

Quarterly Report: 2nd Quarter (January 1 2016 – March 31 2016)

1	Deviations from plan
	None to report for this quarter
2	Progress made since last reporting
	This is the second quarterly report for this project. The progress made during this time are listed below. The team is progressing as per schedule on the several tasks. Details are provided below. Work towards several deliverables are ongoing.
3	Published deliverables and achieved milestones
	PCM selection (both microencapsulated and liquid) has been completed, as is the characterization of thermophysical properties of the PCMs. In this report, work belonging to several work packages that are being carried out are reported.
4	Any problems that occurred and solutions found
	No problems have occurred in the first quarter of this project.
5	Financial Progress
	The partner universities and organizations have been provided the respective share of the pre-financing amount, and the coordinator is monitoring the progress carefully. The project manager for ECLIPS, Lisa Schulze at Arizona State University is overseeing the financial progress and other aspects between all partners.

The following activities are in progress. The activities are detailed below, based on the work packages that they belong to.

WP1: Selection, characterization and optimization of PCMs and delivery strategies:

The PCM selection part of this WP was completed for the range of experimental and numerical studies that will form part of this project. The microencapsulated PCM chosen was the Enfinit series of PCMs, manufactured by Encapsys Inc., who has been providing the research group with the microencapsulated PCM and Entropy solutions, who manufactures the PureTemp series of liquid PCMs. The microencapsulated and liquid PCMs have transition temperatures of 4, 25, and 36°C. We have also used Micronal series of PCMs from BASF for comparative purposes, especially the efficiency of microencapsulation. The results reported here corresponds to microencapsulated PCMs Micronal (PCM-M) and Encapsys (PCM-E) with a transition temperature of ~25°C.

(a) Encapsulating PCMs in silica capsules:

For this work, and taking into account the range of temperatures needed for the final application, two phase change materials with the transition temperature one around 22°C and the second one around 53°C (paraffin)¹ have been chosen. We are researching a synthetic route for the silica microencapsulation of the mentioned PCMs by combining sol-gel reaction and emulsion technique. Initially we have started working with alkoxysilanes as starting materials and the heptadecane phase change material. By the sol-gel method silica materials can be synthesized under very mild solution conditions and by applying emulsion techniques, encapsulation by that silica material can be obtained. Sol-gel mechanism involves

¹ *Renewable and Sustainable Energy Reviews* **13**, 2009, 318-345

hydrolysis and condensation reactions of an alkoxy silane starting material catalyzed by an acid or base. By changing the reaction parameters (such as type of alkoxy silane compound, alkoxy silane-water ratio and pH) materials with different properties can be obtained (different particle size, porosity and morphology among others). We are exploring different synthetic routes and different reaction parameters in order to obtain the best path for the synthesis of silica microencapsulated heptadecane and some of these will be briefly described next. The time of hydrolysis as well as volume of water in the emulsion step have been changed in order to study their effect on the morphology of the product obtained (see Table 1). Overall, microcapsules of different sizes have been obtained in each case as can be seen in the scanning electron microscopy images shown in Figure 1. In the images, spherical particles and also particles/microcapsules that are broken can be observed. The broken microcapsules prove that the spherical particles are indeed hollow. This means that, during the synthesis, the silica shell has been formed around the PCM obtaining thus hollow silica particles (i.e. microcapsules). However, in the images one can also observe that there is a high quantity of broken material and also that the shells of those microcapsules seem to have quite a few pores. The samples were characterized by FTIR spectroscopy and this showed that they contain organic material (heptadecane) as well as silica. However, there is a possibility that part of the organic material is not encapsulated and is outside of the microcapsules. Furthermore, because of the porosity that the silica shells display, the PCM could flow out through the pores as well. Because of this, and with the idea of improving the encapsulation, we are investigating other synthetic paths as well. For example, we are using surfactants to help the emulsion process and so improve the encapsulation yield as well as lower the porosity of the shell of the microcapsules.

Table 1. Synthesis carried out by varying the time of hydrolysis and volume of water in the emulsion step

Starting material	Ratio of the hydrolysis parameters TEOS:EtOH:H ₂ O:HCl	Time of hydrolysis (h)	Heptadecane (mL)	Volume of H ₂ O in emulsion (mL)
Tetraethoxysilane (TEOS)	1:4:1.3x10 ⁻³	1	3	25
TEOS	1:4:1.3x10 ⁻³	1	3	50
TEOS	1:4:1.3x10 ⁻³	3	3	50
TEOS	1:4:1.3x10 ⁻³	3	3	125
TEOS	1:4:1.3x10 ⁻³	5	3	25
TEOS	1:4:1.3x10 ⁻³	5	3	50
TEOS	1:4:1.3x10 ⁻³	5	3	75
TEOS	1:4:1.3x10 ⁻³	≥20	3	50
TEOS	1:4:1.3x10 ⁻³	≥20	3	125

Figure 1 shows SEM images of solids obtained in the experiments. Some of the surfactants that have been used so far in this reaction are Span 80, Tween 65 and a combination of Span 80-Tween 80. The concentration of the surfactant as well as its chemical characteristics are key parameters in order to form a good emulsion. The surfactants have been added in the emulsion step and the solids obtained in the reactions have been characterized by SEM and FTIR.

Next steps: In the following months we will keep studying and characterizing in more detail some of the synthetic routes and materials developed so far, the ones that may give us the most information on how to improve the encapsulation synthesis and we will research also other synthetic pathways. Furthermore, we will also start working on the encapsulation of the paraffin wax.

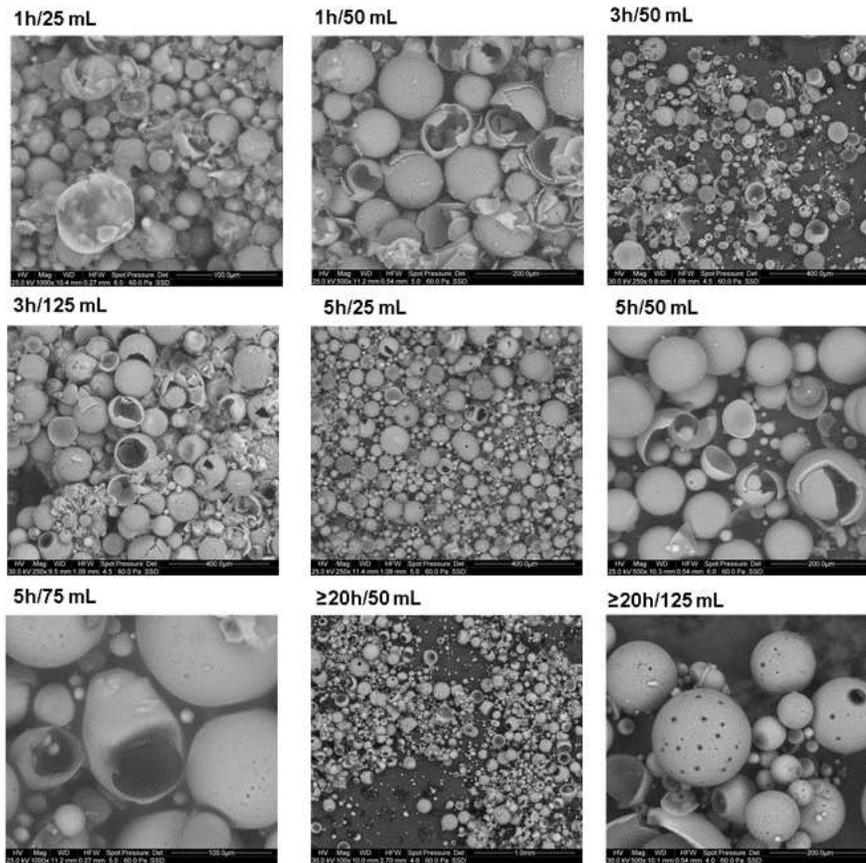


Figure 1. Scanning electron microscope (SEM) images of the solids obtained in the experiments shown in Table 1.

(b) Encapsulating liquid PCMs in lightweight aggregates:

In this stage, we are investigating the use of lightweight aggregates of different types to impregnate PCMs. Figure 2 shows the different lightweight aggregates being investigated, and Table 2 shows their properties.

Table 2: LWAs and their properties.

LWA	S.G. (OD)	S.G. (SSD)	PCM Absorption, % by vol.	Average Pore Diameter (μm)	Porosity
Pumice	1.45	1.75	21.1	516	0.39
Perlite	1.72	1.81	11.2	580	0.15
Exp. Slate	1.77	1.99	10.6	247	0.30
Exp. Shale/Clay	1.07	1.33	15.7	361	0.53

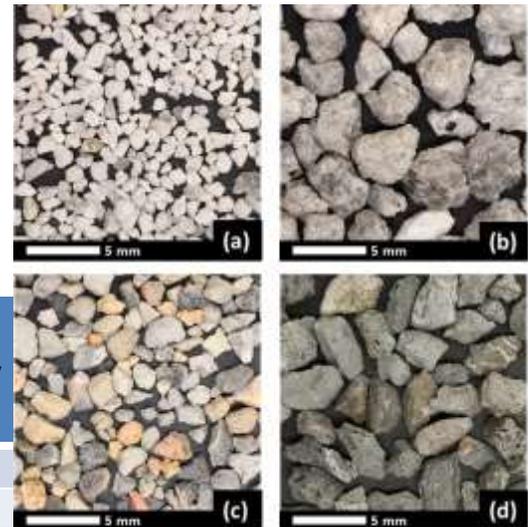


Figure 2: Lightweight aggregates for encapsulation (a) Pumice, (b) perlite, (c) expanded shale and clay, (d) expanded slate

WP2: PCM-cement composites: Microstructural and thermomechanical properties

(a) Dispersion and properties of PCM in pastes and mortars:

The dispersion characteristics of PCM-M and PCM-E in hardened cement paste are presented here through the use of μ CT (computed tomography). Cubic volumes of interest of sizes ranging from $600^3 \mu\text{m}^3$ to $900^3 \mu\text{m}^3$ were extracted from different areas of the original 3D reconstructions, in order to determine the influence of the size of the representative volume element (RVE) on the accuracy of the extracted volume fraction and dispersion parameters of the PCMs. A transition point-based thresholding approach (in the grey scale histogram), where a small increment in the threshold values causes a sharp change in the detected phase quantities, is employed to effectively segment PCM phases in the cement paste. Figures 3(a) and (b) show the distribution of PCM-M and PCM-E respectively in a cubic RVE of $900 \mu\text{m}$ edge length. Figure 3(a) clearly shows large PCM-M capsules which are agglomerated. On the contrary, a more uniform distribution of smaller particles of PCM-E in the cement paste is shown in Figure 3(b), which likely influences the mechanical behavior of these systems.

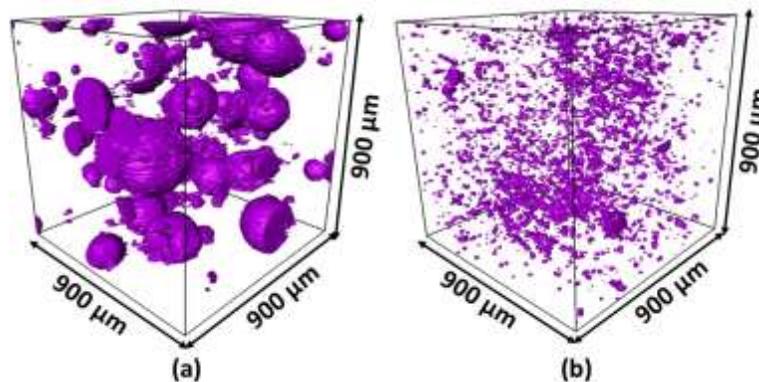


Figure 3: Representative cubical volumes of interest ($900^3 \mu\text{m}^3$ RVE) extracted from the μ CT dataset for: (a) PCM-M and (b) PCM-E.

The influence of PCMs on the cement hydration reactions and the amounts of hydration products formed was evaluated using thermogravimetric (TG) analysis. To evaluate the influence of PCMs on cement hydration, the calcium hydroxide (CH) contents in these pastes, normalized by the mass of OPC in the paste, were determined as a function of the PCM volume fraction. For pastes containing both types of PCMs, the normalized CH content increases with PCM volume fraction, and the effect is more pronounced for the systems containing PCM-E. This indicates that the smaller PCM particles act as nucleation sites for the formation of CH.

The compressive strength development as a function of age for mortars containing different volume fractions of PCM as replacement of the fine aggregate (sand) are shown in Figures 4(a) and (b) for mortars containing PCM-M and PCM-E respectively. While there is a consistent reduction in strength when PCM-M replaces sand in the mortars, the strengths of mortars containing up to 15% of PCM-E by volume are higher than that of the plain mortar at all ages. Similar trends are noticed in flexural strengths, as shown in Figure 4(c). More details are reported in a paper submitted for publication recently².

² Aguayo, M., Das, S., et al., Submitted to Cement and Concrete Composites

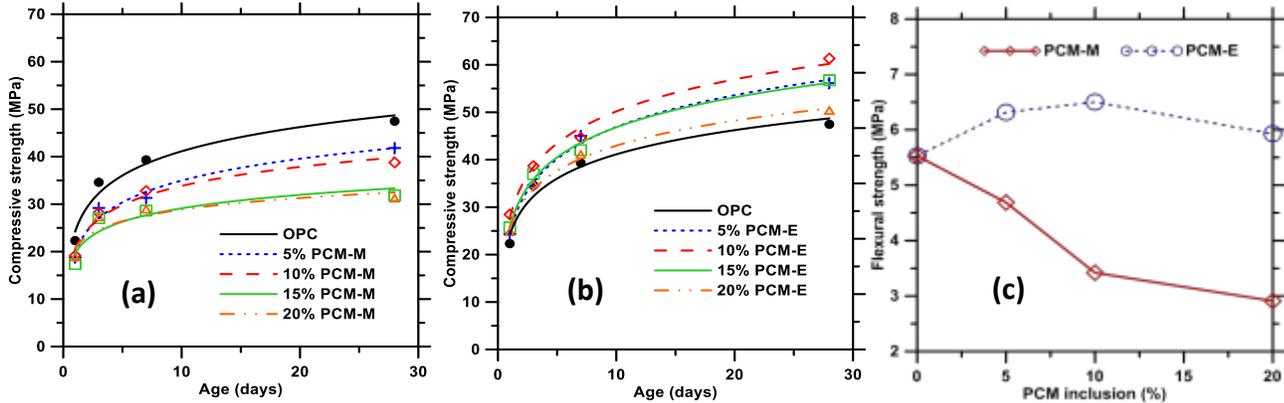


Figure 4: (a) and (b) Compressive strengths as a function of time for mortars containing different volume fractions of PCM-M (a), and PCM-E (b).

(b) Lattice model for temperature evolution:

A lattice-type model has been developed in order to consider temperature evolution in hydrating concrete on the meso-scale. On this scale, the material is considered to comprise cement paste with discrete PCM microcapsules embedded in the matrix. To simulate the heat transport on this scale, the transient heat conduction equation for a stationary medium is used:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \dot{Q}$$

Contribution from the latent heat due to the phase change process is considered by using a piecewise temperature dependent function for the specific heat capacity of the PCM microcapsules. Three different cases are considered:

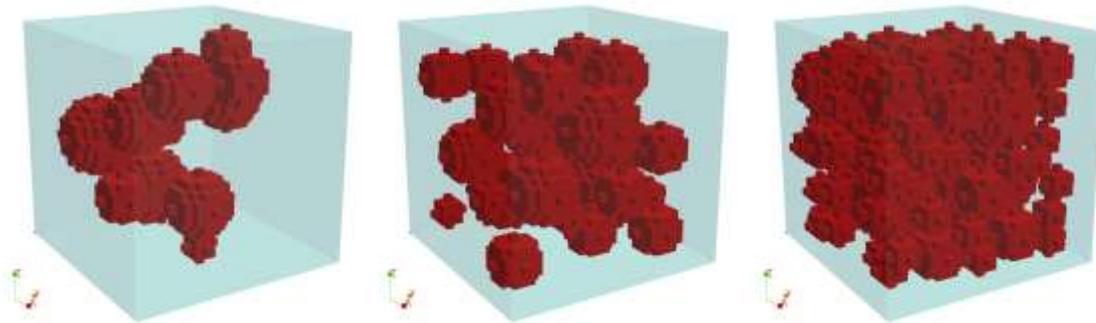


Figure 5. 30x30x30 μm³ material structures comprising PCM microcapsules and cement paste with (left to right) 10%, 20%, and 30% PCM microcapsules per volume

Because the heat production occurs only in the cement paste, the heat source term is applied only in the paste nodes. The phase change capsules have, therefore, a two-fold effect on the internal heat generation in the composite: first, they have a diluting effect due to the fact that they replace a part of the hydrating cement; and second, the phase change effect.

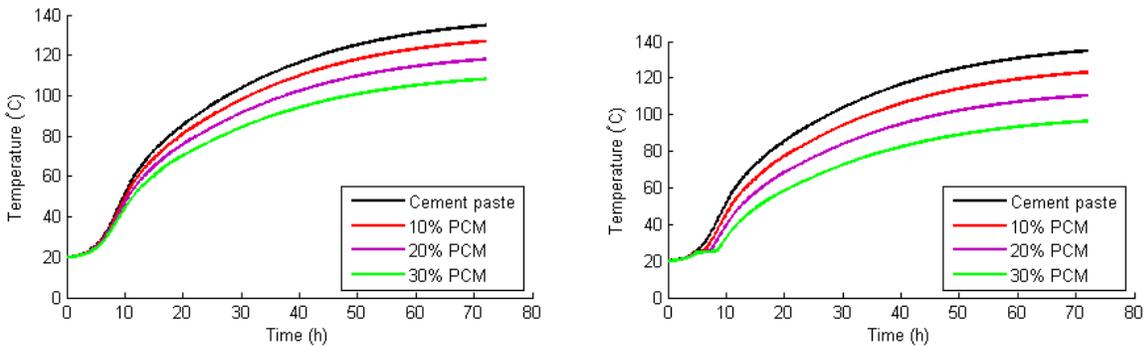


Figure 6. Simulated temperature evolution in adiabatic conditions of a $30 \times 30 \times 30 \mu\text{m}^3$ microstructure containing different amounts of PCM microcapsules. Left- without considering the latent heat contribution; right: with latent heat contribution of PCM microcapsules.

WP4: Numerical modeling of thermal evolution

A numerical model is being used to describe temperature gradients within concrete as a function of binder composition (e.g., w/c, cementitious material content) and environmental conditions. The model assumptions are: (a) Microencapsulated PCM-concrete composite behaves as a homogeneous medium with effective thermal properties, (b) All material properties are isotropic, (c) All properties other than the specific heat of the PCM are constant, (d) 2D heat transfer prevails, (e) Convective heat transfer coefficient remains constant at pavement surface, and (f) Evaporative cooling is neglected. The model schematic is shown in Figure 7.

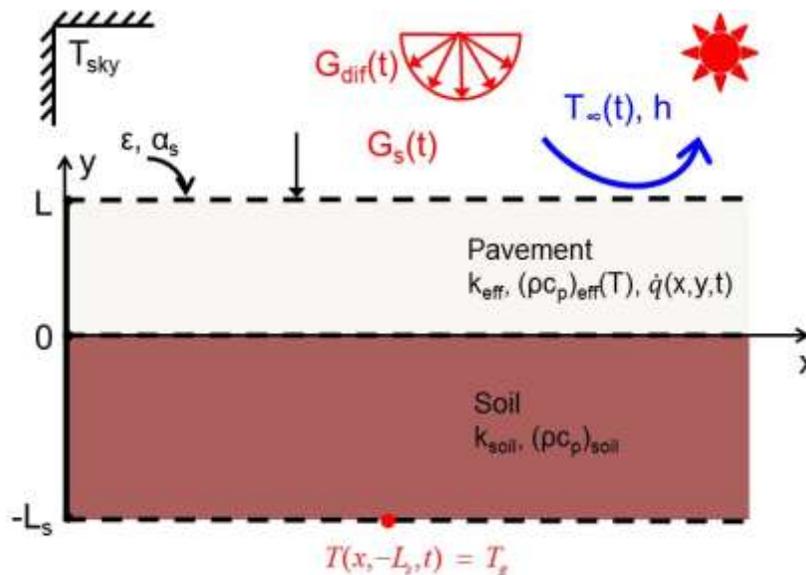


Figure 7: Schematic of the numerical model

This model is being applied to determine the temperature evolution in pavements and the stresses thus generated, in order to determine the effectiveness of PCMs in controlling thermal stresses and thus cracking.

WP5: Cracking sensitivity and deformability response

The concrete for this study has been determined and two trial concrete mixtures have been produced. In addition to temperature evolution during hardening, compressive strength and E-modulus at 2, 7 and 28 days have been determined. These preliminary tests confirm the suitability of the mix design. In the first part of the project, specimens for the concrete ring test will be produced. The concrete is restrained during its thermal expansion by an outer ring made of invar steel. An inner ring provides restraint in the case of cooling and shrinkage. Both rings are equipped with strain gauges. The entire setup is isolated to minimize heat loss during hydration. Heat development is recorded by thermal sensors.

As the PCM will melt at a temperature of 24 °C in an endothermal reaction a dampening of the temperature increase during early hydration is expected. As a consequence, the same type of dampening is expected to be observable in the strain development at the outer ring. After hardening, strain at the outer ring should disappear, but is expected to be recorded at the inner ring due to cooling and shrinkage. After this initial thermal cycle caused by hydration, multiple passive cycles are added by heating up the sample in an oven and subsequent cooling. With this approach the repeatability of the effect of the PCM and their effectiveness in reducing stress and the probability of concrete cracking can be studied. In addition to the ring test, compressive strength, tensile strength and E-modulus of the concrete are determined. The same tests are conducted with a reference concrete without PCM.

WP8: Knowledge Management and Dissemination

- The first ECLIPS newsletter has been developed and is ready for dissemination through our partner agencies as well as through several other outlets
- A technote is being prepared
- Research publications are being prepared by partner institutions based on the respective work