Andreas Kounadis,
Efstratios Badogiannis,
Dimitrios Karonis, Anna Gaki, Maria Taxiarchou

Incorporation of Phase Change Materials in Lightweight Aggregate Concrete

ANDREAS KOUNADIS[1], EFSTRATIOS BADOGIANNIS[1]*, DIMITRIOS KARONIS[2],
ANNA GAKI[3], MARIA TAXIARCHOU[3]
[1] School of Civil Engineering, NTUA, Athens, GREECE
[2] School of Chemical Engineering, NTUA, Athens, GREECE
[3] School of Mining & Metallurgical Engineering, NTUA, Athens, GREECE

Abstract: - An investigation on some methods for the incorporation of phase change materials (PCMs) into concrete and their effect on its properties is presented. PCMs are characterized by high latent fusion heat, which can increase thermal mass of concrete and contribute to the bioclimatic design of buildings. Concrete compositions with different aggregates (limestone, lightweight or their combination), as well as with different PCMs (paraffinic and dodecyl alcohol) were prepared by different incorporation methods (impregnation to lightweight aggregates or immersion of concrete specimens). Properties of fresh and hardened concrete were studied, as well as hydration heat, thermal response and flammability. The results revealed that the selected PCMs do not significantly affect the properties of concrete. Regarding hydration heat, the presence of the PCM in concrete contributes to a decrease of the temperature peak during hydration which also occurs delayed. Thermal response measurements showed that concrete with purely pumice aggregates has a much better thermal behavior than the other two compositions, while the existence of PCM causes large or small increase of concretes heat capacity, in temperature near to each PCM's melting point. Finally, appropriate application of PCMs is needed in order to moderate the reported effect on concrete's fire resistance.

Key-Words: - Concrete, Lightweight Concrete, Phase Change Material (PCM), Hydration Heat, Thermal Response, Flammability

1 Introduction

To date, the greatest percentage of primary energy used world-wide comes from non-renewable sources of energy, such as oil, gas and coal for which the risk of exhaustion is undeniably visible. Moreover, carbon dioxide emissions are among the most dangerous atmospheric pollution causes with incalculable effects on our planet, making a possible turning to renewable energy sources (hydropower, wind, solar, ocean, geothermal, bioenergy) particularly critical and significant. Despite the upward trend in renewable energy sources, mainly from 2005 onwards, they are still far behind when it comes to consumer preferences. It is also known that the building sector requires extremely large amounts of energy. Heating, cooling, lighting and all other indoor activities require about 40% of the total energy used in the European Union [1-5].

What is suggested, appearing in numerous applications concerning the utilization and storage of (mainly solar) energy in the construction sector, is the use of Phase Change Materials (PCMs). Their choice in the building sector among a number of criteria derives from the desired temperature range. In applications in which the main target is human comfort, PCMs with a melting point within the range of user-desired temperature (18-24 °C) are selected. In this way, taking advantage of the high latent heat of fusion and solidification of PCMs, building materials, such as concrete with significantly higher thermal mass, constitute latent energy storage and ultimately contribute to lower cooling and heating needs. This aspect of bioclimatic and energy design leads to the creation of ecologically friendly and economically advantageous structures [6-8].

In respect of other PCM applications, the increase of the heat capacity of concrete leads to a decrease in the temperature peak during the hydration and time lag of its occurrence, which - depending on the place of the concrete and the size of the concrete elements - can play a decisive role in mitigating the phenomenon of early age cracking [9-11].

The first question that arises concerns the materials choice. As mentioned, the basic criterion that makes a PCM suitable or unsuitable for a particular application is the transition point. For example, to improve the indoor climate of a building would require PCM with a melting point of 24°C while to reduce the annual freeze - thaw cycles of a bridge deck in cold climates would require a

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PCM with a transition temperature of 5^oC [12-16]. Latent heat of fusion, physical properties, stability, toxicity and economy constitute also important criteria. Sharma et al bibliographically approached PCMs of a wide range of melting points and formulated an acceptable classification model based on their chemical composition [17]. Hence, PCMs are divided to organic, inorganic and eutectic mixtures. It should be noted that PCMs with common problems such as the appearance of separation and supercooling should be avoided [18].

Since interest in the coexistence of concrete and PCMs appeared, many studies have been carried out and several ideas have been recorded about the way in which PCMs could be incorporated into the concrete. The three main techniques are the immersion, the impregnation of aggregates and the direct mixing [19-30]. The immersion technique is probably the first method appeared. The most common way to apply is to immerse a concrete element in a container full of liquid PCM. In order to achieve the liquid phase of the material, the temperature must be relatively high. The process may take some time until the concrete is completely saturated to the PCM. The absorption capacity and the ability of the concrete to retain the PCM have major role in the duration and effectiveness of this method. D.W. Hawes and D. Feldman conducted experiments to crystallize the time and saturation capacity of two different types of concrete: normal and autoclaved concrete versus different types of PCMs [22]. In the impregnation technique, which is considered to be more effective than the immersion method, the PCM in its liquid phase is impregnated to dried aggregates and then incorporated to the concrete mixture. As in the case of immersion, the basic principle is that the lower the aggregate density (or the greater the porosity), the greater the absorption capacity. D. Zhang et al experimentally demonstrated that it is much more difficult to absorb the amount of liquid from the aggregates by the immersion method compared to impregnation [23]. The main reason for this is the presence of air, which prevents the liquid from entering the pores of aggregates. If the air is removed from the aggregates the method is much more efficient. A particularly important issue when applying the immersion (mainly) and the impregnation technique concerns the stability of PCMs when they are incorporated into high alkalinity concrete. Direct mixing of PCMs into concrete tends to become the most common method, as it attempts to address the main problems of the above methods, i.e. the leakage, evaporation or contact of the PCM with the external environment or the concrete environment. In this

case, the PCMs are stored in chemically and physically stable macrocapsules or microcapsules and mixed in the concrete. It is very important that the capsules are absolutely indestructible to avoid any possible leakage. Nevertheless, creating capsules that remain absolutely intact is quite difficult. M. Hunger et al ran a series of experiments to draw conclusions as to whether and in which parameters the variation in the percentage of microcapsules with PCM content in the concrete mix causes changes [21].

The main problem to be solved by those who study concrete mix design with PCM is the achievement of the optimal combination of upgrading its thermal properties with the minimum possible negative effect on the mechanical properties of the concrete, such as compressive strength, maintaining alongside the required workability. By controlling the negative effects of the incorporation of the various PCMs on concrete, the flammability test should not be omitted. Concrete is considered to be non-flammable, but this is not the case when organic PCMs are used. Thus, PCM-concrete must be tested against ignitability and possible adverse effects should be handled appropriately when designing [17-18, 24-26].

In this study, two different PCMs were used. The first (PCM-P) is a custom-made material consisting of paraffin wax and paraffinic base oil in appropriate proportions derived from experimental processes [31]. This material does not have the thermal performance of commercial PCMs, however it can be deemed to be representative for the investigation of incorporation methods and effect on concrete properties. The other material used (PCM-A) belongs to the category of fatty alcohols [17, 23]. The incorporation techniques chosen were the immersion of concrete elements, composed exclusively of lightweight aggregates to liquid PCM-P and PCM-A, as well as the impregnation of lightweight coarse aggregates and their subsequent incorporation into concrete, consisting of combination of conventional limestone fine aggregates and lightweight coarse aggregates that functioned as PCM carriers. The concrete specimens were tested and compared to reference compositions against properties of fresh and hardened concrete, thermal behavior, heat capacity, hydration heat and products, as well as their flammability.

Finally, to determine the correlation of PCM content, unit weight and compressive strength at the age of 28 days, the values of Pearson's correlation coefficient for the above-mentioned pairs were calculated.

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This work is expected to contribute in methods and techniques for the incorporation and evaluation of phase change materials in concrete, opening further the debate for their rational use in concrete technology. Possible interactions with the concrete ingredients and their influence on the properties of the concrete are also reported and discussed.

2 Experimental

2.1 Materials and Mixtures

Typical Portland cements (CEM I 52.5 R, CEM I 42.5 N) were used, conforming to EN 197-1:2011, for the production of all concrete mixtures. Three nominal grades of locally available crushed calcareous limestone aggregates, conforming to EN 12620:2002 [31], were used: sand (s) 0/4 mm, small gravel (g1) 4/8 mm and medium gravel (g2) 8/16 mm. In addition, three nominal gradings of pumice lightweight aggregates, also locally available, were used: Besser (ls) 0/4 mm, Rice (lg1) 2/10 mm, German (lg2) 8/16 mm.

Two different phase change materials were used for either the impregnation of aggregates or the immersion of the concrete testing specimens: a dodecyl alcohol (PCM-A), with chemical formula $CH_3(CH_2)10CH_2OH$ and an oil mixture of paraffin wax (PCM-P) where their main physical properties are given in Table 1. The synthesis of oil-paraffin wax (PCM-P) mixture, was optimized in respects to cloud and pour points, according to ASTM D-2500 and ASTM D-97, respectively. Cloud point is defined as the highest temperature at which separation of paraffin crystals from the mixture occurs when it is cooled under specific conditions, indicating restricted flowability. In accordance pour point gives the temperature at which paraffin separation is so intense that it prevents fluidity. With these measurements, conclusions about the melting point of the mixture can be derived with a relative accuracy. The optimal ratio of the two components is achieved when a mixture with melting point near the temperature of human comfort (20°C to 26°C) is produced. Thus, for varying mixture proportions, the two temperature points corresponding to the cloud and pour point were measured, respectively. It must be also noticed that the fact that the density of the two substances did not significantly differ (0.82 and 0.87 for paraffin and oil, respectively), makes it possible to create a quite homogeneous mixture without obvious signs of separation [31].

In total, four (4) concrete mixtures (Table 2) were studied, i.e. one mixture (Ca) with limestone aggregates and one with pumice lightweight aggregates (Pu), both used as reference mixtures. In the two remaining mixtures, pumice partially replaces limestone aggregates (CaPu). The effective water to cement ratio for all specimens was kept constant (w/c=0.40) and tap water at 20°C was used. For the production of the concrete mixtures a fixed-pan planetary type cylindrical mixer with rotating blades was used and the same mixing procedure was carefully followed for all mixtures. At first, the aggregates were mixed where in the case of the lightweight concrete, pumice aggregate were pre-saturated. Subsequently, cement was introduced to the homogeneous mixture. Then, 80% of the total water content was added, followed by the rest 20% of the water, in addition with the superplasticizer. The batches were cast at an average temperature of 22°C and an average relative humidity of 50%.

Table 1. Physical properties of PCM-A, PCM-P and of its ingredients

Properties	PCM-A	Paraffin Wax	Paraffin Oil	PCM-P
Density (g/cm^3)	0.82	0.82	0.87	0.82
Melting Point (°C)	24.0	57.6	-6.0	NA

Instead of their usage as reference mixtures, Pu, CaPu and CaPu* mixtures were also used for the incorporation of PCMs. Concrete specimens of Pu mixture were immersed in PCMs, while CaPu mixture was re-produced twice, using impregnated in PCMs lightweight aggregates (CaPu-PCM-P and CaPu*-PCM-A). It is noted that the CaPu*-PCM-A and CaPu* were produced at a different laboratory from the other compositions using only a different type of cement (CEM I-42,5N instead of CEM I-52.5R) in the mixture.

Steel moulds were used for the casting of produced concrete. Standard cubes of 100 mm edge and rectangular moulds of 210*210*35 (or 50) mm3, were cast per mixture in two lifts, applying mechanical compaction. The specimens were demoulded after 24 h and were then water cured, at 20°C, until the age of 28 days. Cube specimens were used for the estimation of the compressive strength, fcc (N/mm^2), while the rectangular specimens were used for the thermal behavior tests.

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Table 2. Concrete mixtures used, either containing impregnated in PCMs aggregates or immersed in PCMs.

Ingredients (kg/m^3)	Ca	Pu	CaPu	CaPu-PCM-P	CaPu*	CaPu*-PCM-A
Cement	400	400	400	400	400	400
ls	-	528	-	-	-	-
lg1	-	58	-	-	-	-
lg2	-	375	434	434	434	434
s	950	-	682	682	682	682
g1	570	-	124	124	124	124
g2	380	-	-	-	-	-
PCM-P	-	-	-	65	-	-
PCM-A	-	-	-	-	-	90
Water	187	335	249	249	249	249
SP	1.22	1.13	1.26	1.26	1.72	1.43

2.2 Incorporation Techniques

In order to incorporate the PCM into the aggregates, a preliminary experimental investigation was carried out to determine the required impregnation time of the aggregates in the liquid PCM until saturation and the maximum absorbed mass of the PCM. Coarse fraction (8-16 mm) of pumice aggregates and (PCM-P) were used in the impregnation procedure. A special testing device (Figure 1) was constructed that would serve the needs and particularities of the experimental work. A rectangular cross sectional container was filled with the liquid PCM up to a point that could completely cover the aggregates. The lightweight aggregates were placed between two thin sheets of a metal sheet of a suitable opening (1.4 mm) so that no grain could penetrate the holes. Two sheets of the metal film were used to counteract any buoyancy in aggregates, which would cause a problem in impregnating them properly, as they would not be fully absorbed in the liquid. The container was permeable by two pins in order to have a further net position. This position was just upstream of the container so that the aggregates can drain when it is desired.

Therefore, coarse fraction (8-16 mm) of pumice aggregates were impregnated with the two PCMs, at 40°C for 24 hours. Afterwards, they were placed in the draining position left to drain for 2.5 hours and they were weighed. This sequence consisted a complete cycle. When the weight change between two sequent cycles was lower than 0.1%, the lightweight aggregates were assumed to be saturated and the required time for saturation was considered the total duration of the immersion in the liquid. The procedure was followed for three different samples of lightweight aggregates of the same fraction. Next, CaPu and CaPu* mixtures were reproduced containing impregnated coarse pumice (8-16 mm)

aggregates with PCM-P and PCM-A respectively. All the other fractions of lightweight aggregates before being incorporated into the concrete were water saturated.
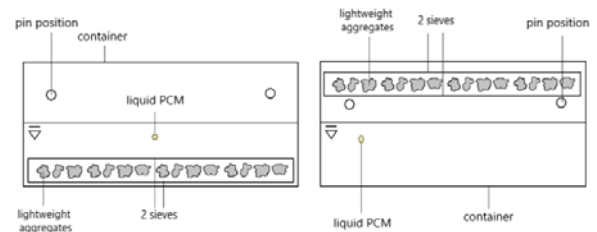

Fig.1. Longitudinal section of the container in immersing and draining position

Accordingly, rectangular concrete plates, sampled from Pu mixture were immersed in the two PCMs, by a similar to the impregnation procedure: dried (100°C, until constant mass) concrete slabs are placed in containers which are filled with PCM in its liquid phase (in oven at 40°C), until being fully covered. Initially, the plates were left in the container for 24 hours and they were then allowed to drain for two hours and then weighed. This procedure is repeated every 24 or 72 hours until the change in the mass of the concrete elements for two successive measurements does not exceed 0.1%.

2.3 Testing

The properties of fresh and hardened concrete, i.e. slump, density, air content and compressive strength at different ages (2, 7, 28 days), were measured in accordance with EN 12350-2-2009, EN 12350-6-2009, EN 12350-7-2009 and EN 12390-3-2009 respectively [32-35].

Hydration heat measurements for cylindrical concrete samples (100 x 200 mm) of the CaPu* and CaPu*-PCM-A compositions were taken, in order to

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indicatively examine the effect that the addition of the PCM-A may have on the hydration heat of CaPu* concrete. Hydration heat was evaluated under semi-adiabatic conditions, using the F-Cal 4000 Semi-Adiabatic Calorimeter and the CalCommander Software for Semi-Adiabatic Calorimeters [36].

In addition, hydration of the CaPu* concrete cement pastes was studied by means of X-Ray Diffraction (XRD) analysis. Samples taken from the concrete specimens that they were used for compressive strength test, were appropriately prepared (ground and sieved at a 75 mm sieve) in order to obtain as much as possible cement paste and they were then analyzed by XRD. Bruker D8 Focus diffractometer in a $\theta - \theta$ configuration employing CuKα radiation (λ=1.54 Å) with a fixed divergence slit size of 0.5° and a rotating sample stage, was used. The samples were scanned between 5 and 75° 2θ. The step size and time per step were set to 0.05° 2θ and 190 s, respectively.

In order to evaluate the thermal response of the concrete, for each of the six aggregate concrete compositions, plates of 210x210x35 (mm) or 210x210x50 (mm) of impregnated lightweight aggregates or of immersed lightweight concrete slabs respectively were studied. The process was carried out in a temperature controlled laboratory environment and the procedure layout shown in Figure 2, was as follows: two by two plates, depending on the desired comparison, were placed at a distance of 30 cm from two identical lamps, which gradually provided them with heat. The plates examined each time were previously cooled to 5°C for 24 hours to ensure that the PCM would be in solid form at the begging of the experiment and therefore that the phase change temperature would be included in the range of measurements. Thermocouples were placed on the plates both on their front and rear surfaces in relation to the exposure to lamps heat. Temperature measurements were transferred to a computer using an appropriate software. Concrete with PCM-P was also tested 18 months after the first measurement in order to investigate the potential instability of the oil – paraffin wax mixture.

The obtained results provide information on the difference in temperature variation of the plates as a function of the exposure time to the same heat source and indicative qualitative conclusions can be drawn regarding the heat capacity and the thermal mass of each concrete composition.

Fig.2. Thermal response assay device

It must be noticed that for all the samples measurements were taken at the age of 28 days after casting and immediately after immersion, depending on the incorporation method (impregnation or immersion, respectively). For the concrete samples containing PCM-P the measurements were repeated after 18 months, in order to evaluate the stability over the time of the oil - paraffin wax mixture that consists PCM-P [37].

Undoubtedly, by incorporating organic phase change materials in the concrete the flammability behavior differs significantly compared to normal concrete which is considered to be non-flammable. Therefore, it is necessary to evaluate the new concrete compositions with PCMs in terms of their flammability. For this reason, two concrete compositions (CaPu-PCM-P, CaPu*-PCM-A) were tested according to EN ISO 11925-2: 2010. According to the procedure of this empirical test, two specimens of each composition of 210x105x35 (mm) were used. The specimens were suspended from a base and then a 2 cm long flame at an angle of 45° was placed on the underside of the specimen at a distance of 0.15 mm from its edge while the tip of the burner is 1.6 cm from its point of application in the specimen. Also, filter paper is placed on the surface under the specimen. The relative humidity during testing reported at 50%. The test time is selected at 30 seconds and the measurement starts from the moment the flame is applied to the specimen. The flame must be stabilized and measured before contact with the concrete. At the end of 30 seconds the burner is removed. The results studied and examined on the basis of the observation relate to whether or not the sample was ignited, whether the edge of the flame exceeded 150 mm above the point of application and the time at which it occurred. The presence of flammable particles that caused ignition on the filter paper as

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well as any other physical observation for the specimen, are also examined [38]. Figure 3 illustrates precisely the experimental setup in which flammability experiments were performed.

To determine Pearson's correlation coefficient between the properties of the same concrete composition (CaPu), the statistical software SPSS, designed to solve business and research problems, was used.

Fig.3. Assay device of flammability experiments

3 Results and Discussion

Applying different ratios between paraffin and oil in the mixture, the diagram of the Figure 4 was produced, showing the variation of the cloud point and the pour point of the mixture in relation to the corresponding change in ratios of the mixture. Based on the results, the material that can be used as a PCM will be a mixture of approx. 6% paraffin wax and 94% paraffin oil. Still, it is useful to emphasize that in such cases as the manufacture of non-commercial/ packaged PCMs, it is useful to carry out a series of tests to ensure the good and safe function of the substance over time as well as to avoid the aforementioned known problems of PCMs.

As far as the impregnation time of aggregates with PCMs is concerned, after the third impregnation cycle, they have measured to carry a liquid amount of 23-25% of their original dry mass. However, the impregnated lightweight aggregates which they have incorporated into concrete compositions they were measured to have absorbed approximately 14.9% and 20.6% of their mass PCM-P and PCM-A, respectively. Additional effort

seems to be needed in order to optimize the saturation time and capacity, employing also vacuum in the pore system of the pumice aggregates [12, 23] in order to increase their capacity.
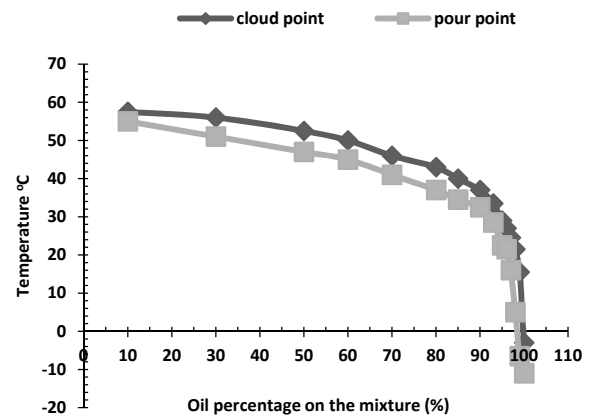

Fig.4. Cloud point and pour point curves for different proportions of paraffin wax and oil

Table 3 shows the results regarding the immersion time of the concrete rectangular specimens to their saturation and the extent to which they are saturated by each PCM. As It can be seen from Table 3, lightweight aggregates concrete can be considered saturated after their third immersion cycle (after 6 days) in the PCM, as their weight change (P %) from their counterpart mass of the previous cycle, was measured to be less than 0.1%. In total, for the tested lightweight aggregate concrete specimens immersed in PCM-P and PCM-A, it was measured to retain 7.7% and 6.0% of each PCM respectively, by their aggregates (mainly pumice) mass (w/w).

Table 4 includes slump classification according to the slump test results and the unit weight and the air content (%) for each of the concrete compositions prepared [32-34].

The comparatively small slump (20 mm) of the CaPu*-PCM-A composition could be regulated using a higher amount of SP in the mix. The differences in unit weight of mixtures can be observed initially depending on the type of aggregates contained in their composition. Thus, the Ca composition comprising only limestone aggregates is clearly heavier than the Pu composition comprising only pumice, with values of 2431 kg/m^3 and 1521 kg/m^3 respectively. The remaining compositions prepared using both lightweight and limestone aggregates have a unit weight between the aforementioned values. CaPu-

PCM-P and CaPu*-PCM-A exhibit a lower unit weight than the CaPu reference composition, as the added PCM-P and PCM-A substances have lower density than water (0.8-0.85 g/cm^3 vs 1.00 g/cm^3). These results conform to the findings met in the literature [7].

Table 3. Immersion measurements and retention percentage of PCM-P and PCM-A by lightweight concrete specimens

Process sequence	Sample with PCM-P		Sample with PCM-A	
	Mass (g)	Weight change P (%)	Mass (g)	Weight change P (%)
Before immersion	3274.1	-	3492.2	-
1st cycle (24h)	3430.9	4.80	3608.8	3.30
2nd cycle (24h)	3464.3	0.97	3643.1	0.95
3rd cycle (72h)	3524.6	1.71	3704.1	1.67
4th cycle (24h)	3527.3	0.08	3706.7	0.07
Dry 24h on absorbent paper	3524.9		3702.4	

Table 4. Slump, slump class, unit weight and air content for each of the six concrete compositions

Property	Ca	Pu	CaPu	CaPu-PCM-P	CaPu*	CaPu*-PCM-A
Slump (mm)	90	50	80	50	43	20
Slump class	S2	S2	S2	S2	S2	S1
Unit weight (Kg/m^3)	2431	1521	1822	1793	1876	1726
Air content (%)	0.9	6.5	4.8	4.0	4.2	-

The results also confirmed that concrete with conventional limestone aggregates entraps much lower percentage of air compared to lightweight aggregate concrete. The composition of Ca contains only 0.9% air, while Pu and CaPu compositions contain 6.5% and 4.8%, respectively. As far as the expected increasing effect that the addition of PCMs has on the entrapped air, the integration of PCM-P and PCM-A into concrete through aggregates, does not cause an increase in air content. There are indications, since only one measurement was taken (in the case of CaPu*-PCM-A, the content of the concrete was not measured, but it is expected to be similar to CaPu-PCM-P), that probably the impregnation application of PCMs might not further affect the air content of concrete.

From Figure 5, useful conclusions are drawn regarding the compressive strength developed by the different concrete compositions prepared, after 28 days. As expected, concrete with purely limestone aggregates (Ca) developed greater strength (79.6 MPa) than concrete containing purely pumice Pu or a combination of limestone and pumice (CaPu) whose strength was measured at 27.7 MPa and 35.0 MPa, respectively. Also, in all formulations containing PCM, a decrease in strength is observed compared to the reference mixture that does not contain PCM. However, the percentage of this drop varies depending on the substance. More specifically, due to the existence of PCM-P and PCM-A the compressive strength decreased by 11% and 39%, respectively.

According to the literature [7], the decrease in compressive strength could be attributed to different reasons, depending on the type of PCMs and their application methods. In the case of impregnation, the incorporation of PCMs could increase the porosity of the paste, decrease the mechanical resistance of the aggregates or retard the cement hydration reactions due to leakage. To the latter, as Sakulich and Bentz reported a quantity of the PCMs leakage to the surface of the aggregates and coat unreacted cement particles during mixing, inhibiting hydration [12].

To this point, results obtained from hydration heat measurements are presented in Figure 6. It is evident that the curve corresponding to CaPu* without PCM is observed to develop its temperature at a significantly faster rate in the first hours (00:00 to 04:00) after mixing, compared to the composition contained the PCM (CaPu*-PC-A). Also, the temperature peak of the two curves differs both in its magnitude and in the time at which it occurred. More specifically, for the CaPu* concrete, the temperature peak is 38.9°C and occurs 14 hours and 20 minutes after mixing, while for the CaPu*-PCM-A concrete the temperature peak is 34.9°C and

occurs 16 hours and 10 minutes after mixing. Therefore, a difference of 4°C, i.e. 10.3% and almost a 2 hours delay, is observed between the appearances of the temperature peaks for the two compositions during the hydration reaction. Finally, 37 hours after mixing, the temperature of the two mixtures equals to 26°C, followed by an interval for which the concrete of CaPu*-PCM-A exhibits a lower temperature than the corresponding reference composition CaPu*, which ceases to occur after 18 hours when the temperature of the samples is again equalized to almost 22°C. From this point to the end of the measurement the CaPu* concrete has a higher temperature than CaPu*-PCM-A resulting in their final temperatures being 20.4°C and 19.8°C respectively.
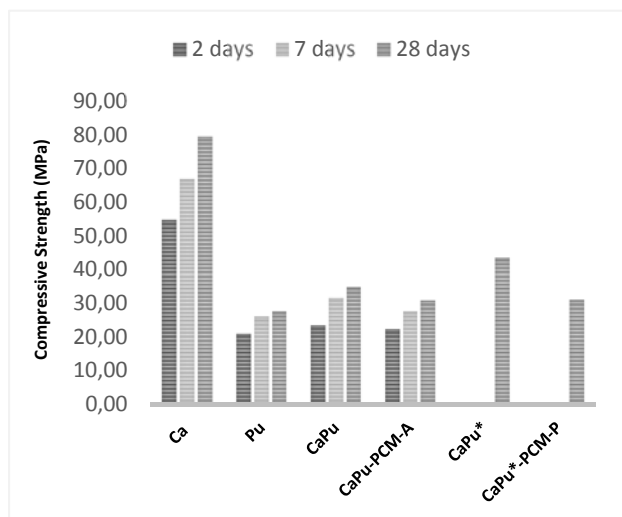
Fig.5. Average compressive strength of concrete compositions, after 2, 7 and 28 days of curing

The above observations on Figure 6 can be explained taking into account both the mode of operation of the phase change materials, namely PCM-A containing one of the two mixtures, and the potential interfere of the PCM to the hydration reactions through coating of the cement particles. By absorbing part of the heat released during the hydration reaction due to the high latent heat of melting, it limits the temperature rise of the mixture and delays the time that CaPu*-PCM-A reaches the maximum temperature, compared to CaPu* mixture. In a similar way, when the samples are cooling, PCM-A ceases to release heat when solidified which explains why the sample without the PCM has reached a greater temperature drop over the phase change temperature of the PCM-A. On the other

hand, the assumed coating of cement particles by drained PCM-A could delay the hydration reaction and therefore the hydration heat curve of the CaPu*-PCM-A is appeared delayed, i.e. righter than its counterpart of the CaPu* sample.
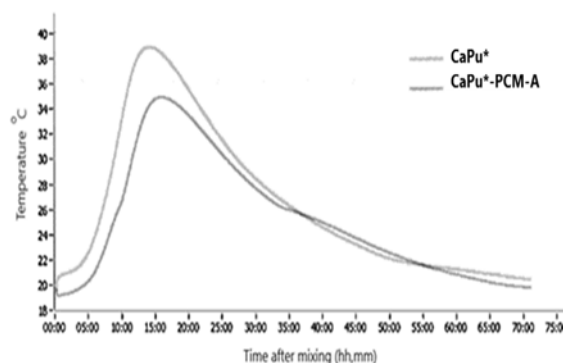

Fig.6. Temperature changes during hydration of CaPu* and CaPu*-PCM-A in a semi-adiabatic environment at the first 72 hours after mixing.

Taking into account the reported differences between CaPu* and CaPu*-PCM-A as far as the hydration heat development is concerned, potential differences on the composed hydration products of the cement paste were accordingly investigated by means of XRD analysis. The resulted XRD diagrams presented in Figure 7, show no significant differences between the two samples, as far as the crystalline products of the hydration reactions are concerned. Ordinary crystalline phases, in terms of hydration reactions are evident after 28 days of curing, as it is shown in Figure 7.

Precise quantification of the phases (Rietveld Method) would offer valuable conclusions as far as the effect of the PCM to the hydration level of the cement is concerned, although it was not able to be performed at this stage of the investigation. Still, there are indications that hydration level is moderated by the incorporation of PCM since some hydration products (i.e. CAH, Portlandite) exhibit lower peaks in the CaPu*-PCM-A sample.
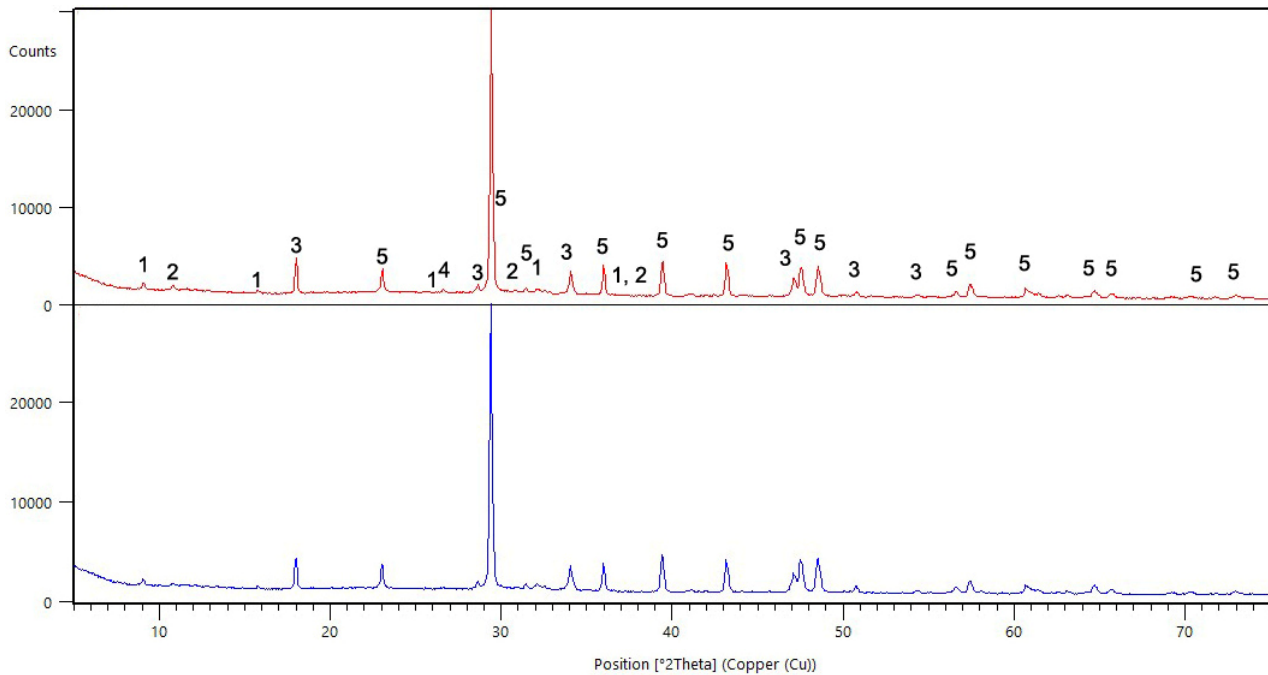
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Fig.7. XRD analysis on CaPu* (up) and CaPu*-PCM-A (down) samples after 28 days of curing (1: Ettringite, 2: CAH, 3: Portlandite, 4:Quartz, 5: CaCO3).

In the Figure 8, the results obtained in terms of the thermal response developed for the different pairs of concrete compositions compared are illustrated. It is clear that lightweight concrete exhibits better thermal response than the conventional concrete compositions containing limestone aggregates and therefore it would be a particularly attractive option for energy efficient design. Although aim of the current study wasn't the assessment of the lightweight aggregate concrete, the study of its thermal response is made only for comparison reasons and they are nor further discussed.

Figure 9 illustrates comparisons made between the concrete syntheses with impregnated aggregates. Useful conclusions were drawn regarding the action of the selected PCMs, as far as the phase change temperature is concerned, as well as the effectiveness of both PCMs. Thus, comparing the reported temperature curves of each concrete mixture with PCM, it is evident that in the case of CaPu*-PCM-A concrete mixture the phase change of PCM-A occurs near to the design temperature of 20°C. In contrast, in the case of CaPu-PCM-P concrete mixture, the phase change of paraffin – wax mixture occurs near to 10°C, a temperature that is far below the designed one. On the other hand, as

far as the effectiveness of the applied PCMs is concerned, the temperature curve of CaPu*-PCM-A concrete is approximately the same to the reference one and only a small alteration is reported after the phase change temperature (20°C), producing however a slight decrease in the temperature measured at the back surface of the concrete plate. Contrarywise, in the case of CaPu-PCM-P concrete mixture the temperature plot differs from its counterpart of CaPu, indicating that the effectiveness of the of paraffin wax mixture (PCM-P). During the phase change of PCM-P the temperature at back surface of the plate maintains at 10°C, presenting a characteristic plateau, although the temperature at front surface of the concrete plate reaches 40°C.

Figure 10 illustrates thermal response test results obtained from plates of the concrete mixture Pu that they were immersed in the two PCMs. As far as the phase change temperature is concerned, same behavior is reported and despite the incorporation method PCM-A and PCM-P were reported to function at approx. 20°C and 10°C, respectively. Comparing the effectiveness of the two PCMs, by the immersion application method PCM-A appeared to be more efficient where at maximum approximately thirty degrees temperature difference
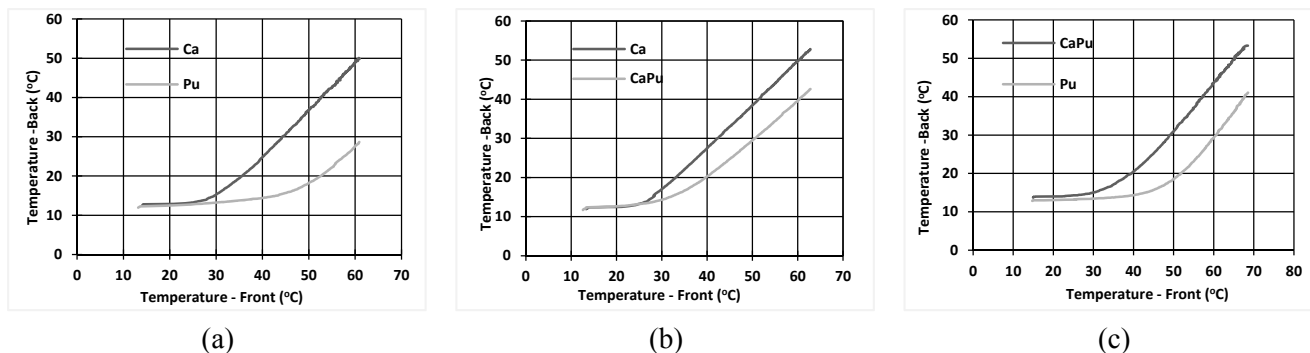
(a)   (b)   (c)

Fig.8. Thermal response of concrete containing lightweight aggregates comparisons: a) Pu and Ca, b) CaPu and Ca, c) CaPu and Pu.
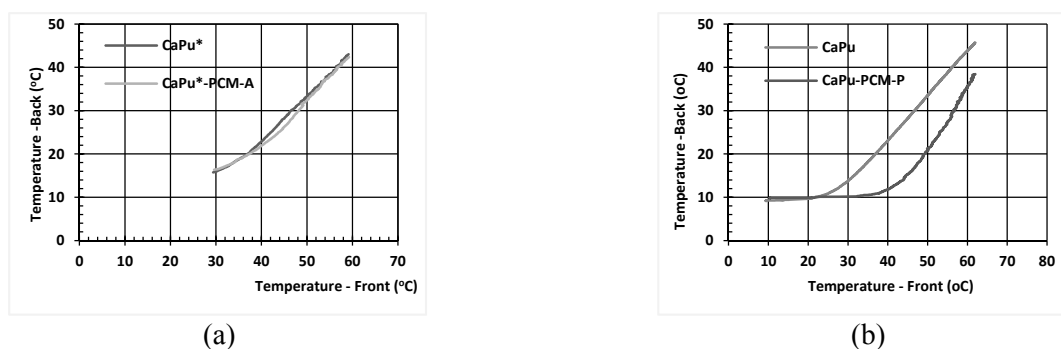

(a)   (b)

Fig.9. Thermal response of concrete compositions CaPu* and CaPu with lightweight aggregates impregnated into PCM-A (a) and PCM-P (b).

is reported between back and front surfaces of the plates, till external temperature of 50°C. Contrarywise, plates of Pu-PCM-P, did not perform significantly improved thermal response and similarly temperature curves are plotted. In addition, as it has been discussed on Figure 8 due to the higher heat capacity and lower thermal conductivity of Pu concrete, for same external (front) surface temperature significantly lower temperature is measured at the back (inner) surface compared to CaPu concrete plates. Therefore, the delayed heat development postpones the phase change of PCMs and regardless of the PCM, their action appears at higher exposure (front) temperatures (>40°C) compared to PuCa concretes with PCMs (>30°C, for the PuCa-PCM-P). Consequently, PCMs function with respect to thermal properties of concrete and their choice and addition amount should be regulated according to thermal

characteristics of concrete, after appropriate experimental or analytical study.

Comparing the two PCMs as far as their efficiency is concerned, PCM-P seems to be superior by the impregnation incorporation method, while PCM-A seems to be superior in the case of the immersion. Moreover, considering the addition percentages, although lightweight aggregates carried greater amount of PCM-A (20.6%) than PCM-P (14.9%) in the impregnation incorporation method, they did not better perform in terms of thermal response. In the case of immersion, PCM-A outweighs to PCM-P, although the latter counts lower addition percentage (6.0 to 7.7%). Nevertheless, the effectiveness of PCM-P need adjustment as the melting temperature is below the designed one. Furthermore, the synthesis of the PCM-P is assumed to be unstable as the results after 18 months showed an adverse effect on concrete's
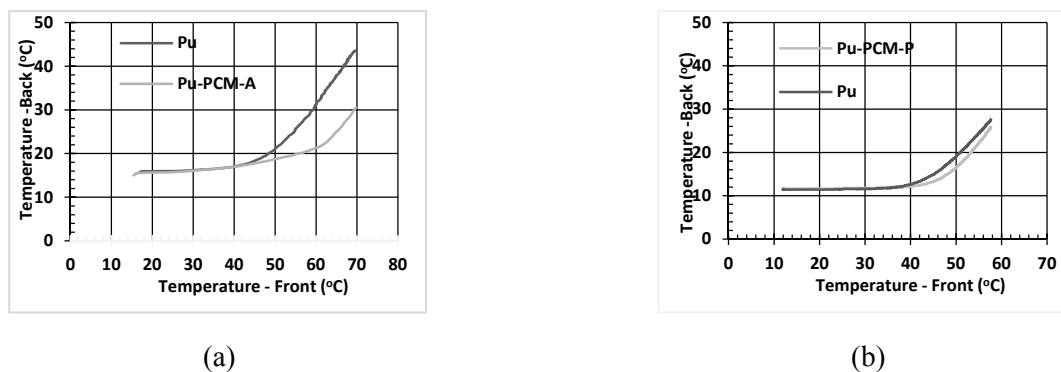
(a)

(b)

Fig.10. Thermal response of Pu concrete compositions, immersed into PCM-A (a) and PCM-P (b).
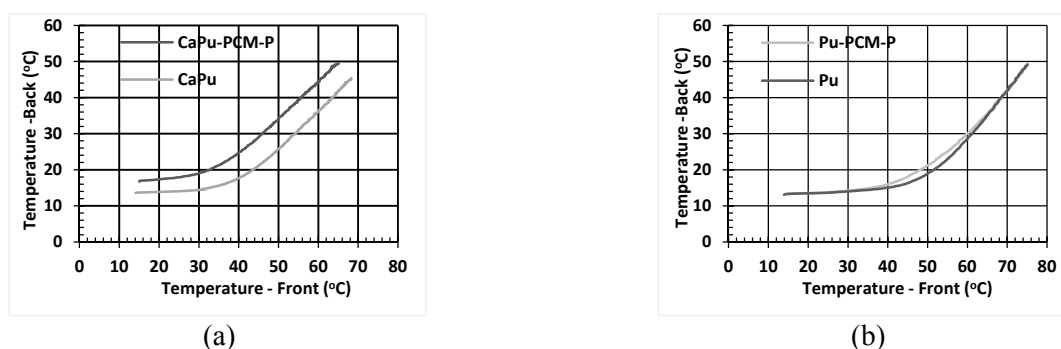

(a)

(b)

Fig.11. Thermal response of lightweight concrete compositions, incorporating PCM-P measured after 18 months (a) impregnation of aggregates to PCM-P, (b) immersion of Pu concrete plates to PCM-P.

thermal properties (Figure 11). In both cooperation methods the effect of PCM-P found to be suspended, probably due to its mixture separation.

The observations obtained from the flammability test are shown in Table 5. It is clear that both concrete compositions were ignited, that is, they continued to burn on their own even after the flame had been removed, causing even a significant amount of smoke. It is noted that the above phenomenon would not occur in a concrete composition which does not contain phase change material. A positive observation is the fact that in any of the two compositions the flame did not exceed 150 mm. It is stressed however, that in the case of CaPu-PCM-P synthesis the flame went up significantly reaching about 100 mm. The specimens of the CaPu-PCM-A composition, that is specimen containing an alcohol, while firing with the burner produced flowing particles.

As expected, both compositions containing an organic PCM make the concrete clearly more flammable. This acts as a restriction on the use of concrete with PCM and therefore additional fire

protection measures (fireproofing, refractory coatings) are required.

Table 5. Observations of flammability tests for the concrete compositions

Observation parameter	Concrete Composition	
	CaPu PCM-P	CaPu* PCM-A
Occurrence of ignition	Yes	Yes
Whether flame reaches 150 mm	No	No
Time to reach 150 mm	-	-
Ignition of the filter paper	Yes	Yes

Table 6 was extracted providing with useful information when it comes to the correlation between the amount of the PCM in concrete, the unit weight and compressive strength at the age of 28 days. According to Table 6, the compressive strength is highly correlated to the unit weight. At the same time, PCM content negatively affects compressive strength to a quite large extent. The

above could be explained by the high correlation between PCM content and the unit weight.

Table 6. Pearson's Correlation between compressive strength at 28 days, PCM content and unit weight

		Compressive strength	PCM content	Unit weight
Compressive strength	Pearson Correlation	1	-0.775	0.866
	Sig. (2-tailed)		0.225	0.134
	N	4	4	4
PCM content	Pearson Correlation	-0.775	1	-0.904
	Sig. (2-tailed)	0.225		0.096
	N	4	4	4
Unit weight	Pearson Correlation	0.866	-0.904	1
	Sig. (2-tailed)	0.134	0.096	
	N	4	4	4

4 Conclusion and Future Work

By varying the proportions in a mixture with paraffin wax ingredients and a paraffin base mineral oil, homogeneous mixtures with different flow and blurring points can be obtained suitable for different applications requiring latent heat storage. Therefore, it was possible to prepare a substance with a melting temperature near the temperature of human comfort with a low production cost compared to other commercial organic PCMs. Nevertheless, the final PCM faces problems such as low latent heat of fusion, not sharp melting point, separation or supercooling, issues that need further investigation.

The impregnation of PCM in lightweight aggregates does not directly affect properties such as slump and unit weight of concrete. On the contrary, PCM seems to negatively affect the compressive strength of the concrete, to an extent however that does not affect the eligibility of concrete for use in most of its structural applications.

The existence of an efficient PCM can make a significant contribution to reduce the temperature peak during hydration and to delay its occurrence, which could mitigate the experience of early age thermal cracking.

The existence of PCM in concrete undoubtedly increases the heat capacity of the concrete around the PCM transition temperature point. This increase varies depending on the efficiency of the PCM, the type of concrete and the percentage of PCM in the mix. PCM-P found to be more effective than PCM-A, in terms of thermal response. However, PCM-P proved unable to retain its action through time, as the thermal response results of the specimens were adverted after 18 months of curing. The reported malfunction could be attributed to the possible separation of the oil – paraffin wax mixture.

The presence of PCM in concrete makes it flammable, which should be taken into account when designing.

Future research should investigate the production of PCMs that combine high latent heat of fusion which in turns leads to high concrete thermal mass with low material cost and low flammability. Also, widely accepted incorporation techniques should be revised to ensure the protection of structures, users and the natural environment in case of conflagration.

Acknowledgements

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