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Granulation of porous materials with phase change material (PCM)

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Abstract: The paper describes the research on the method of production of granulated phase-change materials (PCM) used in construction industry for the accumulation of thermal energy. As mineral materials for the granules preparation zeolite from fly ash Na-P1 and natural diatomite dust were used which were impregnated with paraffinic filtration waste and granulated using a combined granulation method. Obtained granules were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption/desorption isotherm, and differential scanning calorimetry (DSC). Mechanical strength of the materials was determined in a "drop strength" test. Performed analyses revealed that mineral composition and micromorphology of the diatomite and zeolite granules were varied, with zeolite granules having higher mechanical strength.

Keywords: PCM, granulation, zeolite, heat capacity

1. Introduction

Phase Change Materials (PCM) are an element of intelligent building materials, textiles and energy accumulators that absorb or release lateral heat depending on changing environmental conditions. This feature results from the absorption or emission of heat during the transformation from solid to liquid phase and vice versa, hence the heat capacity and phase change hysteresis are extremely important parameters of these materials [1]–[3].

The main function of PCM in construction industry is to minimize the heat flux between the inside of buildings and the outside environment, thus reducing the energy consumption needed to maintain a constant temperature, which significantly increases the interest in materials containing PCM. The reduction of energy consumption in the operation of buildings is one of the most important challenges of the building materials industry, also related to the requirement to reduce emission of CO_2 [4], [5].

The most commonly used in construction industry PCM substances are saturated hydrocarbons of various chain lengths (so-called paraffin waxes), including:

- lanolin (CAS 8006-54-0), with solidification temperature 38 °C and melting temperature 42 °C,
- eikosan (CAS 112-95-8), with solidification temperature 30.6 °C and melting temperature 36.1 °C,
- octadecane (CAS 112-95-5), with solidification temperature 25.4 °C and melting temperature 28.2 °C,
- heptadecane (CAS 629-78-7), with solidification temperature 21,5 °C and melting temperature 22.5 °C,
- hectadecane (CAS 544-76-3), with solidification temperature 16.2 °C and melting temperature 18.5 °C.

Mixtures of these hydrocarbons are also used to extend the temperature range of the phase transition. Due to the low melting points of the mentioned substances, they are closed in microcapsules or granules before introducing them to the target structure [6], [7].

In the granulation process, the comminuted material particles change their size to form groups called granules. The size of the granulated particles is usually in the range from 1 to 10 mm, depending on the production methods, additives used and, above all, their subsequent use. One of the granulation methods is agglomeration. The condition for the formation of a durable agglomerate is the occurrence of sufficiently large forces connecting the grains. Rumpf divided the bonding mechanisms between grains into 5 categories [8]:

1. Permanent bridges, formed at elevated temperatures at the grain junction, as a result of the diffusion of molecules from one grain to another.
2. The forces of adhesion and cohesion occurring in binding substances, which do not allow the free movement of the grains. The highly viscous substances thus form bonds similar to those appearing in solid bridges.
3. Forms of closed mechanical bonds occurring in materials with a fibrous or lamellar structure, as well as in the case of grains, which, undergoing deformation, cause mutual blocking.
4. Capillary pressure forces in loosely arranged grains. These forces in the capillary spaces can form strong bonds, which, however, disappear when the liquid evaporates and there are no other bonding mechanisms.
5. Attractive forces acting between the grains, such as Van der Waals forces, electrostatic or magnetic, which cause the grains to fuse together when they come close enough. These forces clearly increase when the grain size is reduced.

In practice, these categories are combined in the agglomeration process. Bonding of mineral matrix particles with fillers uses the mechanisms described in point 1–3.

So far, a number of attempts have been made to enclose PCM materials in mineral matrix. Sterczyńska et al. [9] used octamethylcyclotetrasiloxane (OMCTS) in the mesoporous Al-SBA-15 structures. Ramakrishnan et al. [10] used commercial PCM paraffin blends in the intramolecular spaces of expanded perlite, using vacuum during saturation. In turn, Sololciak et al. [11] used commercial paraffins RT42 encapsulated in expanded graphite.

On the other hand, there are commercial PCM microgranules encased in polymeric shells (eg Micronal from BASF), which however exhibit a volume change during the phase

change and hence their use in building materials such as flooring, mortar and plaster is limited. A more advantageous solution is to use granules made of mineral matrices soaked in PCM, in which the phase change material remains in a liquid state. Apart from expanded perlite, such structures are characteristic, for example, for diatomite and zeolites.

The basic limitation of PCM application in construction is their liquid form, which forces the use of polymer microcapsules or granules. Due to a thin polymer coating around phase-change substances, PCM microcapsules expand in temperature, which affects the risk of cracking in building materials that use them [12]. Granules using three-dimensional mineral matrix are a much more advantageous alternative because the compensation takes place inside the pores. So far, however, there is little experience in developing a technology enabling the industrial production of PCM granules based on mineral matrix, especially those using waste substrates [9], [13]. This work covers research on the granulation technology of two types of matrices soaked in PCM and a comparison of their properties – natural diatomite and synthetic zeolite made from waste coal fly ash.

2. Materials and methods

2.1. Materials

Two matrix mineral bases were used for granulated PCM preparation: natural diatomite dust (GD) and synthetic Na-P1 zeolite (GZ), obtained as a result of the hydrothermal reaction of fly ash. Fly ash from coal combustion, characterized by the appropriate ratio of SiO_2 to Al_2O_3, was subjected to a NaOH solution at elevated temperature according to the procedure described by Kunecki et al [14]. The post-reaction product was then washed and filtered. The Na-P1 zeolite dust prepared in this way was one of the bases for impregnation with the phase change material. The second base was a natural milled diatomite with a fraction of 0-200 μm.

After initial technological trials, the paraffinic filtration waste (CAS 64742-67-2) was qualified as PCM used for tests. This filtrate was selected due to the melting point, oscillating around 30 °C, and the low cost of obtaining it, which is of key importance for the future possible implementation of the PCM granulate production technology. The filtrate is currently used industrially for the production of paraffin emulsions, anti-caking agents for fertilizers and for impregnation of chipboards in the furniture industry.

2.2. Granulation procedure

The technological tests included granulation of bulk materials (matrices) in a wax with a temperature of 70-80 °C, sprayed together with cooling water. In order to obtain the appropriate mechanical strength, a small amount of cement was used in the final stage of pelleting. Then, the granules were dried in a low temperature microwave oven and aged for 2-3 days.

The samples were prepared with following equipment in R&D test center of Biko-Serwis, Polish producer of granulation equipment:

– fluid bed vibration granulator,
– disc granulator,
– pin granulator,
– high shear granulator.

Despite the pre-selected vibro-fluid technology, other methods resulted in better results in during the tests, due to the expected particle size. The vibro-fluid method allowed for the obtained particles of 1-2 mm in size, which did not allow to enclose a sufficient amount of paraffins inside the granule structure and to cover it with a layer of strengthening cement crust. It was desired to obtain 6-8 mm granules, which were produced using the other tested methods. The best results were achieved by combining two technologies:

– pelleting with the pin granulator, where hot paraffin was added to the base material with cooling water,
– thin cement coating with disc granulator.

Such selection of methods resulted in the shortest sample preparation time, amounting to 3-5 minutes, and the highest proportion of the desired fraction, which was over 80%.

2.3. Characterization methods

In order to fully characterize PCM granules, a number of phase, chemical and textural research methods were used.

X-ray phase analysis (XRD) was performed with the powder method using a Panalytical X'pertPRO MPD X-ray diffractometer with a PW 3020 goniometer. A Cu copper lamp (Cu_{Ka} = 1.54178 Å) was used as the source of the X-ray emission. X'Pert Highscore software was used to process the diffraction data. The identification of the mineral phases was based on the PDF-2 release 2010 database formalized by JCPDS-ICDD.

The morphology and chemical composition in the grain micro-area of the main mineral components of the studied materials was determined using the Quanta 250 FEG Scanning Electron Microscope by FEI.

The textural research included the determination of the most important surface and volume parameters. The texture study was performed on the ASAP 2020 specific surface analyzer from Micromeritics Instrument Corporation on the basis of nitrogen vapor adsorption and desorption isotherms at liquid nitrogen temperature (-194.85 °C). The measurement was carried out in the range of relative pressures p / p_0 ranging from $1.5 \cdot 10^{-7}$ to 0.99.

Differential Scanning Calorimetry was performed using Perkin-Elmer DSC 7 apparatus. By recording the rate of change (0.1-200) °/min in steps of 0.1 °/min.

The mechanical strength of the obtained granules was determined in a test called "drop strength". It best simulates the conditions related to handling and transport that the tested granules may be subjected to. A triple drop of 20 randomly selected granules from each sample was made from a height of 2 m onto a steel plate. Then the broken and crushed mass was screened through a sieve. The size of the screen was chosen such that the mesh size was about 2/3 of the average calculated from the two maximum granule dimensions measured in mutually perpendicular directions. The drop resistance of the granules was determined on the basis of the formula:

$$K = \frac{m_z}{m} \cdot 100\% \tag{1}$$

where: K – the drop resistance of granules, m_z – average weight of pellets after drop, m – average weight of pellets before drop.

3. Results and discussion

The phase analysis showed that the dominant crystalline phase in the zeolite granulate (GZ) is the zeolite with the structure type NaP1 (Fig. 1). It was recognized by characteristic interplanar distances d_{hkl} = 7.10; 5.01; 4.10; 3.18 Å. The second important component is mullite recognized at d_{hkl} = 5.38; 42; 3.39; 2.21 Å. An important sub-component is also calcite recognized by characteristic interplanar distances d_{hkl} = 3.86; 3.04; 2.49; 2.28 Å. The mineral composition is completed by quartz recognized at d_{hkl} = 4.25; 3.34; 2.46; 2.28 Å.

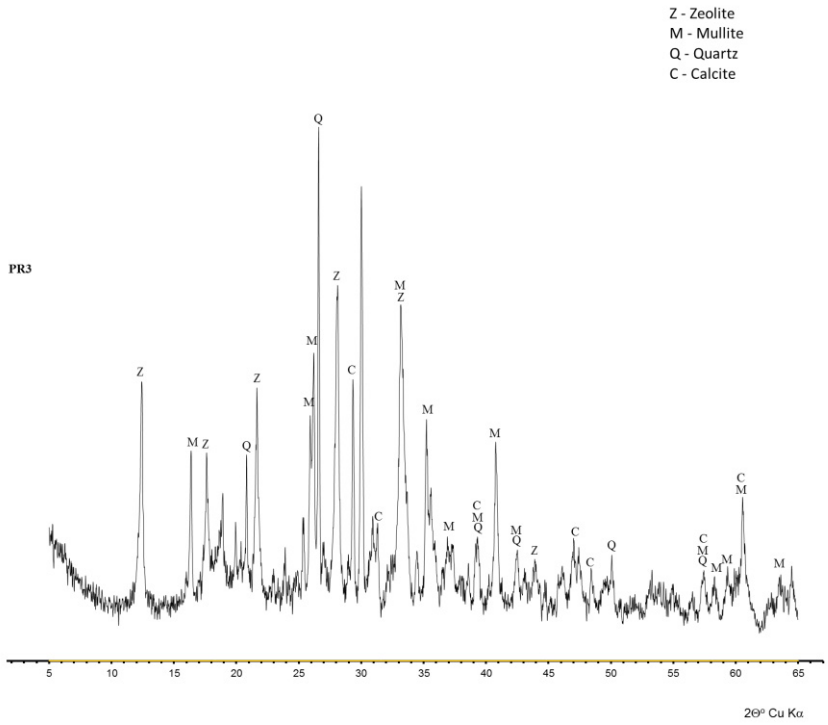

Fig. 1. Phase composition of the GZ sample

Figure 2 shows the XRD patterns of diatomite granulate (GD). In the sample, the dominant crystal phases are Ca_2Al [(Si, Al) $_2O_7$] and cristobalite. The presence of gehlenite is confirmed by the strongest reflections with interplanar distances d_{hkl} = 5.46; 5.08; 2.85 Å. Crystobalite was recognized by d_{hkl} = 4.05; 3.13; 2.48 Å. The sample also shows a clear elevation of the background in the angular range of 15-25 2theta, which proves the presence of amorphous silica. The mineral composition is complemented by quartz recognized by the characteristic interplanar distances d_{hkl} = 4.25; 3.34; 2.46; 2.28 Å.

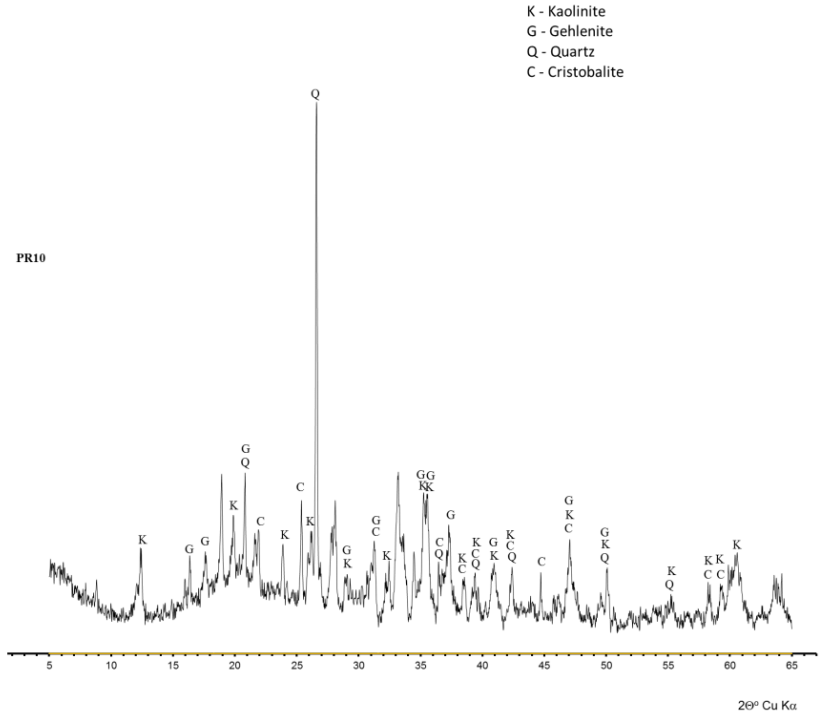

Fig. 2. Phase composition of the GD sample

The presence of zeolite as the main mineral component confirms the presence in microscopic images of spherical plate aggregates with a size of up to 10 μm (Fig. 3). The microscopic observations clearly show the presence of unreacted fragments of fly ash in the form of spheres with smooth surfaces, made of mullite and aluminosilicate glaze, which is confirmed by XRD tests. The zeolite-based granulate sample also shows a significant pore content in its internal structure.

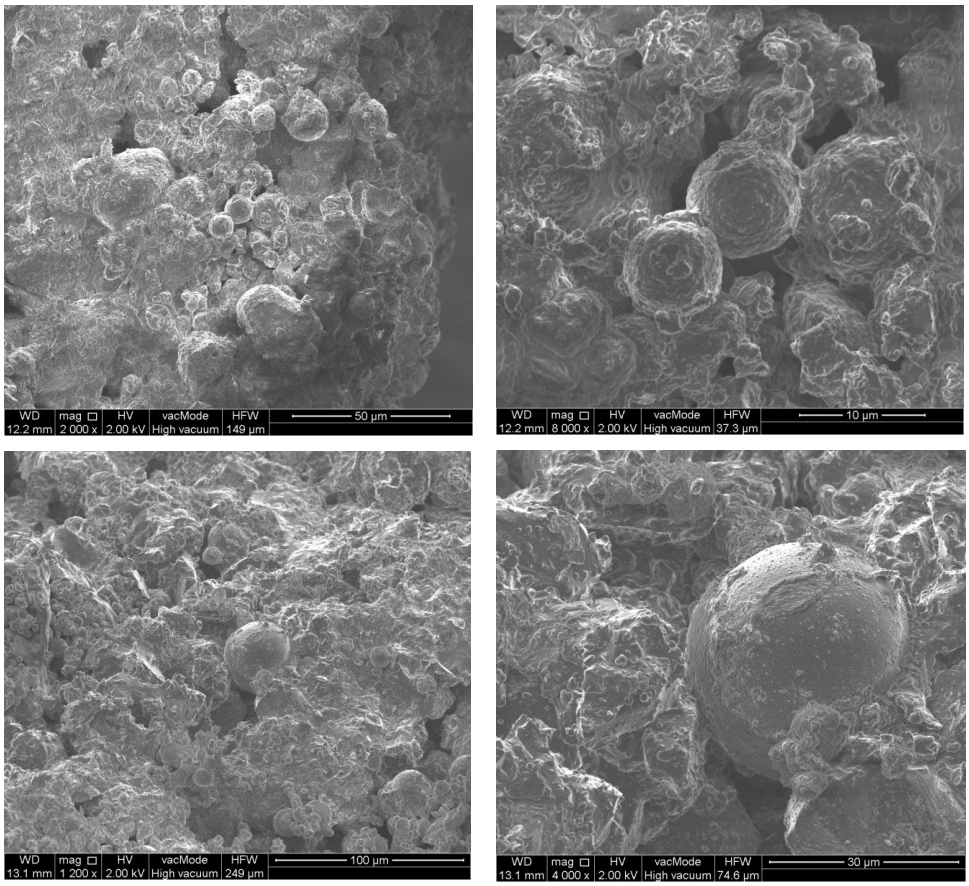

Fig. 3. SEM images of the GZ sample

In the images made with electron microscopy (Fig. 4), the fractures of the diatomite granulate sample showed almost no pores. The microscopic observations clearly show that the main minerals present in this granulate are embedded with an amorphous substance (wax), which masks their morphology and prevents phase recognition using the SEM technique.

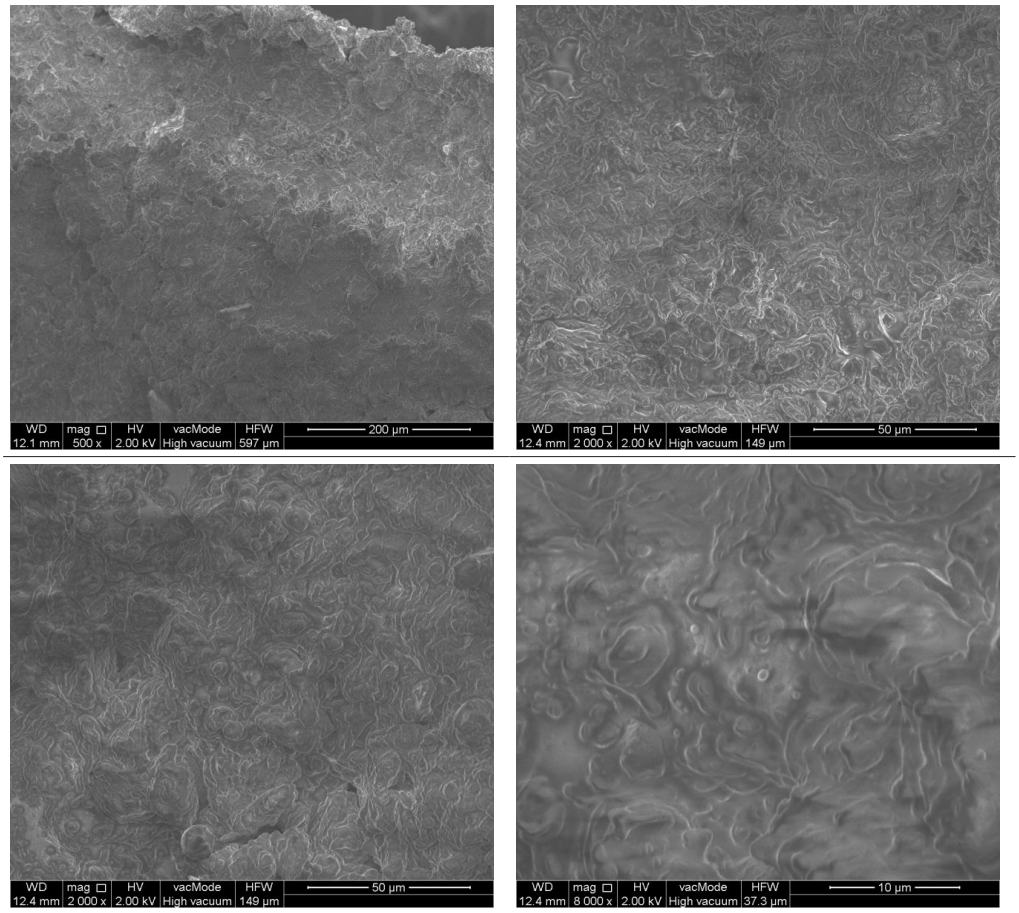

Fig. 4. SEM images of the GD sample

The nitrogen adsorption/desorption analyses performed allowed for the calculation of the specific surface area of the granules tested. The results of these determinations using BET and Langmuir theories are presented in Table 1.

Table 1. Scpecific surface area of PCM granules

Sample	BET Surface Area [m²/g]	Langmuir Surface Area [m²/g]
GZ	0.7581	1.3346
GD	0.3878	0.7484

The studied granules represent materials with low specific surface area. Slightly higher specific surface area parameters were obtained using the Langmuir equation to determine this parameter. The GZ granules obtained from Na-P1 zeolite had the highest surface area.

Table 2 shows the results of the research on the heat capacity of PCM granules obtained from DSC analysis.

In the course of the research, it was found that increasing the working temperature for the samples causes an increase in the energy output, which is directly related to the materials used for their production.

Table 2. The heat capacity of PCM granules

Sample	cp /0°C [J/(g*K)]	cp /30°C [J/(g*K)]
GZ	30.59	-31.83
GD	28.91	-27.23

According to the data presented in the test report, granules with zeolite and diatomite are characterized by a greater difference in the value of specific heat in the temperature range of 0-30 °C. This may indicate their greater energy storage potential. For the sample based on the zeolite matrix, the heat capacity was 62.42 kJ/kg, for the diatomite matrix it was 56.14 kJ/kg. Obtained heat capacities are higher than those for the commercially available Rubitherm GR granules, which have a heat capacity of 55-57 kJ/kg. Table 3 shows the results of the mechanical strength tests for PCM granules.

Table 3. Mechanical strength of PCM granules

PCM granules	Average diameter of granules [mm]	Diameter of screen [mm]	m [g]	m_z [g]	K [%]
GZ	6	4	1.65	0.635	38.48
GD	18	12	65.41	20.58	31.46

Based of the drop resistance of the granules K values it can be stated that zeolite granules exhibit higher mechanical strength that diatomite granules and can be used in construction industry more preferably. Presumably, the higher porosity of the zeolite causes better adhesion of the wax to the mineral surface resulting in increased cohesion and better mechanical performance of the obtained PCM composites.

4. Conclusions

Since the main parameter of PCM materials used in the construction industry is high heat capacity in the range of 0-30 °C with sufficient mechanical strength, it was found that the best material base (matrix) will be zeolites, while the technology of granules production: pin granulator with coating with disc. This is indicated by the better obtained values of heat capacity, as well as the greater share of granules with sizes in the range of 4-7 mm.

The use of waste material, which is fly ash from coal combustion, as a raw material for zeolite synthesis, along with the low cost of the PCM material used in the tests, has a positive effect on the possibility of using the technology in industrial production. The use of ashes is part of the circular economy and will reduce greenhouse gas emissions associated with the extraction of raw materials from natural sources. The use of waste materials to create a matrix and residue wax as a phase-change filling allowed to create assumptions for an economically viable technology for the production of PCM granules with better parameters than those currently available on the market.

References

[1] Bendkowska W., Kudrys J., "Thermal insulation of apparel textiles with PCM", in: *International Symposium Avantex*, Frankfurt am Main, 27-29.11.2000.

[2] Li L. Yu H., Liu R.,. "Research on composite-phase change materials (PCMs)-bricks in the west wall of room-scale cubicle: Mid-season and summer day cases", *Building and Environment,* vol. 123, (2017), pp. 494–503. https://doi.org/10.1016/J.BUILDENV.2017.07.019

[3] Shobo A.B., Mawire A., Aucamp M., "Rapid thermal cycling of three phase change materials (PCMs) for cooking applications", J*ournal of the Brazilian Society of Mechanical Sciences and Engineering,* vol. 40, (2018), pp. 329–341. https://doi.org/10.1007/s40430-018-1253-y

[4] Jeong Y.-G., Park K.-B., Lee H.-S., "An Experimental Study on the Thermal Performance of Cement Mortar with Granulated PCM", *Journal of the Korea Institute of Building Construction*, vol. 12, no. 5, (2012) pp. 548 – 557. https://doi.org/10.5345/JKIBC.2012.12.5.548

[5] da Cunha J.M.P., and Eames P. "Thermal energy storage for low and medium temperature applications using phase change materials –A review", *Applied Energy*, vol. 177, (2016), pp. 227–238. https://doi.org/10.1016/j.apenergy.2016.05.097

[6] Zhang Y., Zhou G., Lin K., Zhang Q., Di H., "Application of latent heat thermal energy storage in buildings: State-of the art and outlook", *Building and Environment*, vol. 42, (2007), pp. 2197–2209. https://doi.org/10.1016/j.buildenv.2006.07.023

[7] Mehling H., Cabeza L.F., "Heat and cold storage with PCM. An up to date introduction into basics and applications". Berlin: Springer-Verlag, 2008. https://doi.org/10.1007/978-3-540-68557-9

[8] Rumpf H., "The strength of granules and agglomerates", in *Aggromeration, Interscience*, Kneper W.A. (ed), New York: John Wiley, 1962, pp. 379-414.

[9] Sterczyńska A., Deryło-Marczewska A., Sliwinska-Bartkowiak M. Piotrowska J.Z., Jarek M., Domin K., "Phase transitions of octamethylcyclotetrasiloxane confined inside aluminosilicate and silicate nanoporous matrices", *Journal of Thermal Analysis and Calorimetry,* vol. 118, no. 1, (2014), pp. 263-276. https://doi.org/10.1007/s10973-014-4008-8

[10] Ramakrishnan S., Sanjayan J., Wang X., Alam M., Wilson J.L., "A novel paraffin/expanded perlite composite phase change material for prevention of PCM leakage in cementitious composites", *Applied Energy*, vol. 157, (2015), pp. 85-94. http://dx.doi.org/10.1016/j.apenergy.2015.08.019

[11] Sobolčiak P., Mustapha, K., Krupa I., AlMa'adeed, M., "Storage and Release of Thermal Energy of Phase Change Materials Based on Linear Low Density of Polyethylene, Parafin Wax and Expanded Graphite", in Proceedings of the TMS Middle East – Mediterranean Materials Congress on Energy and Infrastructure Systems, MEMA 2015, pp. 395-402. https://doi.org/10.1002/9781119090427.ch41

[12] Wang L.L., Tianbo Z., Yang L., Hongjing D., "Method for Control of Particle Size and Morphology of Paraffin/Polystyrene-Divinylbenzene Microcapsules", *China Petroleum Processing and Petrochemical Technology,* vol. 18, (2016), pp. 73–82.

[13] Mitran R.A., Berger D., Matei C., "Phase Change Materials Based On Mesoporous Silica", *Current Organic Chemistry,* vol. 22, no. 27, (2018), pp. 1-45. https://doi.org/10.2174/1385272822666180827125651

[14] Kunecki P., Panek R., Wdowin M., Bień T., Franus W., "Influence of the fly ash fraction after grinding process on the hydrothermal synthesis efficiency of Na-A, Na-P1, Na-X and sodalite zeolite types", International Journal of Coal Science & Technology, vol. 8, (2021), pp. 291-311. https://doi.org/10.1007/s40789-020-00332-1