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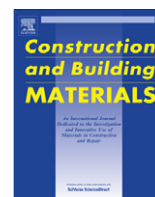
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Contents lists available at SciVerse ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Incorporation of phase change materials in cementitious systems via fine lightweight aggregate

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H I G H L I G H T S

- ▶ A novel apparatus was used to measure absorption of PCM by LWA.
- ▶ High viscosity PCMs were found to be impractical for use with LWA.
- ▶ This technology is most effective across the south and Pacific Northwest.

A R T I C L E I N F O

Article history:

Received 19 January 2012

Received in revised form 14 March 2012

Accepted 25 April 2012

Keywords:

Phase change material

Composite

Freeze/thaw

Lightweight aggregate

A B S T R A C T

A new technique to extend the service life of bridge decks, by reducing freeze/thaw damage through the incorporation of phase change materials (PCMs), has been investigated. The impregnation of two lightweight aggregates (LWAs) with four different PCMs was quantified, and compressive strength, isothermal calorimetry, and thermal property analyses were used to determine the effects of PCM incorporation on the physical properties of mortars. Physical and thermal property data were used to refine a previously-developed model and determine locations in the United States where PCM incorporation to reduce freeze/thaw damage may be a viable technology.

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1. Introduction

Phase change materials (PCMs) are substances with a high enthalpy of fusion (ΔH_f) that can be used to increase the thermal inertia of a system [1]. As solidification is an exothermic process (and melting an endothermic process), as a PCM changes phase, the surrounding environment is maintained at the phase change temperature of the PCM [2]. The length of time that this temperature can be maintained is dictated by the enthalpy of fusion of the PCM; a higher ΔH_f means more energy can be released or absorbed, maintaining temperatures for a greater length of time [3]. PCMs with a phase change temperature in the human comfort range have been investigated for several decades in building envelopes as a way to reduce HVAC energy usage by maintaining comfortable temperatures, and are increasingly being incorporated in commercially available products [4–7].

In addition to maintaining interior spaces at comfortable temperatures, PCMs can be used to reduce the number of freeze/thaw cycles experienced by systems such as bridge decks [8,9]. In a system containing PCM, as temperatures fall, the PCM will undergo an exothermic solidification reaction, the heat from which can delay the freezing of the surrounding concrete pore solution. The effectiveness of a PCM at delaying or preventing freezing is complex and depends on ΔH_f and the phase change temperature of the PCM, thermal characteristics of the concrete or mortar in which it is incorporated, local weather conditions, and incorporation methods [10].

Reducing freeze/thaw cycling is important, as such cycling leads to damage that makes a significant contribution to limiting the service life of a bridge deck [11]. As the pore solution in a concrete freezes it expands, creating pressures that lead to cracking, spalling, and degradation of mechanical properties. Freeze/thaw cycling alone causes a reduction in mechanical properties due to cracking, while the presence of cracks can exacerbate corrosion by providing aggressive media easy access to reinforcing steel and amplifying the amount of damage caused by successive freeze/thaw cycles [12].

Reducing the number of freeze/thaw cycles experienced by a bridge deck, and thus extending the bridge deck service life, would

Abbreviations: PCM, phase change material; LWA, lightweight aggregate; PEG, polyethylene glycol.

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have significant economic impacts. Some \$10 billion is spent on the maintenance of American bridges annually, yet this amount is not enough to maintain the bridge system in good repair [13]. The American Society of Civil Engineers issued a grade of “mediocre” to America’s bridges in 2009, the same year that the American Association of State Highway and Transportation Officials listed “age and deterioration” first on its list of the “top five problems for bridges” [13–15].

Previous studies [8–10] concluded that the use of PCMs to prevent freeze/thaw cycles is a technology that shows promise, and identified two areas (among others) that require further investigation: the carrier that is used to incorporate PCM in concrete, and the thermal properties of the final PCM/carrier/concrete composite. In the current study, two different lightweight aggregates have been investigated (an expanded clay and a naturally porous pumice) as incorporation methods for four different PCMs (PT4, PCM6, PEG400, and PEG600). The abilities of the aggregates to hold PCMs have been investigated, along with the effects of LWA/PCM incorporation on early age properties, strength, and thermal properties of mortars. The data collected during these experiments were used to update a previously developed service life prediction model [10]. It should be stressed that the development of PCM/LWA composites is still in its infancy, and there are many questions that will need to be answered in the future before such composites are ready for real-world applications. This research will help to serve as part of a foundation for such studies.

2. Materials and methods¹

In the preparation of the mortars, the cement used was a commercially available ASTM C150 Type I cement. Distilled water was used throughout. The aggregate was a mixture of four different normal-weight silica sands (‘S16’, ‘ASTM C778 – 20/30’, ‘ASTM C778 – graded’, and ‘F95’ sands) which has previously been used in studies involving LWA [16]. Four different PCMs were used: PCM6, a paraffin wax; PT4, a vegetable oil-based PCM; PEG400, a 400 molecular mass polyethylene glycol; and PEG600, a 600 molecular mass polyethylene glycol. PCM properties [8,10] can be found in Table 1. Two lightweight aggregates were investigated: a commercially available expanded clay and a naturally porous Greek pumice. The particle size distribution and water absorption/desorption properties of the two aggregates have previously been published elsewhere [17].

To measure the ability of PCM to impregnate LWA, a novel apparatus was constructed. The apparatus consisted of hat-shaped wire mesh baskets, the brims of which were supported by rods, allowing the crown/basket area to stand without touching any other surface. LWA was sifted to ensure that no particles finer than the mesh size of the baskets were present, and three replicate baskets were filled with between 20 g and 50 g of LWA. The apparatus was then placed in an oven at 40 °C to dry the LWA; baskets were weighed daily, and after four consecutive mass measurements were recorded that were within 0.1% of each other, the LWA was determined to be dry. The LWA was then submerged in liquid PCM for either one or 7 d. At the end of the soak, the LWA was returned to the baskets, which were allowed to drip-dry under ambient conditions for 2 h. The baskets were weighed, placed in an oven at 40 °C, and weighed with at least 24 h between measurements for at least 7 d thereafter. The average amount of PCM retained by the aggregate after 24 h of soaking in PCM and 24 h in the 40 °C oven was considered the impregnation capacity of the LWA and used for mixture proportioning (discussed below). Any PCM released by the LWA after an age of 24 h is unlikely to interfere with hydration, as the bulk of hydration will have already occurred. Whether any residue has been left on the surface of the aggregates was only addressed with qualitative observations of whether the aggregate appeared ‘wet’ or ‘dry’. However, as there is no other currently accepted method for determining the ability of PCM to impregnate LWA, this method provides a reasonable approximation, and was used in determining mixture proportions.

The composition of each mortar mixture can be found in Table 2. Three controls were produced; a mortar containing only sand aggregate, and two mortars, each containing either the expanded clay or pumice LWA soaked in water. The practice of using pre-soaked LWA in cementitious systems is commonly known as “internal curing” and is used to mitigate early age cracking due to autogenous shrinkage [18].

Table 1

Enthalpy of fusion, melt temperature, and chemical origin of four different PCMs used here. PEG data taken from [8].

Name	ΔH_f (J/g)	T_{MELT} (°C)	Origin
PCM6	162	6	Paraffin wax
PT4	195	4	Vegetable oil
PEG400	48.7	–7.3–3.7	Polyethylene glycol, M_w 400
PEG600	107.9	0–20	Polyethylene glycol, M_w 600

Mortars were prepared as described in ASTM C109, with the exception that the PCM-soaked LWA was added immediately after the regular aggregate. LWA was impregnated with PCM by agitation on a shaker–mixer for one hour followed by immersion for 24 h. The amount of water or PCM introduced via LWA in each mixture amounts to 50 kg/m³ of mortar, or roughly 2 wt.%. This amount is substantially lower than the amount that could be introduced if all aggregate was replaced with LWA, and is used here to provide a conservative estimate of the effectiveness and properties of LWA/PCM composites. Introducing more PCM would lead to higher effectiveness in reducing the number of freeze/thaw cycles to which a bridge deck is exposed, but would have more pronounced effects on strength, etc. and may be the subject of future inquiries.

The water:cement mass ratio was fixed at 0.4; the volume fraction of sand was 55%. The slightly high water:cement ratio was chosen to ensure that if any of the LWA remained unsaturated, it would not be possible for the LWA to absorb enough mix water to effect the overall properties of the final material. LWA was incorporated by replacing equal volumes of the normal-weight sand aggregate at appropriate gradations. In this way, the incorporation of the LWA altered the overall gradation of the aggregate as little as possible. The fresh mortar was cast in cube-shaped steel molds 50.8 mm on a side that were subsequently stored in sealed plastic bags in a constant temperature (25 °C) environmental chamber. Samples were demolded after 24 h and submerged in lime-saturated water until compression testing after 1 d, 7 d, and 28 d. Compression tests were carried out on at least three specimens of each mixture.

Isothermal calorimetry, which measures the rate of heat release from a hydrating mortar, was used to identify possible hydration retardation caused by PCM incorporation. The tests were carried out for 7 d, using between 7.4 g and 8.1 g of mortar, depending on the mixture. Specimens of mortar for isothermal calorimetry were taken from batches used to make specimens for compression testing, placed in a glass specimen vial, sealed, and loaded in the calorimeter, along with a reference vial containing only unhydrated cement powder. A 45 min holding period was used to allow the calorimeter to equilibrate, therefore, data on any very early hydration reactions were not recorded.

Two additional cubes were produced for thermal property analyses using Transient Plane Source (TPS) analysis, which has been described elsewhere [19,20]. Samples were tested at an age of 28 d. A 6.403 mm radius probe (Ni foil encased in Kapton) was placed between the two samples, which were stacked on top of each other and held down with a weight to ensure good probe/surface contact. The samples and probe were then placed inside a plastic bag to minimize evaporation. Subsequent measurements were taken with intervals of at least 45 min. At least five measurements of thermal conductivity and volumetric heat capacity (from which mass-basis specific heat capacity was later calculated, using sample density, measured during compression tests) were recorded. Measurements were taken at ambient temperatures with a power of 0.3 W applied over 10 s. According to the manufacturer, thermal conductivity measurements on homogeneous materials have a standard deviation of less than $\pm 2\%$, while the standard deviation of heat capacity measurements are $\pm 7\%$. No attempt was made to treat the data in such a way as to obtain values that reflect the thermal properties of concretes rather than mortars. Previous research has shown that the heat capacity of mortars and concretes are similar [21]. The thermal conductivities of concretes containing only siliceous aggregates are quite similar to those of (silica sand) mortars, while the heat capacities of those containing only limestone aggregates are typically about 25% lower. Finally, during freeze/thaw cycling, non-porous aggregates are not generally damaged – it is in the cementitious matrix that cracking initiates and propagates. As such, the actual measured data were used as a ‘first approximation’. Further study on concretes may be necessary to allow the drawing of more exact conclusions.

A previously developed, two-part model was used to determine PCM effectiveness. The CONTEMP program developed at the National Institute of Standards and Technology was used to determine the number of freeze/thaw cycles a bridge deck of a given mixture composition would undergo at each of 237 different locations; a service life model developed for the Indiana Department of Transportation was then used to predict the length of the bridge deck’s service life. Full details of these two models, and their use together, can be found elsewhere [10,22,23]. Briefly, service life is a combination of initial service life (the time it takes for a material to become so saturated with water that the volumetric expansion caused during a freezing event will lead to damage) and secondary service life (the time it takes for damage caused by freezing events to add up to a given drop in mechanical performance). In the previous study [10], assumptions were made regarding the heat capacity, thermal conductivity, and density of the concretes; here, the data were experimentally

¹ Certain commercial equipment, instruments, or materials are identified in this report in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 2

Mixture proportions by mass, in grams. Abbreviations: C = control; G = expanded clay; P = pumice; 6 = PCM6; 4 = PT4; 400 = PEG400; 600 = PEG 600. Weights of pumice and expanded clay are dry measures.

Mixture	C1	C2	C3	G6	G4	P6	P4	G600	G400	P600	P400
Cement	1000										
Water	400	480	480	400							
F95 sand	572.7	546.4	572.7	542.4	544.9	572.7	572.7	560.5	557.6	572.7	572.7
Graded sand	435.3	388.0	435.3	380.8	385.2	435.3	435.3	413.2	377.8	435.3	435.3
20–30 sand	435.3	335.4	435.3	320.2	329.5	435.3	435.3	388.7	408	435.3	435.3
S16 sand	847.6	495.6	530.1	441.9	474.6	347.6	514.6	683.3	644.8	493.6	503.6
Pumice	–	–	317.5	–	–	500	333	–	–	354	344
Expanded clay	–	302	–	348	320	–	–	141	174	–	–
PT4	–	–	–	–	80	–	80	–	–	–	–
PCM6	–	–	–	80	–	80	–	–	–	–	–
PEG400	–	–	–	–	–	–	–	–	80	–	80
PEG600	–	–	–	–	–	–	–	80	–	80	–

determined for mortars using TPS analysis. The transition temperature and enthalpies of solidification of the PCMs have previously been published [10,23]. For PEG400 and PEG600, broad transition temperatures were previously reported; therefore, the highest temperature values, of 3.7 °C and 20 °C, respectively, were used. A conservative loading of 50 kg/m³ PCM, roughly 2% by mass and the same as used in the laboratory experiments (compressive strength, isothermal calorimetry etc.), was used in the modeling.

3. Results and discussion

3.1. PCM impregnation

The impregnation of PCM6 and PT4 in two different LWAs were measured (Fig. 1). After the LWA was removed from soaking in PCM and allowed to drain under ambient conditions for 2 h, the aggregate particles were dry to the touch. Both LWAs were impregnated with slightly more PT4 than PCM 6 after 1 d of soaking (Fig. 1a).

A longer soaking times leads to a higher amount of PCM impregnated in the LWA, an effect that is slightly more pronounced

in PCM6. The reason for this difference between PCMs is unclear, but may be related to their slightly different viscosities. However, in real-world applications an extra week of soaking LWA so as to increase the amount of PCM in a mixture by roughly 10–35% may not be practical. Additionally, the uncertainty measured for pumice is generally lower than that for the expanded clay, possibly due to the more homogeneous size distribution of the pumice particles. Although the quantity of PCM absorbed by the LWAs decreases during storage at 40 °C, the internal temperature of a concrete reaches 40 °C only for a brief period during early hydration and possibly during the summer months, depending on location. The release of PCM from LWA is therefore likely, in practice, to be less pronounced.

A second set of impregnation tests were performed using two polyethylene glycols (PEG400 and PEG600). After 1 d of soaking, the expanded clay absorbed substantially more of the PEG PCMs than either of the other two, respectively (Fig. 2a). During storage in the 40 °C oven, neither of these amounts changed appreciably,

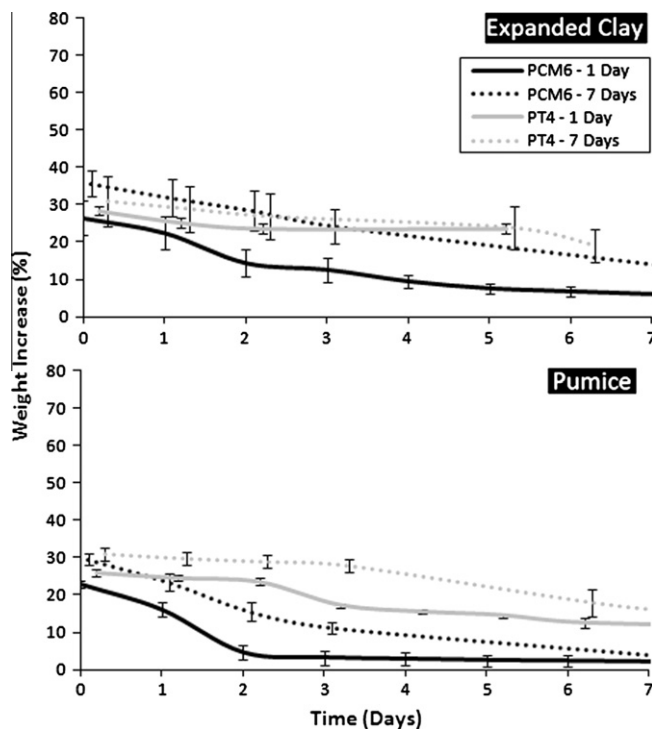


Fig. 1. Weight loss during storage in a 40 °C oven of expanded clay (top) and pumice (bottom) after soaking in PCM6 (black) or PT4 (gray) for 1 d (solid lines) or 7 d (dashed lines). Error bars are slightly offset to avoid overlap and indicate one standard deviation from the average of the measured data.

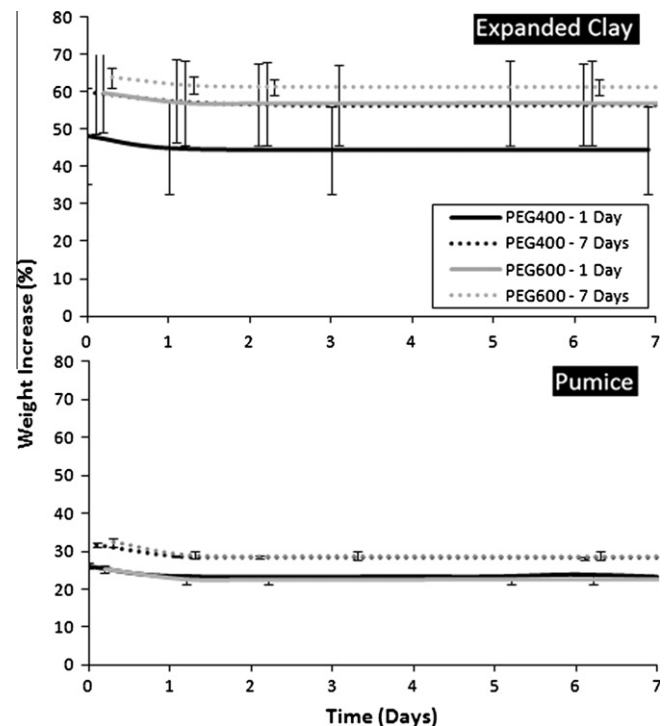


Fig. 2. Weight loss during storage in a 40 °C oven of expanded clay (top) and pumice (bottom) after soaking in PEG400 (black) or PEG600 (gray) for 1 d (solid lines) or 7 d (dashed lines). Error bars are slightly offset to avoid overlap, indicate one standard deviation from the average of the measured data, and may be too small to be clearly observed.

and increasing the soaking period to 7 d resulted in an increase in the amount impregnated that was not statistically significant. Similar behavior was observed in pumice (Fig. 2b). Qualitatively, both the expanded clay and pumice appeared 'wet' or 'sticky' after soaking, implying that the LWA was not only impregnated by the PEG, but that the PEG was also wetting the surfaces of the aggregate. This wetting behavior is due to surface tension and the fact that the long-chain molecule nature of PEG produces a relatively high viscosity, much higher than those of the PT4 or PCM6. This higher viscosity prevents the PEG from evaporating or dripping away from the surfaces of the aggregate during oven storage.

Although the LWAs were impregnated with a much larger amount of PEG, compared with the PCM6 and PT4, the fact that much of this 'impregnation' was simply wetting of the surface could prove to be a problem during cement hydration, as discussed below. It also helps to obscure the amount of additional PEG impregnated when the soaking period is increased from 1 d to 7 d.

3.2. Compressive strength

Compressive strength was measured for a total of 11 different mixtures, including three controls (mixture proportions can be found in Table 2): Control 1, a standard mortar with no PCM or LWA; Control 2, containing expanded clay that had been soaked in water; and Control 3, containing pumice that had been soaked in water (Fig. 3).

All mixtures incorporating LWA showed reduced compressive strengths at all ages (Fig. 3). Generally speaking, the compressive strengths of mixtures containing PT4 are lower than the compressive strength of the control mixture at ages of 1 d and 28 d, while only moderately lower than the compressive strength of the control mixture at an age of 7 d. Mixtures containing PCM6 generally experienced only a small reduction in compressive strength compared to the control mixture at an age of 1 d, but this reduction in compressive strength is larger at 7 d and larger still at 28 d.

Mixture Control 2, which contained water-soaked expanded clay, sees a decrease in strength of 13.7% at 1 d, but levels off to decreases of 5% and 4.6% at 7 d and 28 d, respectively, while Mixture Control 3, which contained water-soaked pumice, sees a consistent drop in compressive strength by roughly 25% at all ages. Replacing normal weight sand with a more porous lightweight sand can certainly contribute to a reduction in compressive strength that can be partially compensated for at later ages via the increased hydration provided by the internal curing water. Finally, the compressive strengths of the four mixtures containing PEG PCM are substantially reduced across the board. All four mixtures are, however, consistent regardless of aggregate or which of the two PEGs were used (PEG400 or PEG600; Fig. 3).

The decreases in compressive strengths observed for mortars with PCMs in LWAs can be attributed to a variety of origins. First, the porous nature of the LWAs make them weaker in compression than the normal weight sand aggregate. Second, only one particle size of pumice (similar to the S16 sand in the normal aggregate) was used, while the expanded clay has a broader size distribution; the pumice therefore altered the particle size distribution and the packing efficiency of the aggregate, which can lower strength. Third, interfacial effects, such as weak bonding between the aggregates and cement paste, cannot be discounted, but were not investigated further here and may not be the same for both expanded clay and pumice. Finally, the PCMs may each have had an effect; it was observed during the drainage tests that a relatively large quantity of the PEG PCMs stuck to the surface of the aggregates, and likely entered the mix water during mortar production, possibly coating unreacted cement particles and inhibiting hydration. The specific trends observed are likely due to some combination of these four effects.

These decreases in strength would be prohibitive in the deployment of LWA/PCM composites in real-world applications, however, they can also be addressed with a variety of countermeasures. Supplementary materials such as silica fume can be used to increase

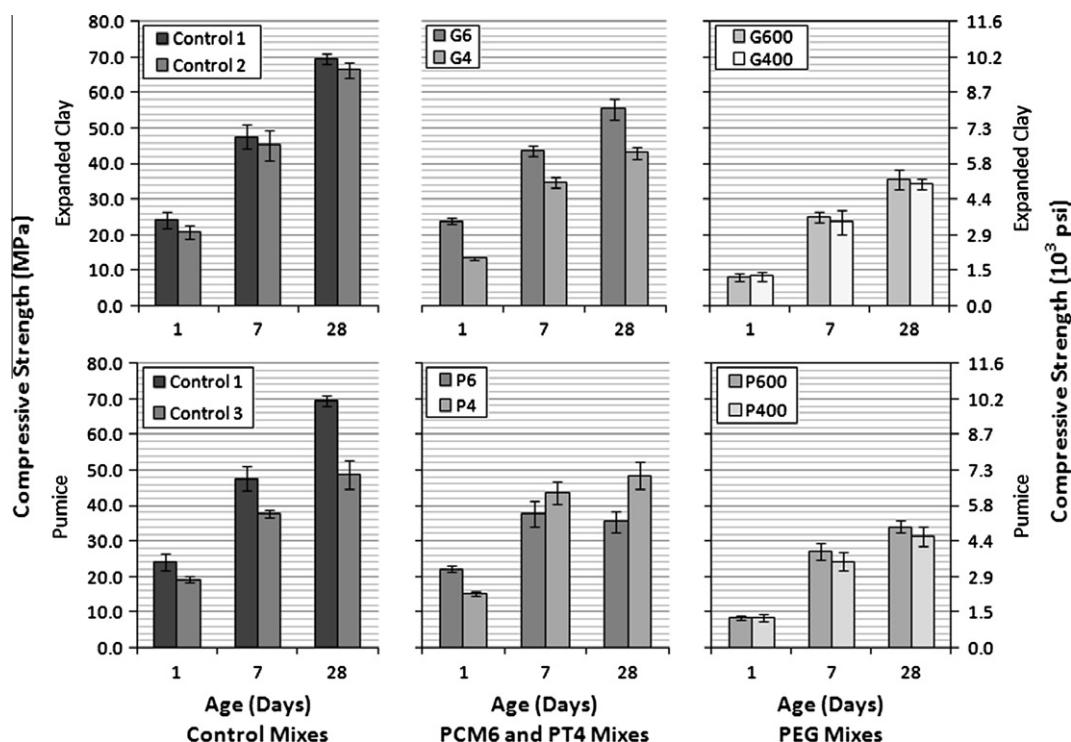


Fig. 3. Compressive strengths of mixtures containing no LWA/LWA with water (left column); PCM6 or PT4 (center column); and PEG400 or PEG600 (right column) in either expanded clay (top row) or pumice (bottom row). The scale is the same on all charts. Error bars indicate one standard deviation from the average of the measured data; abbreviations as given in Table 2.

compressive strength, as can reduced water:cement ratios. Such techniques have their own hazards, such as increased incidences of early-age cracking (which can be countered through the use of internal curing), and may be an important area of future research.

3.3. Calorimetry

To quantify the effects of PCM incorporation on cement hydration, isothermal calorimetry was used to monitor heat evolution, which is directly related to the degree of hydration. In terms of both the rate of heat release and cumulative heat release, the profiles of the three control mixtures are essentially identical (Fig. 4a). A recent review by Bullard et al. notes that the dissolutions of C_3S and C_3A into various ionic species are strongly exothermic ($\Delta H = -137.6$ and -248.3 kJ/mol, respectively), whereas the precipitation of C–S–H(I) and C–S–H(II) from ionic solutions is relatively weak ($\Delta H = \sim -20$ kJ/mol) [24]. The inclusion of water-soaked LWA, therefore, has little effect on the dissolution reactions taking place in the control mixture at an early age (otherwise a decrease in heat evolution would be observed). However, the effect of water-soaked LWA on the ability of dissolved ionic species to produce

strength-bearing C–S–H phases cannot be determined with calorimetry – a large change in C–S–H precipitation would have only a small influence on heat evolution. The decrease observed in the compressive strength of the Control Two and Control Three mixtures are therefore most likely to be due to mechanical causes (i.e. porous aggregates), but chemical causes (i.e. interference in C–S–H precipitation) cannot necessarily be ruled out.

There is one outlier among the heat release and cumulative heat release curves of the four mixtures containing non-PEG PCMs; the mixture containing PT4 in pumice, in which the heat release is slightly elevated (Fig. 4b). This may be due to the heterogeneous nature of the mixture, in which an uneven amount of binder or aggregate was placed in the vial, due to a discrepancy in plotting, or due to some unknown reaction. The discrepancy is sufficiently small, however, to say that the four curves are essentially identical. As with the Control Two and Control Three mixtures, purely mechanical considerations (i.e. due to the incorporation of an aggregate that is not as strong as normal weight silica sand) have an effect on compressive strength. However, the strength loss in the four non-PEG mixtures is greater than that seen in the controls; therefore, the PCM must be having some effect. This may be due to the PCM interfering with the precipitation of strength bearing C–S–H phases, as alluded to above, and/or possibly due to an effect of the PCM on the aggregate/matrix interface. Further chemical analyses of the binding matrix and microstructural analyses of the aggregate/matrix interface are needed to arrive at a conclusive answer.

A previous study observed that the incorporation of expanded clay soaked in PCM6 had no effect on hydration reactions, whereas the incorporation of expanded clay soaked in PT4 had a substantial effect, both retarding and suppressing hydration [10]. That study assumed that the expanded clay could absorb the same amount of PT4 as it could water; here, less PT4 was used as a result of the drainage measurements made above, and substantially less retardation was observed. Substances such as PT4, known to retard cement hydration, can be safely incorporated using LWA, however, an understanding of how much of the substance the LWA can absorb is critical.

The calorimetric data for samples containing PEG, however, show both retardation (delay in peak times) and suppression (reductions in peak heights) of hydration (Fig. 4c). For all mixtures containing PEG, regardless of the molecular weight of the PEG or the LWA used, peak heat evolution decreased by roughly 40%, while the time to peak heat evolution was delayed by several hours. It was observed during the impregnation measurements that the LWA appeared ‘wet,’ with significant amounts of PCM adhering to the particle surface; this non-absorbed PCM is likely to have entered the mixing water and interfered with chemical reactions. This occurs due to the long-chain nature of the PEG molecule; when PEG enters the mix water, it can wrap around or ‘coat’ cement particles, making it more difficult for the particles to react with water and begin producing strength-bearing phases; such effects have been previously observed [25].

The decrease in compressive strength of the mixtures observed above is therefore due to both mechanical reasons (the relative weakness of the LWAs) and chemical reasons (the PEG PCMs interfering in hydration).

3.4. Thermal properties

The thermal properties of PCM/LWA cementitious composites are important factors for practical use, as thermal properties dictate how quickly energy can be released by a solidifying PCM and how quickly a PCM can be ‘refilled’ by absorbing energy from the ambient environment or direct solar radiation. The 11 different mixtures investigated here show little variation, although mixture Control 1, without LWA or PCM, had both the highest thermal conductivity and lowest specific heat by mass (2.69 ± 0.24 W/

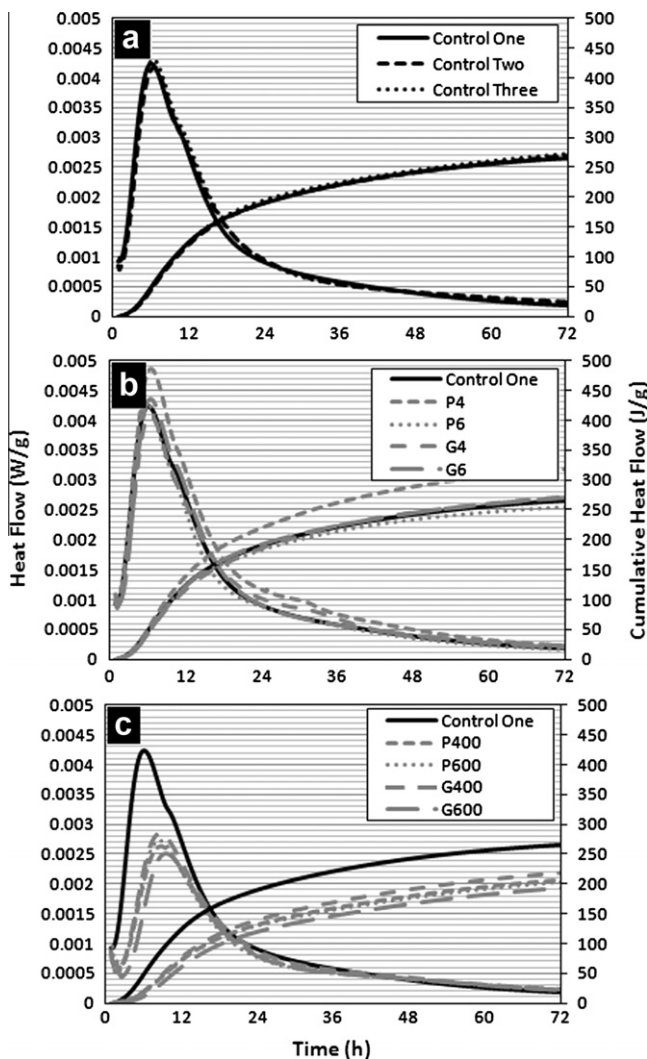


Fig. 4. Isothermal calorimetry of (a) the three control mixtures; (b) mixtures containing either expanded clay or pumice soaked in PCM6 or PT4; and (c) mixtures containing either expanded clay or pumice soaked in PEG400 or PEG600. Primary axis shows heat flow (W/g); secondary axis shows cumulative heat flow (J/g), each normalized by the cement content of the sample. Mix control one is shown in all graphs for comparison purposes. Abbreviations as given in Table 2.

Table 3

Thermal properties and effectiveness of eight mixtures containing PCM. Abbreviations as given in Table 2.

Mix	Thermal conductivity (W/m K)	Specific heat capacity (J/g K)	Volumetric heat capacity (MJ/m ³ K)	Avg. thermal diffusivity (m ² /s)	Locations where effective (#)
Con. 1	2.7 ± 0.24	0.4 ± 0.19	0.9 ± 0.4	3.0	n/a
Con. 2	2.1 ± 0.18	0.6 ± 0.28	1.3 ± 0.6	1.6	n/a
Con. 3	2.4 ± 0.03	1 ± 0.03	2.1 ± 0.1	1.1	n/a
P600	2.2 ± 0.28	0.5 ± 0.33	1.1 ± 0.7	2.0	3
P400	2.0 ± 0.25	0.4 ± 0.24	0.8 ± 0.5	2.4	5
G600	2.4 ± 0.16	0.6 ± 0.19	1.2 ± 0.4	2.0	13
G400	2.3 ± 0.19	0.6 ± 0.23	1.2 ± 0.5	1.9	27
G6	2.1 ± 0.06	0.7 ± 0.2	1.5 ± 0.4	1.4	57
P4	2.0 ± 0.06	0.5 ± 0.16	1.1 ± 0.3	1.8	58
P6	2.3 ± 0.02	1 ± 0.05	2.2 ± 0.1	1.1	88
G4	2.3 ± 0.04	0.9 ± 0.12	1.8 ± 0.3	1.3	101

m K and (0.40 ± 0.19) J/g K, respectively (Table 3; the error reported here represents one standard deviation of the measured data). The lowest thermal conductivity was observed in mixture P4, which averaged (2.02 ± 0.06) W/m K, 25.1% lower than the control; the highest specific heat by mass was observed in mixture P4, which averaged (1.04 ± 0.05) J/g K, two and a half times higher than the control. All samples here were tested in a saturated surface dry condition, as the thermal properties of the system are most prominent when the structure is wet, and thus in danger of damage from a freeze/thaw cycle; drying has previously been shown [10] to lower thermal conductivity by up to 0.3 W/m K, not enough to account for the differences observed here.

3.5. Modeling

The service life model has a number of limitations regarding the two control mixtures containing internal curing. First, the rate at which water desorbs from the LWA and fills the pore system is not taken into account, although this would have a substantial effect on the initial service life (i.e. how long it takes for the material to become so saturated with water that a freezing event will result in damage). Second, after water is desorbed from LWA, the porosity in the LWA may (or may not) provide empty space into which freezing pore solution may expand, reducing the capacity of freezing to cause damage and increasing service life. Finally, calculation of initial service life is influenced by the difference between initial sorptivity and secondary sorptivity. Information regarding systems

in which internal curing has a pronounced effect on internal humidity, and thus sorptivity, is limited [26]. As the model has no mechanism for addressing issues related to internal curing, and assumptions that could be used as workarounds are not immediately apparent, mixtures Control Two and Control Three were therefore not investigated by modeling.

When determining increases in service life due to PCM incorporation, all other mixtures were compared to mixture Control One, the 'standard' system. Modeling of mixture control one shows that there are a total of 58 locations where freeze/thaw damage is not an important factor in deterioration. These locations are either so dry that a system rarely becomes saturated enough for freezing to cause damage (initial service life is greater than 20 years), or so warm that freezing events rarely occur, no matter the saturation level of the system (secondary service life is greater than 20 years). These locations are primarily in the west (Arizona and New Mexico north to Montana) and along the Gulf Coast, Pacific Coast, and overseas territories, respectively. In a further 75 locations, predominantly in New England and the Midwest, the incorporation of PCM has only a minor effect, increasing service life by less than one year,

In a total of 104 locations, one of the eight mixtures incorporating 50 kg/m³ of PCM6, PT4, PEG400, or PEG600 increased service life by at least one year (Fig. 5). By quartile: in 43 locations, only one or two of the eight mixtures increased service life by at least a year; in 35 locations three or four of the eight mixtures increased service life by at least a year; in 22 locations either five or six of the eight mixtures increased service life by at least one year; and in

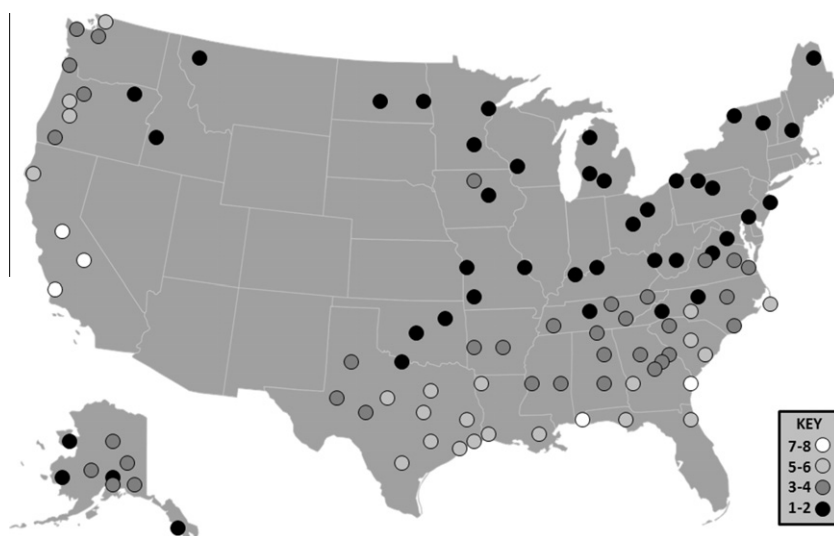


Fig. 5. Map of locations in which the eight mixtures incorporating PCM investigated here increase bridge deck service life by at least 1 year. Point color indicates how many of the eight mixtures were effective, by quartile: black indicates 1 or 2 mixtures increased service life, white indicates 7 or all 8 mixtures increased service life etc. n.b.: not to scale.

five locations either seven or all eight of the mixtures increased service life by at least one year. If all location/mixture combinations are evaluated (not just those where service life was increased), these four quartile groups represent average increases of 0.5 years, 1.2 years, 4.2 years, and 10 years, respectively. More mixtures were effective in regions with milder weather (i.e. the Southeast compared to the Northeast, and the West Coast compared to the inland west). At least 48 of the 100 most populous American cities are in states where an average of two or more PCMs increased service life by at least one year; these cities, combined, have a population of slightly over 26.7 million people [27].

Specific trends regarding the effectiveness of a mixture are difficult to identify (Table 3). Generally, the mixtures containing PEG were effective in fewer locations than mixtures containing non-PEG PCM. Mixtures containing expanded clay as the LWA were effective in more places if PEG400 or PEG600 was used, but performed roughly equal to pumice when non-PEG PCMs were used.

According to the modeling, although there is little correlation between effectiveness and either thermal conductivity or volumetric heat capacity, a distinct trend is observed when effectiveness is compared with thermal diffusivity (i.e. thermal conductivity divided by heat capacity). Mixtures with higher thermal diffusivities are less effective at preventing freeze/thaw cycles, as the mixture will reach thermal equilibrium with the environment more rapidly than a mixture with a low diffusivity. Conversely, if the thermal diffusivity is too low, heat from the solidifying PCM will not be able to spread throughout the entire bridge deck, leading to localized freeze/thaw damage. In the modeling results, this trend was not observed, as the model does not take into account the size of the LWA, or the distance that heat must travel to reach every part of the bridge deck.

In reality, thermal diffusivity must be balanced by the spatial distribution of the PCM, similar to the concept of “protected paste volume” in internal curing studies [28,29]. Composites with relatively fine LWA will have an even distribution of PCM, and the ability of heat to travel through the matrix and reach all corners of the system is not as important. A low thermal diffusivity material can be used, lowering heat transfer from the bridge deck to the environment. In composites with relatively coarse LWA, the distribution of PCM will be less even, and heat will need to be able to move through the matrix more easily, to prevent localization of freeze/thaw damage. In this case, a high thermal diffusivity material must be used, at the cost of increased transfer of heat to the environment. The development of a more detailed understanding of the relationship between the size distribution of the LWA, thermal diffusivity, and effectiveness at reducing freeze/thaw damage will be necessary in the future.

4. Conclusions

A novel method was used to determine the amount of four phase change materials that could be impregnated into two lightweight aggregates. The previously observed detrimental effects on cement hydration of incorporating PT4 [10] were avoided by incorporating this impregnation data into the subsequent mortar mixture proportions. Although all mixtures containing LWA had a lower compressive strength than the control mixture, the strength decrease was only so large as to prohibit practical application in mixtures containing PEG-based PCMs.

The refinement of the previously developed hybrid model, to use more experimental data and fewer assumptions, has shown that the most important property governing the effectiveness of PCM at reducing freeze/thaw cycling is thermal diffusivity, or how quickly the system reaches thermal equilibrium with the environment. The model results show that a low thermal diffusiv-

ity (i.e. slow transfer of heat through the material) is more effective; in reality, it is likely necessary to balance thermal diffusivity and aggregate size, which determines how far heat must travel through the matrix to keep the entire bridge deck warm. In 104 out of 237 locations investigated, a conservative dose of 50 kg/m³ of PCM would increase bridge deck service life by at least one year, primarily throughout the southern United States and the West Coast. These preliminary results suggest that the use of PCM/LWA composites shows promise in reducing freeze/thaw damage in bridge decks and merits further, more detailed investigations.

Acknowledgement

The authors would like to thank Entropy Solutions Inc. for providing samples.

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