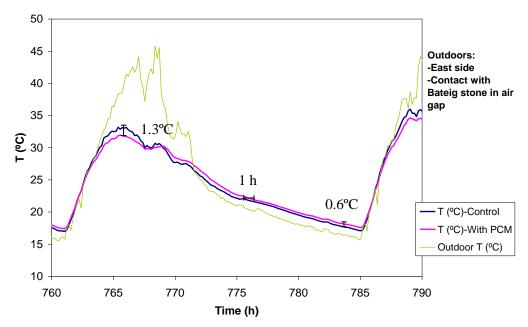


Figure 2. Temperatures in the pilot stations of Bateig azul with and without PCMs as façade materials.

Several differences between the temperatures in the pilot station and the station with PCM-treated Bateig Azul as façade can be observed. The maximum recorded temperature in the PCM treated station – although it occurs at the same time point as in the reference station - it is 1.3°C lower than for the station without PCMs, demonstrating at pilot scale the energy storage potentials of PCMs. The cooling process is smoother for the pilot station with PCMs (the temperatures occurring in the reference station are reached with an hour's delay in the station with the PCM treated stones), indicating that the stored energy is being released. Minimum temperature in the PCM treated station is 0.6°C higher compared to the station without PCMs. These two effects are important because the energy demand due to the heating or cooling systems will be decreased by the reduction of temperature fluctuations between day and night, and also because low or high temperatures are achieved with some time delay (at least one hour in these experimental conditions), and thus the working time of air conditioning systems can be also reduced.

Temperatures have been also registered during winter. For this period, temperature does not rise the melting point of PCM (26°C). Thus, temperatures registered for the control pilot stations are similar to those obtained for the PCM-treated natural stone pilot station. Therefore, PCMs can only be useful for thermal energy storage in a period of the year. To extend the thermal energy storage possibilities of the PCMs to a higher temperature range, natural stone has been treated with PCMs of different melting temperatures: 8°C, 26°C and both 8 and 26°C in the same piece.

PCMs have been characterized by Differential Scanning Calorimetry (DSC) in order to determine the melting temperature and the melting enthalpy (Figure 3 a-c). The information from the provider was confirmed for both PCMs, and melting temperatures of 8 and 26°C were obtained respectively. Natural stone treated with both PCMs shows also the melting processes corresponding to each PCM.

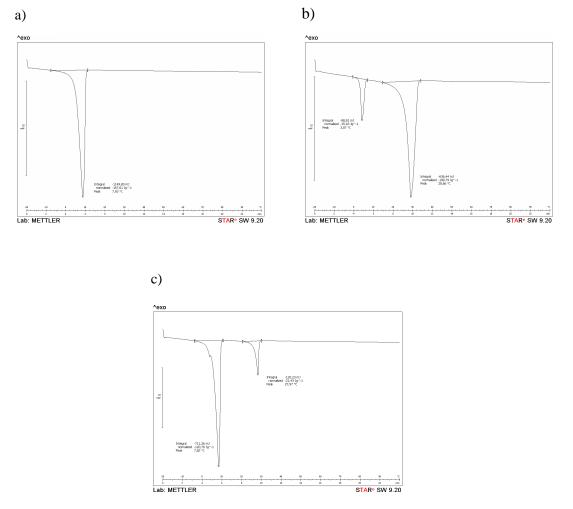


Figure 3. DSC thermographs for a) PCM-8°C, b) PCM-26°C and c) PCM-8+26°C.

The incorporation of both PCMs in the bulk of Bateig azul has been confirmed by mercury porosimetry. Figure 4 shows the pore size distribution for Bateig azul and Bateig azul treated with both PCMs 8 and 26°C. A decrease in the pore size of Bateig azul can be observed when treated with the PCMs, confirming that the natural stone has been impregnated with the PCMs.

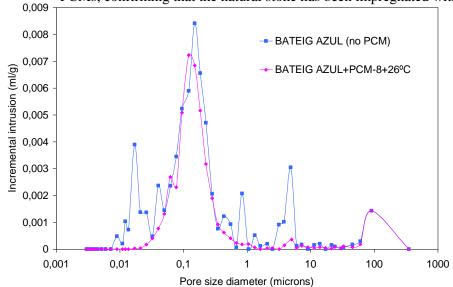
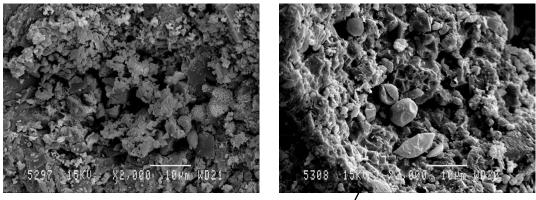


Figure 4. Mercury porosimetry for Bateig azul and Bateig azul treated with PCM-8+26°C.

Figure 5 includes the SEM micrographs of the cross section of Bateig azul and Bateig azul treated with PCM-26°C. The presence of PCMs can be observed in the bulk of Bateig azul.



PCM ⁴

Figure 5. SEM micrographs of Bateig azul and Bateig azul treated with PCM-8+26°C.

An experimental set-up has been designed using natural stone treated with the different PCMs. The experiment consists of adiabatic cubic boxes (30x30x30 cm), made with isolating materials and one side of natural stone. Temperatures inside the boxes have been registered and compared.

Figure 6 shows the temperature inside the control box compared to the PCM-treated box. A day-night cycle has been selected ranging from low temperatures at night to high temperatures during the day, with the objective to analyze the effect of the different PCMs.

During the summer period, when high temperatures are observed, the Bateig azul treated with the PCM with a melting temperature of 26°C is more effective for thermal energy storage compared to Bateig azul with the PCM-8°C, because there is not phase change at this temperature range.

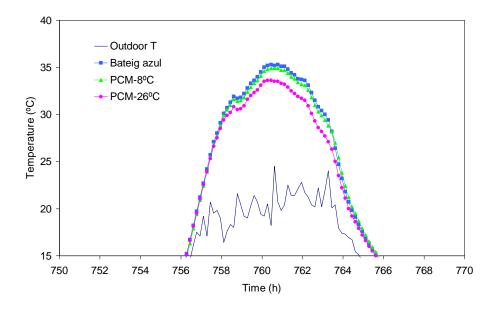


Figure 6. Temperature inside adiabatic boxes with one side of Bateig azul with and without PCMs. Effect of different melting temperature of PCMs during summer.

In order to study the effects of the melting temperature of PCMs in winter, Bateig azul has been treated with both 8 and 26°C PCMs in the same piece. In this period, because the temperature range is 0-25°C, the box with Bateig azul treated with PCM-8+26°C is more effective for thermal energy storage (Figure 7) compared to the PCM-26°C, because at temperatures lower than 26°C there is not phase change and it can not store energy.

When going to low temperatures, the PCM-8°C releases the thermal energy previously stored, and thus not so low temperatures are obtained for the Bateig azul treated with PCM-8°C (Figure 8). On the other hand, and as a consequence of the reduction in the peak temperatures between day and night, the natural stone will be subjected to lower temperature fluctuations. Therefore, it is expected that durability of natural stone treated with PCMs will be increased.

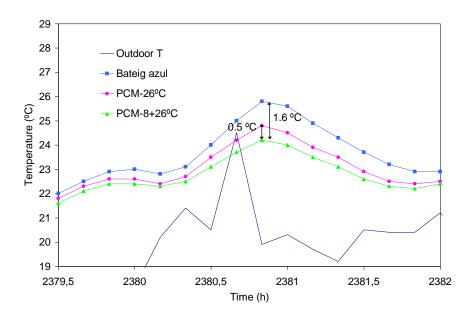


Figure 7. Temperature inside adiabatic boxes with one side of Bateig azul with and without PCMs. Effect of different melting temperature of PCMs during winter.

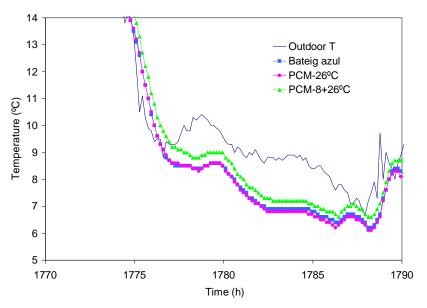


Figure 8. Temperature fluctuations for the box with Bateig azul and Bateig azul treated with PCM-26°C and PCM-8+26°C at low temperatures.

4. Conclusions

As a consequence of the PCM treatment, several effects are observed:

-Reduction on the peak temperatures between day-night.

-Delay in the time to go to minimum or maximum temperatures.

-As a result of the experimental observations, a reduction in energy consumption can be anticipated and an increase in human comfort, due to a reduction of temperature variations during day and night.

However, the effectiveness of PCMs as thermal energy storage systems depends on the selection of the melting temperature of PCM, the place where located (i.e northern or southern climates). Treatment with PCMs with different melting temperatures in the same natural stone piece is recommended in order to cover summer and winter periods.

Together with the reduction in energy consumption, an increased durability of the natural stone pieces is expected as a consequence of the reduction in temperature fluctuations between day and night.

Acknowledgement

Financial support of the E.C., 7th Framework Prog., MESSIB Project, NMP2-LA-2008-211624.

References

Zhang, D., Li Z., Zhou, J., Wu, K., (2004), "Development of thermal energy storage concrete", Cement and Concrete Research, **34**: 927-934.

Khudhair, A.M., Farid, M.M., (2004), "A review on energy conservation in buildings applications with thermal storage by latent heat using phase change materials", Energy Conversion and Management, **45**: 263-275.

Hawes, D.W., Feldman, D., (1993), "Latent heat storage in building materials". Energy and Buildings, 20, 77-86.

Hawes, D.W., Banu, D., Feldman, D., (1990), "Latent heat storage in concrete". Solar Energy Mater, **21**: 61-80.

Salyer, I.O., Sircar, A.K., Kumar, A., (1995), "Advanced phase change materials technology: evaluation in lightweight solite hollow-core building blocks". In: Proceedings of the 30th Intersociety Energy Conversion Engineering Conference, Orlando, FL, USA, pp.217-224.

Sharma, S.D., Kitano, H., Sagara, K., (2004), "Phase Change Materials for low temperature solar thermal applications", Res.Rep.Fac.Eng.Mie Univ, **29**: 31-64.

Moldal, S., (2008), "Phase change materials for smart textiles", Applied Thermal Engineering, 28, 1536-1550.

Salyer, I.O., (1999), "Phase change materials incorporated throughout the structure of polymer fibers, US Patent 5.885.475.

Kowata, H., Sase, S., Ishii, M., Moriyama, H., (2002), "Cold water thermal storage with phase change materials using nocturnal radiative cooling for vegetable cooling", Proceedings of the World Renewable Energy Congress WII, Cologne (Germany).

Agyenim, F., Hewitt, N., Eames, P., Smyth, M., (2009), "A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). Renew Sustain Energy Rev, doi:10.1016/j.rser.2009.10.015.