Lime-Pozzolan Plasters with Enhanced Thermal Capacity

Z. Pavlík, A. Trník, M. Pavlíková, M. Keppert, R. Černý

Abstract—A new type of lightweight plaster with the thermal capacity enhanced by PCM (Phase Change Material) addition is analyzed. The basic physical characteristics, namely the bulk density, matrix density, total open porosity, and pore size distribution are measured at first. For description of mechanical properties, compressive strength measurements are done. The thermal properties are characterized by transient impulse techniques as well as by DSC analysis that enables determination of the specific heat capacity as a function of temperature. The resistivity against the liquid water ingress is described by water absorption coefficient measurement. The experimental results indicate a good capability of the designed plaster to moderate effectively the interior climate of buildings.

Keywords—Lime-pozzolan plaster, PCM addition, enhanced thermal capacity, DSC analysis.

I. INTRODUCTION

HISTORICAL as well as newly developed buildings suffer from surface layers damage that is caused usually by coupled moisture, salt concentration, and temperature changes. The worst durability problems can be observed for pure lime based plasters that were often used for restoration of historical buildings within the last twenty years. Here, in the reconstruction works, such materials are required which are as close as possible to the original materials in their chemical composition and physical properties which determine their technological compatibility with original materials. On that account, there was not able to apply highly durable plasters on cement basis since these materials were not used in the past.

However, the original materials cannot be replaced in an identical way, because nowadays the technology of lime production achieved a very high level so that very pure lime can be produced. In a comparison with lime produced in the past on imperfect devices, without sorting of the raw material and with ash matter presence, the current lime has a different quality and different bonding properties. Current lime creates the solid structure by carbonation and the final product, calcium carbonate, has lower strength than the products of hydraulic or pozzolan hardening. In mortars and renders, this feature is presently eliminated by addition of Portland cement. However, as stated above, this way of modification of mechanical properties of mortars and renders is not preferred by cultural heritage authorities, because cement is not a historic material which could be used in the time of construction of the original building. Therefore, alternatives are to be found in the production of replacement render materials.

Pozzolan admixtures in lime renders can be considered one of reasonable alternatives in this respect. As the chemical analyses of many plasters from historical buildings show, the past centuries external plasters that are preserved until today contain products formed by lime reaction with pozzolanic or hydraulic admixtures. Pozzolanic admixtures appeared to have positive effect on properties of lime binder in the past [1]. According to the composition of the applied pozzolan, compounds similar to Portland cement products were formed. Even compounds of zeolite character were found, such as phillipsite ($3CaO \cdot 3Al_2O_3 \cdot 10SiO_2 \cdot 12H_2O$) and analcime ($Na_2O \cdot Al_2O_3.4SiO_2.2H_2O$), in connection with microcrystalline calcite [2]. These compounds are the cause of the plaster resistance against environmental conditions and in this way of the durability of these plasters.

Present age lays great emphasis on decrease of energy consumption for buildings conditioning, e.g. energy for heating in cold year period and energy for air conditioning in hot year seasons. Environmental protection and achieving sustainable development requires energy efficient solutions and energy conservation in buildings. The high demands on thermal insulation function of buildings led to the construction of passive and low energy buildings that are known to outperform conventional buildings in terms of living conditions and energy efficiency due to their heat recovery, good thermal insulation, and the overall optimization of the house [3].

There are number of technical standards and recommendations on the proper indoor temperature and relative humidity of buildings. According to [3], [4], the internal temperature is the best to be kept between 20-26°C and the indoor relative humidity between 30% and 60%.

In order to meet the above given requirements on low energy consumption for buildings operation and to keep optimal conditions of interior climate, new sophisticated thermal insulation materials and systems are under development and testing that should find application in construction of new building as well as in restoration of older and historical buildings.

Within the optimal design of buildings, the concept of ideal energy conservation building envelope must be accepted [5], [6], which is that if the storage and insulation properties of the building envelope have a suitable role in the delay and decay for outdoor temperature fluctuations, the indoor air temperature can stay in a comfortable range without heating

Z. Pavlík, A. Trník, M. Pavlíková, M. Keppert, and R. Černý are with the Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague, 166 29 Prague, Czech Republic (phone: +420-2-2435-4371, +420-2-2435-5436, +420-2-2435-4688, +420-2-2435-7126, +420-2-2435-5044; fax: +420-2-2435-4446; e-mail: zbysek.pavlik@fsv.cvut.cz, anton.trnik@fsv.cvut.cz, anton.trnik@fsv.cvut.cz, martin.keppert@fsv.cvut.cz, cernyr@fsv.cvut.cz, respectively).

and air conditioning. This kind of building is called passive ideal energy conservation building, and the envelope is called passive ideal energy conservation building envelope. It is evident that the newly designed as well as older buildings must be adopted on ideal energy conservation principles, what will bring the huge energy savings in the near future. The concept of ideal energy conservation buildings is from the inverse way to study how to rely on the building envelope self temperature regulation, fully used natural renewable energy, to meet the requirements of human thermal comfort without or less additional conventional energy.

For the thermal energy storage, the use of phase change PCMs has received a great interest in recent years [7]-[9]. Application of latent heat storage building envelope systems using the PCMs represents an effective way of storing the thermal energy and has the advantages of high energy storage density and the isothermal nature of the storage process [10]. Since the energy storage in the walls, ceilings, floors and other building components may be effectively enhanced and moderated by suitable PCMs [11], [12] it is possible to maintain the internal temperature of buildings closer to the desired comfort temperature for a longer period, without any other additional energy for cooling and heating.

Theoretically, the latent heat storage can be accomplished through the solid-liquid, liquid-gas, solid-gas, and solid-solid phase transition [13]. However, for the practical point of view, taking into account the real conditions of building structures, only the PCMs working on phase change from the solid to liquid or solid to solid phase can be used.

In this work we combined two above given requirements on enhanced durability of plasters due to the pozzolan admixture usage and on enhanced thermal energy storage due to the PCM effect. On this account, new type of more durable lightweight plaster with enhanced thermal capacity is studied in the paper. This material is based on hydrated lime as main binder and its durability is enhanced by pozzolan addition. The paraffinic wax enclosed in polymer microcapsules is added to the dry mixture as PCM.

II. EXPERIMENTAL

In the performed experiments, basic physical, mechanical, hygric, and thermal properties were determined to evaluate the effect of PCM admixture on plaster behavior. All the experiments were realized in the air conditioned laboratory at constant temperature $23°C \pm 1°C$ and relative humidity $30\% \pm 5\%$.

A. Studied Lightweight Plaster with PCM Addition

Lime plaster modified with PCM and pozzolan based on calcined kaolin mixed with milled mudstone was the analyzed material. For the evaluation of PCM contribution to the heat storage capacity of the developed material, the reference plaster without PCM addition was studied as well. The applied pozzolanic material is very fine, having specific surface area $14.56 m^2/g$ and D50 $4.09\mu m$. The used powdered PCM is based on paraffinic wax encapsulated in polymer spherical microcapsules. Lime hydrate was produced by the lime kiln

Čertovyschody, Inc., Czech Republic, whereas the silica sand (fraction 0–4mm) was coming from sand pit Hlavačov, Czech Republic. The water/dry substances (w/d) ratio was slightly modified in order to keep the workability of fresh mixtures on the same level. Composition of the studied plasters is given in Table I. Here, reference plaster without PCM addition is denoted PR, and plaster with PCM addition is denoted PPCM. The samples were cast from the fresh mixture of studied plasters into the moulds having dimensions of 70/70/70mm, 50/50/50mm.

TABLE I
COMPOSITION OF STUDIED PLASTERS MIXTURES

Material	w/d	Lime hydrate (kg)	Pozzolan kg	Sand (kg)	PCM (kg)
PR	0.21	1.5	1.0	7.5	-
PPCM	0.24	1.5	1.0	7.5	0.5

B. Basic Physical Properties

At first, powder density and particle size distribution of PCM were measured. The powder density was measured gravimetrically, weighing the known mass of material in the measuring cylinder. The particle size distribution was measured on laser diffraction principle using the device Analysette 22 Micro Tec plus. The particle size distribution was measured also for the reference dry mixture, as well as for the mixture with PCM addition.

For the researched plasters, measurements of bulk density, matrix density, and total open porosity were performed. The experiments were done on 5 cubic samples of side 50mm. The relative expanded uncertainty of applied testing method was 5% and was mainly due to material nonhomogeneity. Bulk density was determined from the measurement of sample sizes (using digital length meter) and its dry mass. The matrix density was accessed by helium pycnometry using apparatus Pycnomatic ATC (Thermo Scientific). The accuracy of the gas volume measurement using this device is $\pm 0.01\%$ from the measured value, whereas the accuracy of used analytical balances is $\pm 0.0001g$. On the basis of bulk density and matrix density measurements, the total open porosity was calculated.

C. Pore Size Distribution

For measurement of pore size distribution, mercury porosimeters Pascal 140 and Pascal 440 (Thermo Scientific) were used. Within the evaluation of the measured data, the circular cross section of capillaries was assumed, whereas mercury contact angle was assumed to be 130°.

D. Mechanical Properties

The effect of PCM admixture on mechanical properties of the plaster was investigated by compressive strength measurement. The compressive strength was measured according to the standard ČSN EN 12390-3 [14] on the cubic samples. The loading area was 70 x 70mm.

E. Liquid Water Transport Parameters

For the characterization of liquid water transport in the tested materials, sorptivity concept was used. On this account, a free water intake experiment [15] that represents the simplest

technique for the characterization of the ability of porous materials to absorb water and transport it by capillary forces was performed. Using this experiment, the water transport in the studied materials was characterized by water absorption coefficient A (kg/m^{2}s$^{1/2}$) and sorptivity S (m/s$^{1/2}$).

Experimental arrangement of the sorptivity test consisted of tank filled with water and the material sample, water and vapor-proof insulated on four lateral sides, hung on automatic balance and immersed 1-2 mm in the water. The automatic balance allowed continuous recording of increase of mass of the sample. On the basis of measured results, the water absorption coefficient and water sorptivity were calculated according to the procedure described in [15]. In the measurements, 5 samples of each tested material were tested, having the size of 50x50x50mm. The samples were insulated on all lateral sides by epoxy resin in order to ensure 1-D water transport and dried in vacuum drier.

F. Heat Transport Parameters

Among the heat transport properties, measurement of thermal conductivity and thermal diffusivity were done. For that purpose, device ISOMET 2104 [16], [17] working on the dynamic measurement principle was used. The measurement is based on the analysis of the temperature response of the analyzed material to heat flow impulses. The measurements were performed in laboratory conditions at constant temperature 23˚C ± 1˚C and relative humidity 30% ± 5%. The samples had cubic shape of dimensions 70/70/70mm, whereas 5 samples of each material were tested.

G. DSC Analysis

Differential scanning calorimetry (DSC) analysis was performed using apparatus DSC 822e (Mettler Toledo) with the cooling device Julabo FT 900. The measurements were performed for the PCM, the reference plaster and plaster modified by PCM addition. For the measurement, the particular samples were first crushed in laboratory mill. The following temperature regime was applied: 5 minutes of the isothermal regime; 5 minutes of the isothermal regime; heating of 10°C (283.15K)/min from the temperature -10°C (263.15K) to the temperature 40°C (313.15K); 5 minutes of isothermal regime. On the basis of DSC analysis, the temperature dependent specific heat capacity was accessed.

III. RESULTS AND DISCUSSION

Figs. 1–3 show the cumulative curves of particle size distribution of the researched materials measured by laser diffraction. Here, the very fine and uniform particle size distribution of PCM was observed. One can see the particle size distribution of PPCM was only slightly affected by the PCM addition.
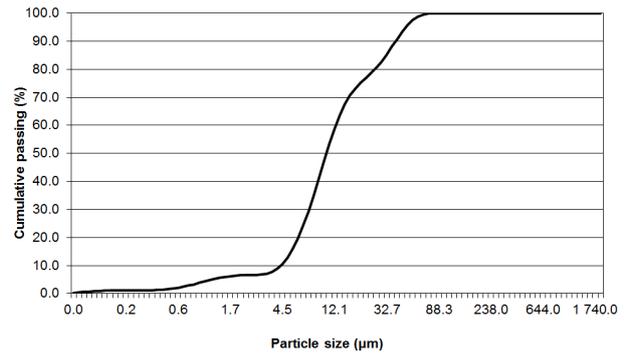

Fig. 1 Particle size distribution of PCM – cumulative curve
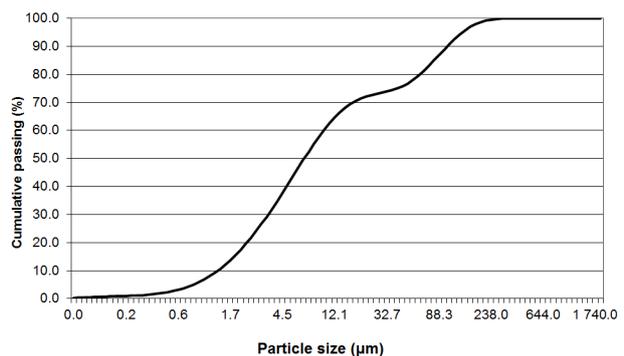

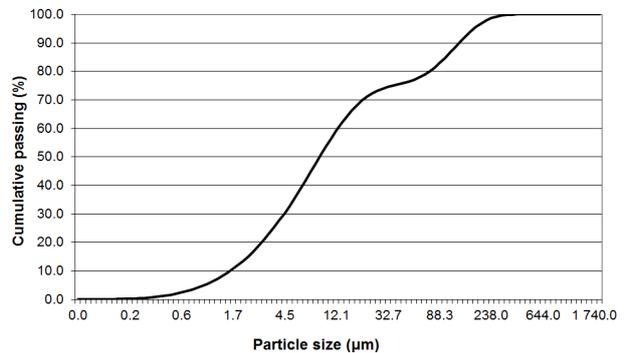
Fig. 2 Particle size distribution of PR dry mixture

Fig. 3 Particle size distribution of PPCM dry mixture

Basic material properties of investigated materials are summarized in Table II. We can see very low powder density of PCM that affected the matrix density and bulk density of the plaster modified by PCM addition. The total open porosity of the modified plaster was in comparison with the reference plaster about 20% higher, which was in accordance with its higher w/d ratio. Here, also the workability of the fresh mixture with PCM addition played an important role in formation of final solid structure. The higher porosity can be explained also by the transition zone formation between PCM and lime-pozzolan plaster hydration products.

The pore size distribution is graphed in Fig. 4. These data clearly support the results of total open porosity measurement.
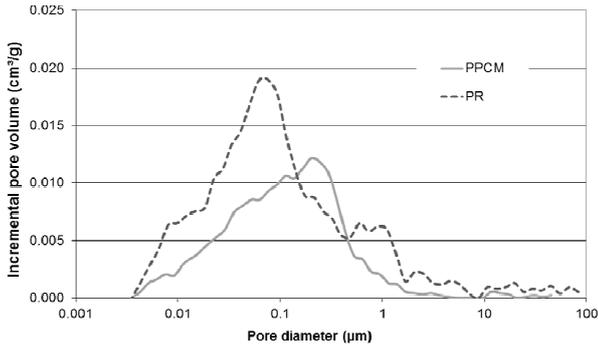
Fig. 4 Pore size distribution

Compressive strength of investigated plasters is given in Table II. Here, the application of PCM into the composition of lime-pozzolana plaster led to the slight decrease of mechanical resistivity. However, from the quantitative point of view, the decrease of compressive strength of PPCM compared to the reference material was < 8%, what is not significant decline.

TABLE II
COMPRESSIVE STRENGTH OF RESEARCHED PLASTERS

Material	Compressive strength (MPa)
PR	3.9
PPCM	3.6

Results of free water intake experiment are given in Table III. We can see significant effect of PCM application on high increase of resistivity against liquid moisture transport. This feature can be attributed to the not wetted surface of polymer encapsulated paraffinic wax used as PCM admixture and to the higher volume of smaller pores compared to the reference plaster. One can observe sharp peak on pore size distribution curve of PPCM at pore diameter of 0.08μm that can be explained by filling the smaller air voids formed within hydration process by fine particles of PCM. On the other hand, for bigger pores, is this effect only secondary.

TABLE III
WATER TRANSPORT PARAMETERS OF RESEARCH PLASTERS

Material	Water absorption coefficient $(kg/m^2s^{1/2})$	Sorptivity $(m/s^{1/2})$
PR	0.086	$8.6 \cdot 10^{-5}$
PPCM	0.057	$5.7 \cdot 10^{-5}$

Results of impulse method measurements are presented in Table IV. We can see much lower thermal conductivity of the PCM modified plaster in comparison with the reference one. This finding corresponds with the results of total open porosity measurement and may be attributed on one hand to the higher amount of batch water in composition of the developed plaster and on the other to the low thermal conductivity of PCM capsules.

TABLE IV
HEAT TRANSPORT PARAMETERS OF RESEARCHED PLASTERS

Material	Thermal conductivity (W/mK)	Thermal diffusivity (m^2/s)
PR	0.86	$0.54 \cdot 10^{-6}$
PPCM	0.55	$5.34 \cdot 10^{-6}$

In Figs. 5–7, there are given results of DSC analysis measured during the heating of the studied materials.
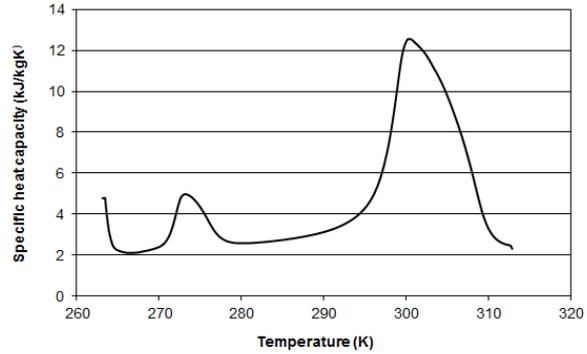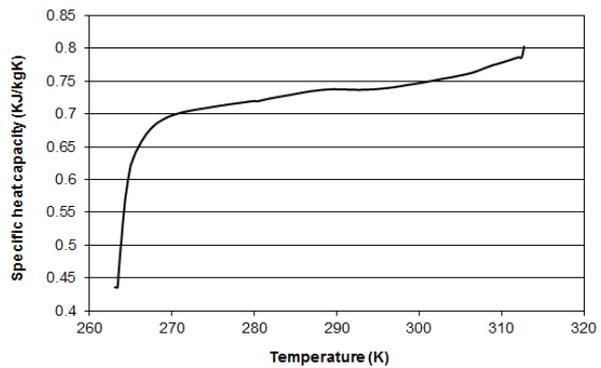

Fig. 5 Specific heat capacity of PCM

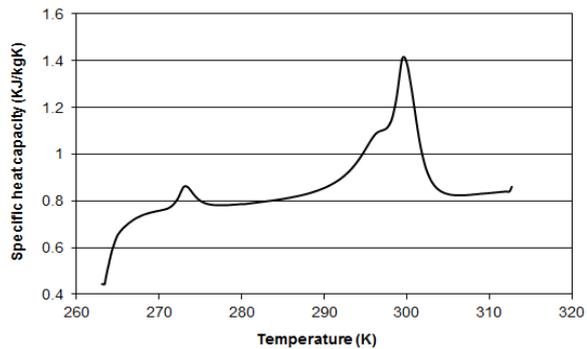Fig. 6 Specific heat capacity of reference plaster

Fig. 7 Specific heat capacity of PCM modified plaster

The measured specific heat capacities of researched materials give clear evidence of high thermal storage of used PCM at the temperature of phase change and of contribution of PCM admixture to the enhanced heat capacity of modified lime-pozzolana plaster. The temperature of the phase change

of the PCM during the heating process was 26.97°C(300.12 K). The solid-liquid transition of the modified plaster was detected at 26.31°C (299.46), whereas the both measured temperatures of phase change are beneficial for the latent heat storage in building structures.

IV. Conclusions

The experimental investigation of material parameters of the designed lime-pozzolan plaster containing incorporated polymeric microcapsules with paraffinic wax revealed the positive effect of PCM admixture on the thermal capacity of the plaster which should find application in thermal insulation of building envelopes.

However, not only thermophysical parameters were subject of the investigations. Also the basic physical, mechanical, and hygric properties were tested, in order to access the applicability of the tested plaster in building practice. Summarizing the obtained results, the application of PCM admixture led to: higher porosity, slightly lower mechanical resistivity, lower thermal conductivity, higher resistivity to moisture ingress, and higher thermal capacity, compared to the reference material.

Since the applied pozzolan admixture based on calcined kaolin mixed with milled mudstone proved its applicability in energy storage plasters with limited moisture ingress, also other types of pozzolan admixtures should be tested in order to evaluate their possible usage in such types of building materials. Here, especially the industrial by products as ceramic powder coming from bricks manufacturing could find utilization. On this account, the waste ceramic powder will be studied in future work as possible pozzolanic admixture in energy storage plasters.

References

[1] M. F. Rojas, J. Cabrera, "The effect of temperature on the hydration rate and stability of the hydration phases of metakaolin-lime-water systems", *Cem. Concr. Res.*, vol. 32, pp. 133-138, 2002.
[2] J. Cabrera, M. F. Rojas, "'Mechanism of hydration of the metakalolin-lime water system", *Cem. Concr. Res.*, vol. 31, pp. 177-182, 2001.
[3] J. Mlakar, J. Štrancar, "Temperature and humidity profiles in passive-house building blocks", *Build. Environ.*, vol. 60, pp. 185-193, 2013.
[4] P. Wolkoff, S.K. Kjaergaard, "The dichotomy of relative humidity on indoor air quality", *Environ. Int.*, vol. 33, pp. 850-857, 2007.
[5] X. Wang, Y. P. Zhang, R. L. Zeng, Q. L. Zhang, H. F. Di, "Review on thermal performance of phase change energy storage building envelope", *Chinese Sci. Bulletin*, vol. 54, pp. 920-928, 2009.
[6] Y. P. Zhang, K. P. Lin, Q .L. Zhang, "Ideal thermal physical properties for free-cooling (or heating) buildings with constant thermal physical property material", Energy Build., vol. 38, pp. 1164-1170, 2006.
[7] Y. Zhong, Q. Guo, S. Li, J. Shi, L. Liu, "Heat transfer enhancement of paraffin wax using graphite foam for thermal energy storage", *Solar Energy Mat. Solar Cells*, vol. 94, pp. 1011-1014, 2010.
[8] A. M. Kudhair, M. M. Farid, "A review on energy conservation in building applications with thermal storage by latent heat using phase change materials", *Energy Conserv. Manag.*, vol. 45, pp. 263-275, 2004.
[9] A. Sharma, V. V. Tyagi, C. R. Chen, D. Buddhi, Review on thermal energy storage with phase change materials and applications", *Renew. Sustain. Energy Rev.*, vol. 13, pp. 318-345, 2009.
[10] M. Koschenz, B. Lehmann, "Development of thermally activated ceiling panel with pcm for application in lightweight and retrofitted buildings. *Energy Build.*, vol. 36, pp. 567-578, 2004.
[11] T. Lee, D. W. Hawes, D. Banu, D. Feldman, "Control aspects of latent heat storage and recovery in concrete", *Solar Energy Mat. Solar Cells*, vol. 62, pp. 217-237, 2000.
[12] M. Hadjieva, R. Stoykov, T. Filipova, "Composite salt-hydrate concrete system for building energy storage", *Renew. Energy*, vol. 19, pp. 111-115, 2000.
[13] A. Pasupathy, R. Velraj, R.V. Seeniraj, "Phase change material-based building architecture for thermal management in residential and commercial establishments", *Renew. Sustain. Energy Rev.*, vol. 12, pp. 39–64, 2008.
[14] ČSN EN 12390-3, Testing of hardened concrete - Part 3: Compressive strength (Prague: Czech Standardization Institute 2007)
[15] E. Vejmelková, M. Pavlíková, M. Jerman, R. Černý, "Free Water Intake as Means of Material Characterization", *J. Build. Phys, vol.* 33,pp. 29-44, 2009.
[16] M. Jiřičková, Z. Pavlík, L. Fiala, and R. Černý,, "Thermal Properties of Mineral Wool Materials Partially Saturated by Water", *Int. J. Thermophys.*, vol. 27, pp. 1214-1227, 2006.
[17] Z. Pavlík, E. Vejmelková, L. Fiala, and R. Černý, "Effect of Moisture on Thermal Conductivity of Lime-Based Composites", *Int. J. Thermophys.*, vol. 30, pp. 1999-2014, 2009.