

Potential applications of phase change materials in concrete technology

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Abstract

In internal curing, pre-wetted lightweight aggregates (LWA) serve as internal reservoirs to supply the extra water needed by the cementitious and pozzolanic components of the concrete during their hydration processes. Due to their porous nature and reasonably high absorption capacity, the LWA can also be filled with other materials, such as phase change materials (PCMs). In this paper, three potential applications of PCM-filled LWA in concrete technology are presented. In addition to the previously explored application of increasing the energy storage capacity of concrete in residential and commercial construction by using a PCM with a transition temperature near room temperature, applications for higher and lower temperature PCMs also exist. In the former case, a PCM can be used to reduce the temperature rise (and subsequent rate of temperature decrease) of a large concrete section during (semi)adiabatic curing, to minimize thermal cracking, etc. In the latter case, a PCM can perhaps reduce the number or intensity of freeze/thaw cycles experienced by a bridge deck or other concrete exposed to a winter environment. In this paper, these latter two applications are preliminarily explored from both experimental and modeling viewpoints.

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1. Introduction

In many areas of the world, concrete is used extensively for residential as well as for commercial construction. In moderate climates, the relatively large thermal mass of the concrete walls can be an advantage, as they store up energy during the day and release it at night, reducing the need for auxiliary cooling/heating. Of course, in more tropical climates, this nocturnal release of energy can be most unwelcome to residents trying to sleep in a room without forced cooling. However, the energy storage capacity of concrete can be further modified by the incorporation of phase change materials (PCMs) into the concrete mixture [1–4]. Two potential applications of PCMs in concrete have been highlighted in the recent works of

Zhang et al. [4] and of Mihashi et al. [3]. In the former case, porous lightweight aggregates (LWA) were successfully impregnated with a butyl stearate PCM that melts at around 18 °C. Such a concrete could be used in construction to maintain interior temperatures near 18 °C, as the melting and solidification of the PCM would delay and, perhaps, avoid temperature excursions above/below this value. Even when a temperature excursion can not be avoided, its delay can be extremely beneficial if it shifts heating/cooling loads to time periods when power is available at a lower cost. Such a technology is now being commercially employed in aerated cement blocks, using microencapsulated PCMs, and plaster, using wax-filled spheres [5], for example.

In the second application [3], a paraffin microcapsule that contains a hydration retarder was incorporated into concrete to drastically reduce the temperature rise experienced during the early-age curing of massive concrete structures. The melting of the wax absorbs energy (partially

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reducing the temperature rise) and the release of the hydration retarder further reduces hydration rates and concurrent heat release from the mixture. Maximum achieved temperatures under (semi)adiabatic curing were significantly reduced in both small cement paste and larger concrete specimens. While early age concrete strengths were significantly reduced, 91 d strengths were actually increased by the incorporation of the PCM/retarder microcapsules, as it is well known that higher curing temperatures, while significantly accelerating hydration and strength gain at early ages, can actually lead to lower long term concrete strengths [6].

Because numerous PCMs are readily available with a wide range of transition temperatures, as summarized extensively in [7], a third (but untried to date) application of PCMs in concrete would be to utilize a PCM with a transition temperature of around 5 °C to avoid a fraction of the freeze/thaw cycles normally experienced by a concrete bridge deck or pavement. This could improve both the durability of the concrete and provide improved skid resistance, improving safety in cold climates. In this paper, the physical properties of a variety of PCMs of potential usage in concrete will be presented and the latter two of the three proposed applications will be explored in more detail.

2. Experimental and computer modeling

2.1. Differential scanning calorimetry

The following PCMs were obtained from chemical suppliers: three different polyethylene glycols (of different average molecular masses, MM), octadecane, and paraffin wax. All of the materials were evaluated in bulk form and two of them (the paraffin wax and one of the polyethylene glycols) were also impregnated into (porous) lightweight fine aggregates (expanded shale) nominally 3 mm in diameter. The “saturation” of the aggregates was performed by simply first drying them at 40 °C and then immersing them in a (melted) solution of the appropriate PCM for a minimum of 24 h. Small samples of each PCM (or of the PCM embedded in LWA) were used for each differential scanning calorimetry (DSC) experiment. In a given experiment, sample mass was typically between 10 mg and 100 mg. For each DSC experiment, the sample was placed in a small open stainless steel pan. The pan with the sample, along with an empty reference pan of similar mass to the empty sample pan, was placed in the calorimeter cell. A temperature range expected to encompass the transition temperature(s) of the specific PCM was selected and a cyclic cooling/heating/cooling scan conducted at a scan rate of 0.5 °C/min, with a 10 min isothermal hold at both the minimum and maximum temperatures comprising the scan. For temperatures between –100 °C and 500 °C, the equipment manufacturer has specified a constant calorimetric sensitivity of $\pm 2.5\%$ and a root-mean-square baseline noise of 1.5 μ W. For comparison, typical measured peak signals

for the PCM phase transitions were on the order of several milliwatts. Enthalpies of melting and solidification were quantitatively estimated by manually identifying each peak in the DSC scan and using a linear approximation for the baseline below/above the peaks.

2.2. Semi-adiabatic calorimetry

A home-built semi-adiabatic calorimeter was used to preliminarily evaluate the second proposed application of PCMs in concrete, namely reductions in the temperature rise and subsequent rate of temperature decrease during the first few days of hydration. For this portion of the experiment, mortar specimens with a water-to-cement ratio by mass of 0.4 were prepared and mixed by hand according to the proportions provided in Table 1. In the control mortars, a nonporous coarse silica sand was employed and the proportions were adjusted to obtain a temperature rise to near 70 °C in the semi-adiabatic calorimeter setup. In the LWA/PCM mortar, the paraffin wax PCM was first absorbed into the expanded shale LWA, with an obtained absorption of 13.8% by mass of dry LWA. The LWA/PCM was then used to replace the sand on a volumetric basis. Finally, in the pure PCM mortar, the paraffin wax particles (about 1 mm in size) were added directly to the cement paste, totally replacing the coarse sand on a volumetric basis. Each mortar was cast into a cylindrical plastic mold with an inner diameter of 47 mm and a height of 97 mm. The mold could thus hold about 330 g of the control mortar. By performing volumetric replacements for the sand, each mold should contain the same mass of hydrating (heat generating) cement paste to enable a realistic comparison amongst the three investigated mixtures. A filled mold was immediately placed in an insulative holder (constructed of microporous insulation) and a single Type J thermocouple inserted into the center of the mortar volume. The temperature was then monitored during the course of several days of “semi-adiabatic” hydration.

2.3. Concrete temperature modeling (CONCTEMP)

For the third potential application of PCMs, namely limiting the number of freeze/thaw cycles of bridge deck concretes (and pavements), a computer simulation approach was employed to evaluate its potential feasibility. An existing one-dimensional finite difference computer code (CONCTEMP) that predicts the temperature distri-

Table 1
Mixture proportions for the mortars employed in the semi-adiabatic calorimetry experiments

Material	Mass (g)
Type I cement	210
Distilled water	84
Coarse sand or #8 LWA with PCM or PCM	70 g sand or 48 g LWA/PCM or 27 g PCM

bution, time-of-wetness, and number of freeze/thaw cycles of a bridge deck in a user-specified geographical location [8] was modified to include the enthalpy of the phase transition of the PCM at a single fixed temperature (5 °C in this study). The model makes use of typical meteorological datafiles (TMY2DATA) that have been compiled for numerous locations throughout the US [9] and includes heat transfer modes of conduction, convection, and radiation [8]. In this study, twelve specific locations were utilized, spanning the range of typical US climatic conditions (hot and dry, hot and humid, cold and wet, etc.). The twelve selected locations will be presented in the results section to follow.

The basic modification to the computer code consisted of monitoring the nodal temperatures in the finite difference grid to note when an excursion across (from above or below) the phase transition temperature was projected to occur. When such an excursion was noted, instead, the nodal temperature was held constant at the phase transition temperature and the enthalpy “into or out of” the PCM was computed. Once the enthalpy reserve of the (local) PCM was exhausted or built back up to its maximum value, the nodal temperature was free to vary once more. For the modified codes, new user inputs included the PCM density (content) in the concrete mixture (kg/m^3), the enthalpy of its phase change (J/kg), and the phase change temperature.

The values for the thermal properties of the base concrete were the same as those presented in reference [8] with a heat capacity of 1000 J/(kg K) , a thermal conductivity of 1.5 W/(m K) , a density of 2350 kg/m^3 , an emissivity of 0.90, and a solar absorptivity of 0.65. A concrete bridge deck with a thickness of 0.2 m was considered. For the bridge deck, both surfaces of the concrete were assumed to be exposed to the environment, which is generally the case when temporary wooden forms are used [8]. It was further assumed that the convection coefficient for heat transfer is the same for both the top and bottom surfaces, and that no heat transfer by radiation (incoming sunlight or emitted radiation) occurs at the bottom surface of the bridge deck, assuming that the bottom of the bridge deck is in radiative equilibrium with the surroundings below it. This is not the case at the top surface, where substantial incoming solar radiation and outgoing radiative emissions to the night sky both are accounted for in the CONCTEMP model [8]. In the formulation examined in this paper, it was also assumed that the PCM is distributed uniformly throughout the concrete thickness. For the simula-

tions conducted for a PCM-containing concrete, the following additional characteristics were assumed: PCM content = 300 kg/m^3 , transition temperature (for both solidification and melting) = 5 °C, enthalpy of phase change = 250 J/g . The latter two properties were selected based on a best case but realistic scenario from values provided in the literature [7]. Specifically, *N*-tetradecane has a melting point of 5.5 °C and a latent heat of fusion of 226 J/g while the corresponding properties for formic acid are 7.8 °C and 247 J/g , respectively [7].

3. Results and discussion

3.1. Differential scanning calorimetry

3.1.1. Phase change materials

For this preliminary study, five PCMs were identified and obtained for further evaluation. DSC scans and the corresponding quantitative analyses of transition temperatures and enthalpies are provided in Fig. 1 and Table 2, respectively. In Fig. 1, the melting and solidification transitions for octadecane are seen to be much sharper than those for the polyethylene glycol (PEG) and paraffin wax PCMs, the latter actually exhibiting two separate peaks for both melting and solidification (30–40 °C and 50–60 °C). It can also be observed that the phase transition temperature of the polyethylene glycol PCM can be conveniently controlled by varying its molecular mass (e.g., chain length), with higher molecular masses providing a higher transition temperature. In Table 2, for each PCM, the enthalpies measured during melting and solidification are within 5 J/g of

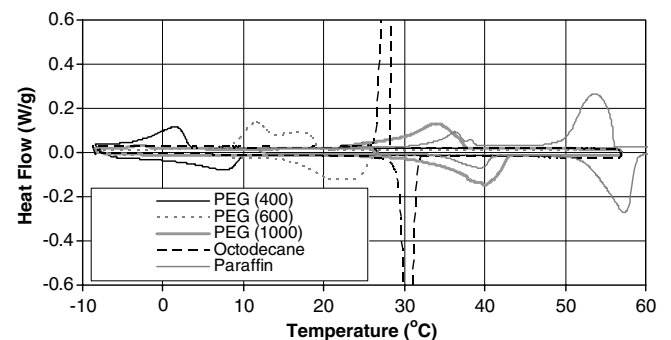


Fig. 1. DSC heating and cooling scans for the various PCMs investigated in this study. For the octadecane, the positive and negative peak values (not shown on this scale) were 1.29 W/g and -1.17 W/g , respectively.

Table 2
DSC analysis of phase change materials

Material	$\Delta H_{\text{cooling}}$ (J/g) (solidification)	Temperature range (°C)	$\Delta H_{\text{heating}}$ (J/g) (melting)	Temperature range (°C)
PEG: 400 MM	48.7	3.7 to -7.3	53.3	-5.6 to 10.7
PEG: 600 MM	107.9	20–0	112.6	3.6–28
PEG: 1000 MM	102.2	38.2–22.3	107.6	23–44
Octadecane	208.7	28.3–24.8	208.7	27.7–32.5
Paraffin wax	153.1	56.2–31.2	150.4	31.6–60.6

one another, an acceptable agreement. Previously, paraffin wax has been shown to be very stable during aging when impregnated into a variety of hardened concretes [2].

3.1.2. Phase change materials in LWA

A second set of DSC experiments were performed on two of the PCMs impregnated into individual LWA particles. Results obtained for the higher molecular mass PEG and the paraffin wax are provided in Figs. 2 and 3, respectively. For the PCM in the LWA, two scans are presented in Figs. 2 and 3 to provide some indication of the repeatability of the phase transitions. In the case of the paraffin wax PCM, peak temperatures were shifted to slightly higher values for both melting and solidification. In concrete, an added advantage of filling the porous LWA with the PCM as opposed to adding the PCM alone directly to the concrete is that because many PCMs, such as paraffin, have a low thermal conductivity [10], embedding them in a more thermally conductive material (e.g., certain LWA) will enhance the necessary heat transfer between the PCM and the bulk concrete.

3.2. Semi-adiabatic calorimetry

Initially, the MM = 1000 PEG was evaluated in the semi-adiabatic calorimetry setup. However, when impregnated into the porous LWA, this PCM was found to sub-

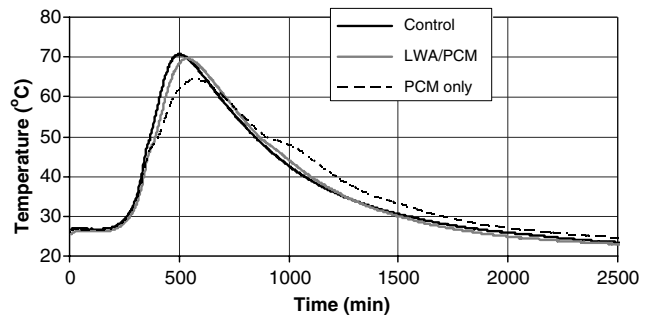


Fig. 4. Semi-adiabatic temperature curves for the three mortar mixtures investigated in this study.

stantially retard cement hydration. Thus, it appears that for successful utilization in fresh concrete, the PEG PCMs may have to be encapsulated by an inert material. Next, the paraffin wax PCM was considered. The semi-adiabatic temperature vs. time curves were measured for the control mortar, the mortar with LWA/PCM, and the mortar with the PCM added directly to the mixture (no aggregates). The second and third mixtures thus contained about 6 g and 27 g of PCM in their mixtures. Results are presented in Fig. 4. The influence of the PCM is clearly observed, producing “shoulders” at a temperature of about 50 °C on both the heating and cooling curves, delaying the peak temperature by up to slightly more than one hour, and lowering it by about 8 °C. As would be expected, the effects of the PCM are greater at increased addition rates.

A typical ASTM International Type I portland cement will have an ultimate heat of hydration of about 500,000 J/kg. Considering a concrete with a cement content of 400 kg/m³ and assuming a heat capacity of 1000 J/(kg K) and a density of 2350 kg/m³, the expected temperature rise under totally adiabatic conditions at complete hydration would be $(500,000 \times 400) / (1000 \times 2350) = 85 \text{ K (}^\circ\text{C)}$, enough to possibly boil any free water remaining in the concrete, if the concrete were placed at temperatures near 25 °C. Such a concrete, proportioned according to the guidelines of the American Concrete Institute (ACI) would contain about 1750 kg/m³ of fine and coarse aggregates. If it is assumed that about 20% of the aggregate mass could be comprised of (impregnated) paraffin wax, there could potentially be 350 kg/m³ of PCM in such a concrete. Taking the enthalpy of the PCM as 150,000 J/kg (Table 2 for paraffin wax), the expected adiabatic temperature rise would be reduced to $(500,000 \times 400 - 150,000 \times 350) / (1000 \times 2350) = 63 \text{ }^\circ\text{C}$, a reduction of over 25%. The actual efficiency of the PCM in a field concrete should be even greater, as few field conditions actually achieve totally adiabatic hydration conditions. Any heat losses to the surroundings will further decrease the energy source term (from hydration) for the control specimen, leading to a higher efficiency for the PCM than in the totally adiabatic case. For example, while one would calculate about a 4% reduction in peak temperature rise for the PCM only mixture presented in Fig. 4, in the curing conditions employed

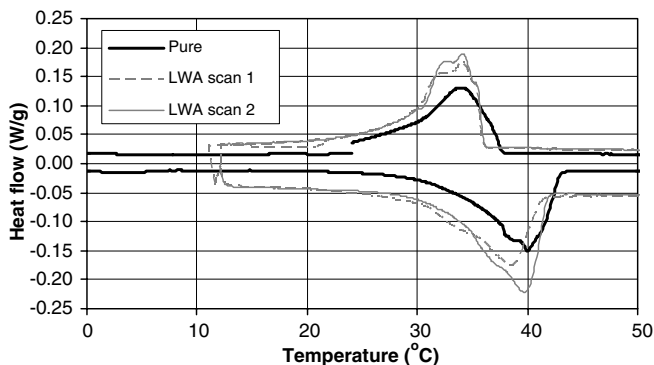


Fig. 2. DSC scans for a single PCM (polyethylene glycol with a molecular mass of 1000) in its pure form and when contained in a porous LWA.

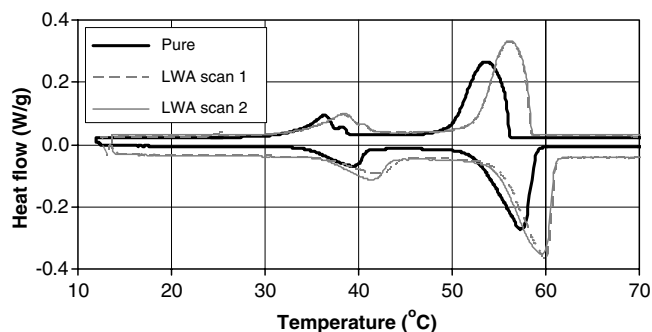


Fig. 3. DSC scans for a paraffin wax in bulk and when contained in a porous LWA.

Table 3

Simulated reduction in annual number of freeze/thaw cycles due to the presence of a PCM in the concrete

US city	National renewable energy laboratory (NREL) code	Number of freeze/thaw cycles for control concrete	Number of freeze/thaw cycles for PCM concrete	Simulated reduction with PCM (%)
Kansas city, MO	03947	81	63	22.2
Tampa, FL	12842	4	0	100.0
Lubbock, TX	23042	71	44	38.0
Tucson, AZ	23160	16	3	81.3
Cheyenne, WY	24018	131	106	19.1
Pierre, SD	24025	100	75	25.0
Seattle, WA	24233	34	18	47.1
Fresno, CA	93193	20	5	75.0
Baltimore, MD	93721	104	71	31.7
Bridgeport, CT	94702	104	83	20.2
Alpena, MI	94849	107	81	24.3
Waterloo, IA	94910	86	61	29.1
Total cycles		858	610	28.9

in this study, about a 15% reduction was actually observed. Of course, for successful field application of this technology, it must be further assured that the ultimate properties of the PCM concrete such as strength and durability will be similar or superior to those of the original concrete without PCMs.

3.3. Simulations of freeze/thaw cycling

The modified CONCTEMP computer model [8] was utilized to simulate the number of expected freeze/thaw cycles for bridge decks in twelve different climates available in the TMY2DATA files [9]. Simulations were first conducted for a control concrete containing no PCMs and then with the PCM as specified previously. The simulation results are summarized in Table 3 which provides the number of freeze/thaw cycles expected for the control and PCM concretes for the twelve different geographical locations, along with the projected reduction achieved in this quantity due to the addition of the PCM.

Table 3 indicates that on average about a 30% reduction in the number of freeze/thaw cycles might be achieved by the addition of the PCM to the concrete. Many of these avoided cycles would have occurred in late fall/early winter and late winter/early spring when temperatures are generally milder and both the amplitude (max–min) and duration of temperature cycles are reduced. Previously, simulations have indicated a greater number of freeze/thaw cycles for bridge decks relative to pavements [8] (which supports the old adage that bridges freeze before roads), further emphasizing bridge decks as the most likely candidates for the utilization of low temperature PCM concrete technology. Table 3 indicates that the efficiency of adding PCMs will be highly geography (climate) dependent. In locations with “extreme” winters, such as Cheyenne, WY, only about a 20% reduction in freeze/thaw cycles is to be expected. Conversely, in milder climates such as Tampa, FL, Tucson, AZ, or Fresno, CA, most or even all (for Tampa FL) of the freeze/thaw cycles might be avoided. The ideal situation for using low temperature

PCMs is when numerous freeze/thaw cycles occur (possibly even more than one per day), but the cycles are not extreme in that the temperature of the concrete falls only slightly below the freezing point of the pore solution. In such a case, the heat of solidification released by the PCM might provide enough energy to consistently maintain the concrete temperature above the freezing point.

4. Conclusions

Phase change materials hold promise in enhancing the performance of concrete technology in several applications. While PCMs may be added directly or in a microencapsulated form to concrete, porous lightweight aggregates can also be utilized as the “carrier” for the PCM. For example, an LWA with an absorption capacity of about 20% by mass could provide 350 kg/m³ of PCM in a typical concrete. As was demonstrated for mortars under semi-adiabatic curing conditions in this study, such addition rates could be used to limit the temperature rise (and subsequent rate of temperature decrease) of a large concrete section. Additionally, by using a lower transition temperature PCM, a significant fraction of the freeze/thaw cycles experienced by a bridge deck, for example, could potentially be avoided. While the preliminary feasibility of utilizing PCMs in such applications appears promising, further research and field testing will be needed to ultimately prove, disprove, and/or improve upon these concepts.

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