The Effect of Phase Change Materials on the Physical, Thermal and Mechanical Properties of Cement

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Abstract: When focusing on materials science in civil engineering, the current trend is to investigate the use of innovative solutions in order to enhance thermal and energy performances. This trend is amplified with the need for a sustainable development strategy for the construction sector. This paper assesses the integration of a Phase Change Material (PCM) in cement intended for building construction. The key characteristic of PCMs is their capacity to absorb energy and restore it. In building construction, this feature could be harnessed to save energy by incorporating PCMs in the materials used. In this study, passive integration of PCM in cement was tested and thermal properties of such an integration was assessed. The results provide insights into how PCMs affect cement as part of the concrete mixture, thus identifying the contribution of PCM-based cements in concrete mixtures.

Keywords: phase change materials; cement; smart material; energy storage; buildings; thermal performance; DSC; thermal conductivity

1. Introduction

1.1. Phase Change Materials

The Smart Materials concern a large panel of materials: self-healing materials, magnetic shape memory, piezoelectric materials, etc. Smart materials are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields [1].

Our research focuses of Phase Change Materials (PCMs) as a type of Smart Materials. PCMs exhibit a high enthalpy of fusion. Indeed, compared with sensible heat storage materials, latent heat storage materials present a higher energy storage density, per unit of temperature gradient, while requiring less mass of material [2–4].

Over a limited temperature range, a PCM is capable of changing its physical state. Thanks to their great variety, some PCMs have a fusion temperature range that is suitable for building incorporation (thermal insulation, building envelope, walls, slab ceiling . . . ). Building’s temperature exposure ranges between 0° to 55° approximately depending on the geographic location. Many research projects focused on the application of PCMs in building construction. For instance, the authors of [5] experimented with microencapsulated PCM integration in concrete walls. They found that the comparison with conventional concrete without PCMs leads to an improved thermal inertia as well as lower inner temperatures.

1.2. PCM Incorporation Methods in Building Components

PCMs could be incorporated using mainly three methods:
- Direct impregnation: this is the simplest method since it consists of mixing the PCM directly with the material. The latter could be: plaster [6], concrete, etc.
- Microencapsulation: this is a commonly used method of incorporation. It consists in enclosing the PCM in a microscopic polymer capsule. The microcapsules have spherical structures and are constituted by (generally) an oily core surrounded by a thin polymer wall whose thickness does not exceed a few nanometers. Those microcapsules are mixed with the material that we seek to improve (concrete [7], cement, wood, etc.)
- Shape Stabilized PCM: Shape-stabilized PCMs are prepared from a liquid mixture of the PCM and a supporting material. The most common supporting materials found in the literature are high-density polyethylene (HDPE) and styrene-butadiene-styrene (SBS) [8].
- Form-stable composite PCM [9–11].

2. Materials and Method

2.1. Materials

The PCM used is microencapsulated and composed of vegetal wax in a powder format. Its industrial reference is INERTEK 23 P. Microencapsulation consists of forming a resistant envelope around the phase change material. The size of microcapsules is within the range of 5–25 microns. Figure 1 represents a 1000 magnification of the microcapsules provided by the manufacturer. Table 1 presents the fusion and solidification ranges of the PCM as well as its latent heat.

<table>
<thead>
<tr>
<th>Powder PCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Range (°C)</td>
</tr>
<tr>
<td>Solicitation Range (°C)</td>
</tr>
<tr>
<td>Latent Heat (J/g)</td>
</tr>
</tbody>
</table>

Cement material used in this research study has a classification: “CEM II”.

Mixture preparation was realized by mixing cement with different percentages of PCM powder.

2.2. Thermal Conductivity Test

Samples composed of cement were tested according to different percentages of PCM integration: 0%, 10%, 20%, and 30%. Each percentage of PCM is assigned to a configuration. Each configuration
was tested three times and the average was noted. Sample dimensions are (35 × 35 × 3 cm). Samples were realized using a mold of Styrofoam for its good insulation properties as shown in Figure 2.

![Figure 2. Mold and sample used for the thermal conductivity tests.](image)

Ratio water to (cement + PCM) was taken equal to 0.5 for the three configurations. Total mass of samples is 4 kg.

Thermal conductivity is measured after 7 days of drying. The measuring device is Fox600 as shown in Figure 2. The optimal Delta of temperature between the plates (lower and upper) suggested by the manufacturer is 20 °C.

Temperature of the lower plate is equal to $T_{\text{low}} = 35$ °C and $T_{\text{up}} = 15$ °C for the upper plate.

According to [12] for steady-state measurements, the arithmetic mean of temperature $(T_1 + T_2)/2$ was adopted as the representative temperature for measuring thermal conductivity. According to [13], the effective thermal conductivity of PCM within the range of melting temperature located between thermal conductivity of PCM solid state and liquid state as in Equation (1):

$$k_f < k_e < k_s$$ (1)

$k_f$: Thermal conductivity of liquid phase of PCM, W·(mK)$^{-1}$

$k_s$: Thermal conductivity of solid phase of PCM, W·(mK)$^{-1}$

$k_e$: Effective thermal conductivity of solid–liquid, W·(mK)$^{-1}$

Since the objective of the study is to assess how the thermal performance of cement evolves with PCM integration, we considered the average temperature for measuring thermal conductivity of 25 °C, which is within the range of the PCM’s melting point. The behavior of the PCM in solid and liquid states could be then evaluated. In addition, 25 °C is an acceptable estimation of the environment of the exposition of cement material in use.

Styrofoam is placed around the sample (Figure 3) covering the entire surface of the plates. The sample covers completely the sensor (measuring range 30.5 × 30.5 cm). To ensure proper contact for conductivity, a rubber was placed between each plate and the sample: it is assumed that temperature of the plate (lower, upper) is equal to the sample’s surface temperature (lower, upper). Two thermocouples were arranged on both sides of the sample to monitor the upper and lower temperatures. Sample’s thermal conductivity is calculated using the measured thermal conductivity provided by the device, which is for the sample and rubber:

$$\lambda = \frac{(d_{\text{sample+rubber}} - d_{\text{rubber}})/[(d_{\text{sample+rubber}}/\lambda_{\text{sample+rubber}}) - (d_{\text{rubber}}/\lambda_{\text{rubber}})]]}$$ (2)

where “d” is the thicknesses (mm) and “$\lambda$” the thermal conductivity (W/mK).
2.3. DSC Test

A Differential Scanning Calorimetry (DSC) test was performed with the aim to quantify the variation of heat flow exchange of PCM incorporation in cement.

DSC is a thermal analysis technique that measures the differences in heat exchange between a sample and a reference. The reference is an empty, hermetically sealed aluminum pan. All DSC experiments were carried out using a Perkin Elmer calorimeter (Figure 4). Samples were treated using nitrogen as the liquid. Samples’ total mass (cement + PCM) is 15 mg.

The testing protocol is described in Table 2. Initial temperature was set at 20 °C and final temperature at 80 °C with a constant rate of 5 °C/min. Temperature is then left stable at 80 °C for 10 min before being reduced to the initial temperature.

Table 2. PCM characteristics: fusion–solidification-latent heat.

<table>
<thead>
<tr>
<th>Initial Temperature (°C)</th>
<th>Final Temperature (°C)</th>
<th>Speed (°C/min)</th>
<th>Material Sample Composition</th>
<th>Material Ref #</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>80</td>
<td>5</td>
<td>Cement (%)</td>
<td>PCM (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>0</td>
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<td></td>
<td></td>
<td></td>
<td>90</td>
<td>10</td>
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<td>80</td>
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<td>70</td>
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<td></td>
<td></td>
<td></td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
2.4. Compressive Strength Testing

The compression test was carried out using the “INSTRON” mechanical press. Sample dimensions are: 4×4×8 cm.

The measurement protocol is as follows:

- Preparation of samples (Figure 5).
- Demolding of samples after 24 h
- Drying for 8 days at an ambient temperature of 20 °C
- Placing samples on the compression machine for testing.

![Figure 5. Preparation of samples in the mold.](image)

2.5. Water Porosity Test

Sustainability indicators act as input data into models for predicting the life of structures. Porosity is considered a relevant sustainability indicator for a wide range of degradations. The cement samples were tested according to different percentages of PCM: 0%, 10%, 20% and 30% (Figure 6). Several tests were conducted on each sample. Each percentage was tested three times and the arithmetic mean was considered in this study. Porosity was measured on samples of dimensions; 4×4×8 cm.

![Figure 6. (a) Samples after demolding, (b) The vacuum saturation procedure, (c) Drying at 60 °C.](image)

An imbibition technique is used for the determination of water porosity (P). It consists in saturating a sample in a solution of demineralized water. After 48 h of drying at room temperature, samples were placed in an air suppression desiccator for 10 days. All the voids in the sample must be filled with water. The sample is then saturated when two consecutive weighing operations spaced 24 h apart do not differ by more than 0.05%.

This procedure allows the sample to be degassed and therefore completely saturated with water. Whatever the shape of the sample, the exact volume can be determined by the hydrostatic weighing method. Then the weight of the water-saturated sample \( M_{\text{sat}} \) (g) is measured, as well as the total volume \( V_1 \) (m³). All weighing operations were carried out with an accuracy of ±0.01 g. Some experimenters use high temperatures (105 °C or 80 °C) to accelerate the drying process, however, this can lead to changes in the internal structure of cementitious materials (dehydration) and the creation of microcracks.
Finally, the samples were placed in a heat chamber with moderate drying at 60 °C to minimize the effects stated earlier. Drying is stopped when the sample weight stabilizes at a dry weight ($M_{sec}$) (g). The period for this study was 6 days and 3 h. The dry state is reached when the variation between two successive weighing operations did not exceed 0.05%. The water porosity is obtained by Formula 3 (%):

$$P (%) = \frac{(M_{sat} - M_{sec})}{V \times \rho_{water}} \times 100$$ (3)

3. Results and Discussion

3.1. Thermal Conductivity Analysis

Thermal conductivity test was conducted to assess the effect of PCM integration in cement material. For each PCM percentage, the sample was tested 3 times and the average was taken. Figure 7 presents the results. For 0% PCM integration, we found 0.724, 0.696 and 0.683 W/Km. It is noticeable that the results are too close which validates the experimentation. For 10%, 0.605, 0.5965 and 0596 W/Km. 20% PCM integration resulted in the following thermal conductivity values: 0.578, 0.57 and 0.547 W/Km. Finally, for 30% PCM integration: 0.544, 0.533 and 0.526 W/Km. For all the percentages, the 3 values tested are close to each other.

![Figure 7](image)

Figure 7. Conductivity of cement as a function of PCM percentage of integration: 4 points of measure (0%, 10%, 20%, 30%).

Thermal conductivity (average) was taken for each configuration and drawn in Figure 7 which expresses cement’s thermal conductivity of cement as a function of PCM percentage of integration.

Thermal conductivity of pure cement (0% PCM integration) is 0.7 W/mK. If 10% of PCM is integrated in cement, thermal conductivity drops to 0.6 W/mK. With 20% of PCM integration, thermal conductivity continues decreasing till 0.56 W/mK. Finally, 30% PCM gives a value of 0.53 W/mK. Thermal conductivity decreases when the integrated PCM in cement increases. This proves that thermal insulation of cement could be enhanced with PCM integration.

In their research, [14] investigated the evolution of Portland concrete cement with 0%, 1%, 3% and 5% PCM integrations. They found that thermal conductivity of the PCM-concrete is quite constant with the addition of PCMs (about 0.02 W/mK change). Our research shows that thermal conductivity is relatively stable in the 0–5% PCM range as well (0.05) and evolves even slower with 10% integration and more. In the same scope, [15] research investigated thermal conductivity of a wall (Cement mortar-SSPCMs bricks) with the following proportion: cement mortar (37.5%), yellow sand (22.5%) and a Shape-Stabilized Phase Change Material (40%). They found that the effective thermal conductivity decreases when increasing the percentage of the phase-changed amount of the wall.
Figure 8 presents percentage of thermal conductivity decrease as a function of percentage of PCM integration. For 10% PCM, thermal conductivity of cement decreases by around 14%. For 20% PCM integration, thermal conductivity decreases by 20%, and for 30%, it decreases by 24%. The dotted line “reference curve’ in the figure represents the equality Percentage of thermal conductivity = Percentage of PCM decrease. For PCM percentage under 20%, cement material thermal conductivity gain is superior to the PCM integration percentage. In other words, we increase thermal conductivity while using a minimum quantity of PCM. The zone under 20% PCM integration could be assigned to “the optimum use” of PCM. For values superior that 20% PCM integration, thermal conductivity decrease is very limited, for instance, we gain only around 5% thermal conductivity for 10% PCM integration.

From Figure 6, it is possible to conclude that the optimal PCM integration in term of thermal conductivity decrease is located in the zone under 20% PCM integration.

3.2. DSC Analysis

Cement-based materials are commonly used in civil engineering. Cement has a plenty of unique and distinguished properties: high strength, easily workable and harden early etc. However, it does have poor thermal properties. Figure 9 describes cement heat flow variation according to temperature. Temperature range is [0:80 °C] which describes common building’s temperature exposition (In hot climate, building façade temperature could exceed 55 °C [16]). For pure cement “Heat flow 0”, heat flow curve ranges from 2.4 to 1.6 mW in the interval (20-40 °C). Heat flow variation is 0.8 mW.

Figure 9. Heat flow as a function of temperature for 5 configurations of PCM integration in cement: 0%, 10%, 20%, 30%, 100%.
«Heat flow 10» curve expresses heat flow of cement with 10% PCM integration. Heat flow curve ranges from 2.4 to 0.75 mW in the interval (20–40 °C), which adds up to a 1.65 mW variation. The curve is convex, starting from 2.4 mW for 20 °C and reaching a bottom at 29.84 °C before increasing to the initial value. The curve contains a small cavity in its heat flow variation (20–80 °C): A massive heat is absorbed via an endothermic reaction.

«Heat flow 20» curve is composed of 20% PCM and 80% cement. Its Heat flow ranges from 2.4 to 0.2 mW, which adds up to 2.2 mW total variation. The latter is higher than that of cement alone. An absorption phenomenon is present since a clear cavity is found in the measured heat flow curve, bigger than that of the one cement alone.

«Heat flow 30» curve presents heat flow of cement with 30 M PCM integration. The curve ranges from 2.4 to 0 mW in the interval (20–40 °C), which adds up to a 2.4 mW variation. This variation is greater than the two previous ones and the curve has more cavity as well.

«Heat flow 100» curve expresses heat flow of the PCM. The curve ranges from 2.4 to −0.65 mW in the interval (20–40 °C). Total heat flow variation is 3.05 mW.

Heat flow variation of cement alone is 0.8 mW compared to 2.4 (for 30% PCM integration), three times more heating capacity (2.75 times for 20% PCM and twice for 10%) which means that pure cement capacity to absorb or release energy by heat exchange is very limited and could be profoundly enhanced. From those results, we deduce that PCM integration in cement increases the phase change enthalpy in the interval (20–40 °C) and the cavity is more noticeable. This translates into a thermal absorption capacity increase. PCM integration in cement enhances its thermal performance by adding a new feature: “thermal absorption feature”. Absorption capacity, however, is less than that of PCM but higher than that of cement alone.

Previous researches focus on the effect of PCM on concrete mix (Aggregates, cement and water). While those research studies proved the benefits of PCM integration, no insights were given to the effect of PCM on each single component of concrete or mortar. This information will help identify which component generates the “thermal absorption feature” in concrete mixture.

PCM absorbs energy in order to change its phase. This characteristic is desirable for building applications. Indeed, when temperature rises (in summer for instance), cooling is needed. By absorbing heat, PCM helps reduce the incoming heat flow. Thus less energy is needed for cooling. The capacity to absorb heat is proportional to cavity extent. Since cement has a very limited absorption capacity, outdoor temperature (exterior) and indoor temperature (in the building) is theoretically the same (if buildings were erected only with thin cement layers). PCM integration could generate an additional absorption capacity is mixed with cement.

Determination of PCM fusion temperature could be deduced from “Heat flow 100” curve in Figure 5. Graphically, $T_f = 31.4 \, ^\circ\text{C}$ for the PCM. The PCM fusion temperature is a good fit for some of building applications. Even for the same climate, different applications in the buildings require different melting ranges to maximize the PCM efficiency. For instance, if the inner mortar layer of a wall is considered, the PCM to be incorporated must have its melting point close to the human temperature comfort range which ranges from about 23 to 26 °C. In summertime, the human comfort zone is between 23 °C and 27 °C, which is inferior to 31.4 °C.

Table 3 presents the temperatures corresponding to the minimum heat flow per configuration. We notice that the PCM depression point decreases when integrated to cement. For 30% integration, $T_f = 31.4 \, ^\circ\text{C}$, for 20% integration, $T_f = 30.69 \, ^\circ\text{C}$ and for 10% integration, $T_f = 30.37 \, ^\circ\text{C}$.

Energy is released around fusion temperature of the PCM without any change depending on the PCM quantity integrated. In addition, the more PCM is integrated, the more energy is released.

However, it is worth noting that PCM integration could affect the structural mechanical strength. Since cement is mainly used as a structural binder, the real stake is to consider a good compromise between the mechanical testing and the percentage integration.
Table 3. Temperatures corresponding to the minimum heat flow per configuration.

<table>
<thead>
<tr>
<th>Percentage of PCM Integration in Cement (%)</th>
<th>Minimum Heat Flow Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>32.27</td>
</tr>
<tr>
<td>10</td>
<td>29.84</td>
</tr>
<tr>
<td>20</td>
<td>30.69</td>
</tr>
<tr>
<td>30</td>
<td>30.37</td>
</tr>
<tr>
<td>100</td>
<td>31.4</td>
</tr>
</tbody>
</table>

3.3. Compressive Strength Tests

Figure 10 shows the variation of the normalized constraint as a function of the elongation (mm). The shape of the curve bends and the slope declines as a function of the PCM percentage integration. The maximum compressive strength is achieved for 0% PCM (pure cement). The more PCM is integrated, the less strength the material has.

3.4. Water Porosity Tests

Measurements of water porosity were made on samples with different percentages of PCM. Figure 11 illustrates the variation of water porosity as a function of the percentage of PCM in the cement paste. Porosity values range from 15.32% for the lowest percentage to 31.17% for the highest. When the percentage of PCM increases from 20% to 30%, porosity increases from 20.40% to 31.17%. For compositions with percentages between 0% and 20% of PCM, the measured porosity values increase from 15.32% to 20.40%. The graph shows that the relationship is not linear. We observe that porosity increases when the percentage of PCM increases, and this increase could be explained by the presence of vegetable waxes. The structure of the sample at 30% PCM is more porous than that of 0%, 10% and 20% MCP.
3.5. Possible Explanation of the Porosity and Mechanical Testing Results

G. Hüsken et al., 2008 [17] carried out a particle size analysis on cement CEM I 52.5. The particle diameter is between 0.1 µm and 50 µm. 80% of the cement particles have a diameter less than 20 µm. In our study, the diameter of the vegetable wax particles varies from 0.6 µm to 200 µm as shown in Figure 12. For 80% of PCM particles have a diameter of less than 40 µm. From this data, one potential explanation is that the integration of vegetable wax increases the porosity in the cement paste, and diminishes the compressive strength.

![Figure 11](image1.png)

**Figure 11.** Variation in porosity as a function of the percentage integration of PCM.

![Figure 12](image2.png)

**Figure 12.** Particle size distribution of the studied PCM.

By way of comparison, Guochen Sang et al., 2016 [18] used Ethylene Vinyl Acetate (EVA) at different percentages (0.03, 0.06, 0.10, 0.13, 0.20, 0.27 and 0.33) with a W/C ratio fixed at 0.9. The results showed that the porosity of each sample is greater than 90% and the variation in EVA content does not have a significant effect on porosity. On the other hand, Elie Kamseu et al., 2015 [19] have shown that semi-crystalline and amorphous polymers contribute to reducing porosity in concrete.

4. Conclusions

Phase Change Materials (PCMs) integration in building materials reduces the need for air conditioning use in summer and brings comfort and well-being throughout the seasons. This research study proved that PCM incorporation in cement material enhance its thermal efficiency by adding a new feature: “thermal absorption feature”. The latter absorbs energy to restore it when needed (day vs. night).
While the warm climate in Africa (and worldwide) is increasing year after year, the introduction of this type of Smart materials (PCM) could be a solution to store energy for reproduction in the next decades. The results revealed that thermal conductivity decreases when the integrated PCM in cement increases. Thermal conductivity of pure cement (0% PCM integration) was found to be 0.7 W/mK. If 10% of PCM is integrated in cement, thermal conductivity dropped to 0.6 W/mK. With 20% of PCM integration, thermal conductivity continued decreasing till 0.56 W/mK. For 30% PCM, the value is 0.53 W/mK. In addition, heat flow variation of cement alone is 0.8 mW compared to 2.4 (for 30% PCM integration) three times more heating capacity (2.75 times for 20% PCM and twice for 10%). Fusion temperature of the studied PCM is included within the range of the building temperature exposure. According to the results, Phase Change Materials incorporation allow an increase in thermal amortization of heat picks. Further studies should focus on the assessment of PCM integration in each component individually (mortar and concrete). Regarding future research, a focus should be set on the optimal compromise between energy efficiency and mechanical performance of PCM integration in construction materials.

Author Contributions: Z.L. managed the research, Z.D. conducted the literature search, K.C. conducted the experimentations, Z.D. Analyzed the results and drafted the manuscript, Z.L. & Z.D. critically reviewed the content of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References


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