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Application of lightweight aggregate and rice husk ash to incorporate phase change materials into cementitious materials

Naser P. Sharifi^{a*}, Hajar Jafferji^a, Savannah E. Reynolds^b, Madison G. Blanchard^b and Aaron R. Sakulich^a

^aDepartment of Civil and Environmental Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609-2280, USA; ^bDepartment of Civil Engineering, Wentworth Institute of Technology, 550 Huntington Avenue, Boston, MA 02115, USA

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Using phase change materials (PCMs) in buildings and pavements improves their thermal performance. However, PCMs cannot be directly added to cementitious media due to the interference of PCMs with hydration reactions. This study aims to evaluate the practicability of lightweight aggregate (LWA) and rice husk ash (RHA) to be used as PCM carrier agents in Portland cement-based mortars. The results show that LWA and RHA can absorb and contain liquids in their porous structures; and since these materials are compatible with cementitious media, they can be used as PCM carriers. However, a portion of the PCM may stick to the surface of the carriers or leak out of them and subsequently affect different properties of the binder. Incorporation of LWA presoaked in PCM decreased the compressive strength of the mortar by about 10%; however, when RHA was used as the carrier, the compressive strength was reduced by more than 35%.

Keywords: phase change materials; lightweight aggregate; rice husk ash; cement mortar; internal curing; interfacial transition zone

1. Introduction

Phase change materials (PCMs) are substances with specific melting temperatures and high latent heats of fusion.[1] PCMs are divided in three main groups: organic compounds, inorganic compounds, and eutectic mixtures.[2] Each group has its own typical range of melting temperature and its own range of melting enthalpy. Thus, a large number of PCMs with different melting temperatures, from $-33\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$, and different latent heats of fusion are industrially available.[3] For the PCMs with the solid/liquid phase transition, when the ambient temperature goes above

the melting point, a PCM absorbs the heat energy and turns into liquid; and when the temperature drops below the melting point, the PCM releases the absorbed energy and solidifies.[1,4] Considering the capability of PCMs to absorb, retain, and release heat energy, they can be used as passive heat storage units to improve the thermal performance of cementitious materials.[5,6]

The application of PCMs in buildings has been widely investigated.[7–9] Using PCMs in buildings reduces energy consumption and thus reduces the associated emission of CO_2 to the environment.[10]

*Corresponding author. Email: npourakbarsharif@wpi.edu

The utilization of PCM-impregnated gypsum wallboards has been shown to reduce maximum room temperatures by about 4 °C during the day, and reduce the heating load during night.[11] Other studies show that by incorporating PCMs in floor tiles, the annual heating costs of a building can be greatly reduced.[12] The use of PCMs also increases occupant comfort by reducing extreme changes in the inside temperature.[2,6,9,13]

In addition to buildings, PCMs can be used in pavements, where extreme temperature changes can cause various modes of failure.[4,14] Cyclic changes in temperature in cold and humid climates increase the number of freeze/thaw cycles experienced by the pavement, producing damage in the binder.[15–17] On the other hand, very high temperatures increase the likelihood of deformation related to shear stresses.[18,19] Using PCMs in pavements increases the thermal inertia of the media and reduces the potential of thermally induced deterioration, thus increasing the service life of the pavement.[14,20,21]

However, PCMs cannot be directly added to a cementitious system because they interfere with the hydration reactions occurring in the binder that produce calcium silicate hydrates (C–S–H), the primary strength bearing phase in concrete, thus reducing mechanical strength.[5,22,23] To prevent the PCM from interfering with the hydration reactions, it should be encapsulated in a carrier agent, such as high-density polyethylene balls,[24] rectangular steel pipes,[25] or diatomite.[26]

Lightweight aggregate (LWA) is one of the materials that has been suggested as a PCM carrier agent.[5,27,28] Because of its porosity, LWA can absorb the PCM into its structure; it is also compatible with the cementitious media. The effects of incorporating PCM on the thermal performance of cementitious materials was investigated in details in other studies.[5,27] However, little information is

available in the literature regarding the problems associated with using LWA in this manner, such as the potential leakage of PCM out of the LWA, and the effect of incorporation of LWA presoaked in PCM on the non-thermal properties of the mortar, such as autogenous shrinkage, total shrinkage, and chemical composition. In addition to evaluating the practicability of LWA as PCM carrier, this study aims to investigate the ability of rice husk ash (RHA), a common material never before used to encapsulate PCM, as an alternative carrier agent. The effects of incorporating LWA and RHA presoaked in PCM on the chemical, physical, and mechanical properties of a mortar are presented.

2. Materials and methods

2.1. Materials¹

Type I ordinary Portland cement (OPC) conforming to ASTM standard C150/C150 M, and ordinary sand from a local source with specific gravities of 3.15 and 2.61, respectively, were used. Expanded shale light weight aggregate (LWA) (from Northeast Solite Corporation), with a specific gravity of 1.5 and 1.675, before and after presoaking in water, respectively, was used. The water absorption capacity of LWA was reported by the manufacturer to be equal to 17.5 wt.%. Scanning electron microscopy (SEM) imaging of the porous structure of LWA is shown in Figure 1(a). The surface-accessible pores of each LWA particle provide space to indirectly incorporate liquids to cementitious media. The methodology of SEM sample preparation is described in Section 2.3.9.

Rice husk was burned in an electric furnace at 650 °C for 6 h to produce RHA. The produced ash was white in color and had a weight loss of 81%. After burning in the furnace, the ash was stored in a dry atmosphere to prevent the absorption of moisture from the air. The

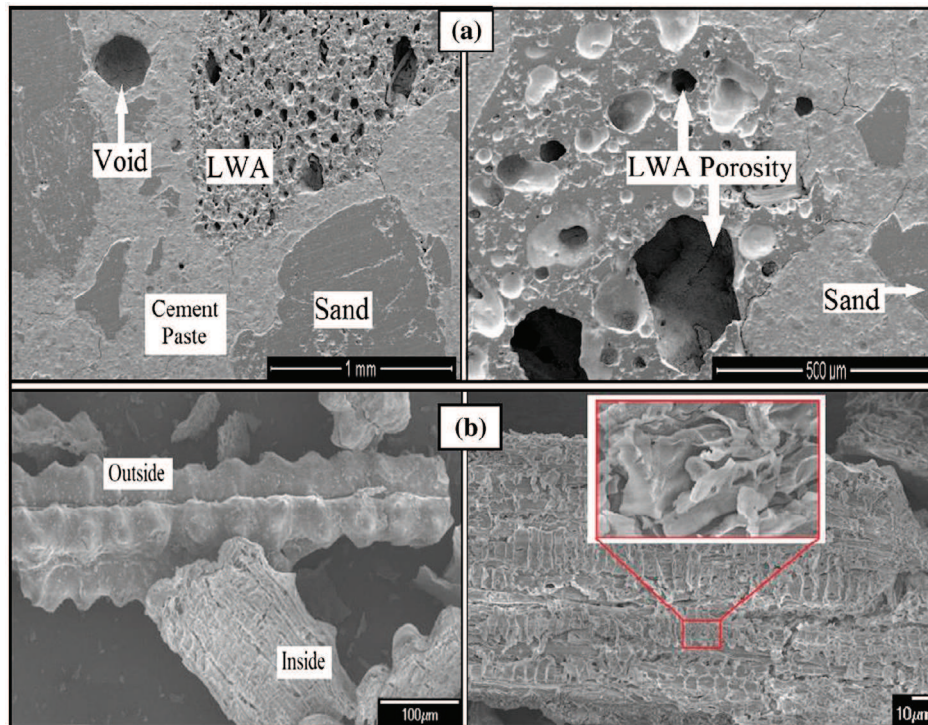


Figure 1. SEM imaging of the carriers. (a) Lightweight aggregate. (b) Rice husk ash burned at 650 °C.

SEM imaging of the porous structure of RHA is shown in Figure 1(b). The images appear to show that RHA powder had two sides with different levels of porosities. However, the exact volume percentage of the pores was not known and therefore, different percentages of water and PCM were added to the RHA, and the results of the experiments such as autogenous shrinkage, semi-adiabatic calorimetry, and isothermal calorimetry tests (described below) were used to estimate the absorption capacity of RHA.

The result of X-ray diffraction test performed on the RHA powder shows that the ash has mostly an amorphous structure (Figure 2). However, there is an amorphous hump created at $23^{\circ}-2\theta$, which is related to silica. This peak matches with the XRD results of RHA presented in other studies.[29,30] Another

study reported that RHA contains about 90 wt.% of silica.[31] The results presented in another study show that for a RHA burned at a higher temperature, in addition to the hump at $23^{\circ}-2\theta$ that is related to amorphous silica, there is a smaller hump at $27^{\circ}-2\theta$ that is attributed to crystalline silica in the form of quartz.[32] These results suggest that burning rice husk at higher temperatures results in a more crystallite structure. The methodology of XRD sample preparation is described in Section 2.3.7.

Fourier transform infrared spectroscopy (FTIR) was conducted to study the chemical composition of the RHA. The results show a broad peak around 2700 cm^{-1} indicating C-H, a broad hump centered around 2100 cm^{-1} that could indicate C=C, a hump around 1700 cm^{-1} indicating bending vibrations in water, a

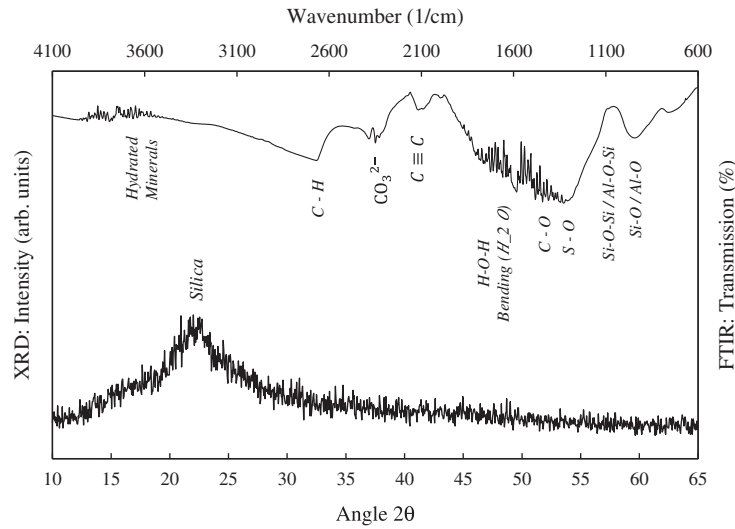


Figure 2. XRD diffractograms and FTIR spectra of RHA burned at 650 °C.

hump around 1300 cm^{-1} indicating S–O, and a hump centered around 900 cm^{-1} indicating Si–O and/or Al–O stretching vibrations (Figure 2). The methodology of FTIR sample preparation is described in Section 2.3.8.

Finally, PCM 6, a paraffin blend produced by Microtek Laboratories, with a specific gravity of 0.76 and a melting point of 6 °C , was used. This PCM is widely available, stable under normal conditions of handling and storage, inflammable below 400 °C , and liquid at room temperature. PCMs with higher melting point, i.e. above 15 °C , will turn solid during mixing on cold days, which not only creates practical problem during mixing, but also affects the results of any given experiment. This PCM has a specific heat of 2.08 J/g K and latent heat of fusion of 160 J/g . [5]

2.2. Mix proportioning

Four sets of mixes, with six total mixes, were prepared. No coarse aggregate (gravel) was used in order to more accurately discern the effects of PCM on the cementitious binder. In Mix 1, only sand,

cement, and water were used. This mix was used as the control. For Mix 2, LWA was used as the carrier for the PCM. LWA replaced sand on a volumetric basis; as such, the aggregate size distributions were the same in specimens with and without LWA. The size distribution of the aggregate for sieves #8, #16, #30, #50, and #100 was 30, 25, 20, 15, and 10% of the total mass, respectively. For samples containing LWA, two different factors may affect the properties of the mortar: the presence of the carrier (which has a different composition and is relatively weak, mechanically) and the incorporation of the PCM (which may interfere with hydration reactions). In order to distinguish between the effects of incorporating the PCM and the carrier, two mixes were prepared: Mix 2W in which LWA was presoaked in water and Mix 2P in which LWA was presoaked in PCM. The mass of added water was 17.5 wt.% of the mass of LWA, as the water absorbance capacity of LWA was reported be equal to 17.5% by the manufacturer. An equal volume of PCM (13.3 wt.% of LWA due to the lower specific gravity) was used in Mix 2P.

Reduced strength in Mix 2W would be due to the first factor described above; reduced strength in Mix 2P would be due to a combination of both factors.

The mass of incorporated LWA was calculated using the equation commonly used to determine mix proportions for systems in which water-soaked LWA is used to provide 'internal curing' [33]:

$$M_{LWA} = \frac{C_f \times CS \times \alpha_{max}}{S \times \phi_{max}} \quad (1)$$

where M_{LWA} is the mass of dry LWA per unit volume of mortar (kg/m^3), C_f is the cement factor of the mortar (kg/m^3), CS is the chemical shrinkage of the cement (g of water/g of cement), α_{max} is the maximum expected degree of hydration of cement, S is the saturation degree of LWA, and ϕ_{LWA} is the absorption of LWA ($\text{kg water}/\text{kg dry LWA}$). For all mixes, C_f was 585 (kg/m^3), CS was calculated by the chemical shrinkage test (following ASTM method C1608-07), α_{max} and S were assumed to be equal to 1.0 and 0.95, respectively, and ϕ was reported to be 0.175 (kg/kg). This amount was chosen to reflect an amount of LWA that could be practically used in the field.

For Mixes 3–5, RHA was used as the PCM carrier agent. RHA has been widely used in concrete as a cement replacement due to its pozzolanic properties,[34–36] but it has never before been used as a carrier agent to indirectly incorporate liquids to concrete. For use as a cement replacement, rice husks should be burned at a very high temperature and be ground to a very fine powder in order to encourage pozzolanic behavior [35]; however, the RHA used here was not ground since its behavior as a PCM carrier was the focus of this study. For these mixes, RHA replaced 10 wt.% of the cement.

The capacity of RHA to absorb liquids was not known, and thus, three different quantities of water and PCM were

presoaked in the RHA. For Mix 3W, the mass of added water was equal to 80% of the RHA mass; for Mix 4W, the mass of added water was equal to 40% of the RHA mass; and for mix 5W, the mass of added water was equal to 20% of the RHA mass. The same volumes of PCM were added to Mix 3P, Mix 4P, and Mix 5P, respectively. For Mix 6, PCM was added to the mortar without using a carrier. Only the compressive strength test was conducted on this mix, to show the need for a PCM carrier. For all mixes, a water/cement ratio of 0.4 by mass and an aggregate/mortar ratio of 0.55 by volume were used. The air content of all mixes (necessary for some of the experiments described below) was set to be equal to 3 vol.% of the mortar.[5] The mix proportions of all mixes are provided in Table 1.

2.3. Test methods

2.3.1. Presoaking LWA and RHA in water or PCM

Before addition to the mix, the LWA was completely dried in an oven at 105 °C for 24 h and then presoaked in water or PCM for 24 h at room temperature. RHA was completely dry due to the burning process and thus was only presoaked in water or PCM for 24 h at room temperature.

2.3.2. Chemical shrinkage test

Cement hydration products occupy less physical volume than the reactants; thus, the cement paste undergoes a shrinkage known as chemical shrinkage. To measure the chemical shrinkage of the cement paste, ASTM method C1608-07 was followed. Five ampules were partially filled with cement paste with a water/cement ratio of 0.4 by mass. Then, the ampules were completely filled with water and covered by a cap with a capillary tube. The samples were kept in a

Table 1. Mix proportioning for 1000 cm³ of mortar (g).

Mix	Sand	LWA	RHA	Cement	Water	Presoaked water	Presoaked PCM
1	1435.5	–	–	585.3	234.1	–	–
2W	1160.6	158.1	–	585.3	234.1	27.7	–
2P	1160.6	158.1	–	585.3	234.1	–	21.1
3W	1435.5	–	58.5	526.8	210.7	46.8	–
3P	1435.5	–	58.5	526.8	210.7	–	35.6
4W	1435.5	–	58.5	526.8	210.7	23.4	–
4P	1435.5	–	58.5	526.8	210.7	–	17.8
5W	1435.5	–	58.5	526.8	210.7	11.7	–
5P	1435.5	–	58.5	526.8	210.7	–	8.9
6	1435.5	–	–	585.3	234.1	–	21.1

water bath at 25 °C and the drop in the height of the water in the graded capillary tube was recorded over the first 115 h. The chemical shrinkage per unit mass of cement at time ‘ t ’ was computed as:

$$CS(t) = \frac{h(t) - h(60 \text{ min})}{M_{\text{Cement}}} \quad (2)$$

in which $CS(t)$ is the chemical shrinkage (mL/g of cement) at time t (min); $h(t)$ is the water level in capillary tube (mL) at time t (min); $h_{60 \text{ min}}$ is the water level in capillary tube (mL) at time 60 min; and M_{Cement} is the mass of the cement (g).

2.3.3. Autogenous shrinkage test

According to ASTM method C1698-09, autogenous shrinkage is ‘the bulk strain of a sealed specimen of a cementitious mix, not subjected to external forces and under constant temperature, measured from the time of final setting until a specified age.’ Chemical shrinkage produces voids in the cementitious binder of a mortar. If these voids are partially filled with water, meniscus forces will be generated that cause the matrix to undergo autogenous shrinkage. However, if the pores are kept filled, autogenous shrinkage does not take place.

In order to record the autogenous shrinkage of the cement paste for each mix, five samples were produced using

flexible corrugated tubes. The samples were placed in zipped plastic bags and kept in a moist curing room for 28 days. The curing room had an almost constant temperature of 23 °C and a high level of humidity to prevent water loss from the samples. Also, because of the specific design of the shelves, no water was accumulated on the top of them. The length of each sample was recorded at the final setting time and at intervals during the first 28 days for use in the following equation:

$$L(t) = L_{\text{ref}} + R(t) - 2 \times L_{\text{plug}} \quad (3)$$

in which L_{ref} is the length of the reference bar (mm); $R(t)$ is the length reading of the mortar at each time (mm); and L_{plug} is the average length of the end plugs (mm). Using the length reading at any time period, the autogenous strain was calculated using:

$$\begin{aligned} \text{Autogenous strain} \\ = \frac{R(t) - R(t_{\text{sf}})}{L(t_{\text{sf}})} \times 10^6 \frac{\mu\text{m}}{\text{m}} \end{aligned} \quad (4)$$

in which $R(t)$ is the length reading of the mortar at each time (mm) and $R(t_{\text{sf}})$ is the length reading of the mortar at the final setting time.

LWA presoaked in water provides internal curing for the mortar since it has the ability to absorb and keep the water inside its porous structure.[37] When the

mix water is consumed during hydration reactions, the LWA releases its water into the media due to the induced osmotic pressure; this liquid fills pores, eliminating or reducing the meniscus forces and decreasing the autogenous strain.[38]

2.3.4. Total shrinkage test

Total shrinkage tests were conducted based on ASTM method C596-07. Six samples were prepared using $25.4 \times 25.4 \times 292.1$ -mm prism molds. The molded samples were kept in zipped plastic bags in a curing room for 24 h. Once demolded, samples were submerged in water to cure for 48 h and then were taken out and kept at room conditions for 25 more days. Measurements were taken on the day of demolding and periodically for the first 28 days. This experiment was conducted on the samples with LWA and RHA presoaked in water and PCM to examine the effect of internal curing and incorporating PCMs on the total shrinkage of mortars, respectively.

2.3.5. Semi-adiabatic calorimetry and isothermal calorimetry

The hydration reactions between cement and water are exothermic; therefore, anything that interferes with these reactions reduces the amount of heat generated. To evaluate the effect of incorporating PCM on the hydration reactions, semi-adiabatic calorimetry tests were conducted in which 101.6×203.2 -mm cylinders were filled with mortar and insulated on all sides. A K-type thermocouple connected to a data acquisition was used to record sample temperature (Figure 3).

Isothermal calorimetry was also used to study the same effects. For each mix, ampules were partially filled, capped, and the caps were crimped in order to be sealed. The operation temperature of the machine was 25°C and initial and final baselines were acquired over a period of

30 min. In order to provide an indication of variability, two specimens from the same mix were tested in neighboring calorimeter cells.

For all samples, reference ampules contained 10 g of cement powder. The amount of material in the experimental samples was selected so that the specific heat of each sample was equal to the specific heat of the reference. To calculate the equivalent sample mass, the specific heat of sand and LWA, cement, water, and PCM was taken as 0.76, 0.75, 4.18, and $2.08 \text{ J/g }^\circ\text{C}$, respectively. The results were normalized per unit mass of cement in the sample.

2.3.6. Compressive strength test

ASTM method C109/C109 M was followed for the compressive strength test. After mixing, mortar was placed in 50.8-mm cube stainless steel molds for 24 h and after demolding, the cubes were kept in a curing room. For each mix, three specimens were tested at ages 3, 7, and 28 days. The loading rate was 13.8 MPa/min for all samples.

2.3.7. X-ray diffraction

X-ray diffraction (XRD) experiments were conducted on the samples that contained LWA, RHA, and PCM to examine if incorporation of these materials affects the crystal structure of the mortars. After 28 days of curing, a specimen of Mix 1, Mix 2P, or Mix 3P was ground to a very fine powder (mesh #200) to prepare samples for XRD experiments. Mix 3P was selected because it had the highest amount of PCM. For the XRD tests, about 0.5 g of powder was placed in the sample holder and was packed down tightly by spatula to prepare a relatively flat surface. A range of 2θ from 10° to 65° with the intervals of 0.05° was used. The same procedure was followed for the RHA powder.

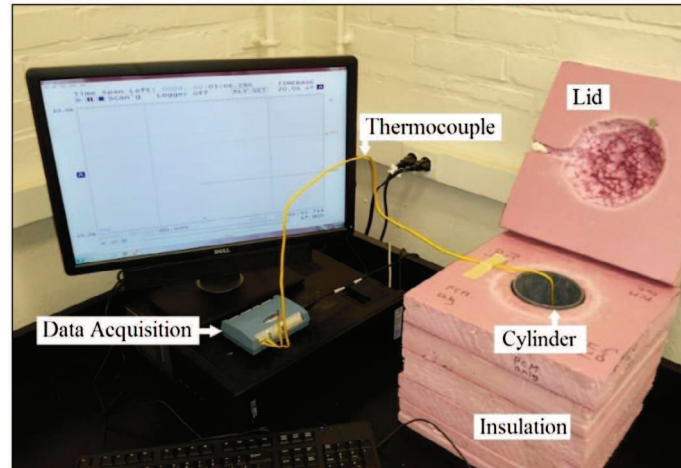


Figure 3. Semi-adiabatic calorimetry setup.

2.3.8. Fourier transform infrared spectroscopy

FTIR experiments were conducted on the samples that contained LWA, RHA, and PCM to examine if the incorporation of these materials affects the chemical composition of the mortars. As with XRD, specimens of Mix 1, Mix 2P, and Mix 3P were ground to very fine powder (mesh #200) after 28 days of curing to prepare samples for FTIR experiments. The sample size for the FTIR test was about 5 mg, studied in the range of the wavenumber (λ) from 600 to 4100 cm^{-1} , with intervals of 2 cm^{-1} . The same procedure was followed for the RHA powder.

2.3.9. Scanning electron microscopy

To create specimens for SEM, a small piece of the sample was placed in a plastic mold which was then filled with epoxy resin. After solidification, the sample was removed and a series of six sandpapers (#120, #240, #600, 1 μm , 0.3 μm , and 0.05 μm) were used to polish the surface of the specimen. The surface was sputter coated with a thin layer of gold.

For SEM sample preparation of RHA, small particles of the powder were stacked on a specimen stub with double-sided conductive tape.

SEM was also used to study the interfacial transition zone (ITZ) between the aggregate particles and the bulk cement paste. When LWA was incorporated in the mix, because of its porous structure, it could lead to a different ITZ, and thus affect some of the mechanical properties of the binder. To investigate that, the ITZ between LWA particles and cement paste was compared to the ITZ between sand particles and cement paste by conducting SEM tests on crushed pieces of Mix 1 and Mix 2.

3. Results and discussion

3.1. Chemical shrinkage

The final chemical shrinkage of the paste was calculated to be equal to 0.042 mL/g, which is similar to the values of 0.046 and 0.039 mL/g determined in other studies, Refs. [39] and [40], respectively. The result of this test was not directly used to make a conclusion; rather, the results of that were used for mix proportioning.

3.2. Autogenous shrinkage

Autogenous shrinkage causes macroscopic volume changes in the media that can lead to early age cracking.[41,42] For Mix 1 (the control), autogenous shrinkage increased over time to a level of $-436 \mu\text{m/m}$ (Figure 4(a)). Autogenous shrinkage can be eliminated by internal curing, where the water supplied by internal reservoirs keeps pores fully saturated.[37,43] This can be observed in Mix 2W, where not only was the autogenous shrinkage completely mitigated, but slight autogenous expansion was observed (Figure 4(a)).

Another study also argued that internal curing not only eliminates the autogenous shrinkage, but also causes expansion in concrete because the incorporation of LWA in the Saturated Surface Dry (SSD) condition reduces the tensile force generated in the mix and thus causes expansion.[44] Based on another research, the water provided by LWA allows the curing of the cement paste to take place in a saturated condition; thus, adsorption of water lowers the surface tension between the cement gel particles, and therefore no capillary pressure develops to oppose the expansion of the solid phase.[45]

Similarly, Mix 2P (containing LWA presoaked in PCM) underwent autogenous expansion (Figure 4(a)). Since the volume of PCM in which the LWA was soaked in was equal to the volume of LWA porosity, this result suggests that a portion of PCM has been released by LWA to the media or that some PCM from the surface of LWA entered the mix. The pores are thus less empty, meniscus forces reduced, and shrinkage mitigated. When the hydration reaction proceeds, fine pores are generated in the solid structure of the bulk cement paste. Therefore, difference in relative concentration of PCM between the LWA's pores and the surrounding area is generated that causes

increase in the osmotic pressure. This causes the cement paste to suck a portion of the PCM out of the LWA's pores. This shows that LWA cannot completely keep the PCM inside its porous structure.

The same pattern was observed for the mixes with RHA presoaked in water or PCM (Figure 4(b)). For all of these mixes, autogenous expansion occurred, implying that water and PCM had been released by the RHA. More expansion was observed in the mixes that more water or PCM had been incorporated.

The level of expansion of mortar for Mix 5W, where the water/RHA was 20 wt.%, was close to the level of expansion of mortar for Mix 2W, where water/LWA was 17.5 wt.%. The water absorption capacity of LWA was reported by the manufacturer to be equal to this percentage; thus, this suggests that the capacity of RHA to absorb water is close to 20 wt.%. However, when the RHA was presoaked in more water, the rate of expansion of the mortar was more.

The two forces that are involved in the water leakage out of RHA pores are the adhesion force between RHA surface and the osmosis force from the bulk cement paste. Leakage of water out of the RHA particles depends on the suction force from the cement paste.[46] At early ages, the water content of the cement paste is still high; thus, only water in big pores of the RHA particles will be released. However, when the hydration reaction proceeds, it consumes the water in the paste and reduces the water content of the paste. Therefore, the difference in relative humidity between the cement paste and RHA pores increases, which leads to the increase of the osmotic force. This causes the cement paste to suck the water out of the finer pores of RHA.[47] However, the much finer pores, i.e. smaller than 4 nm in diameter, in RHA particles remain water-filled for a very longer period of time.[48]

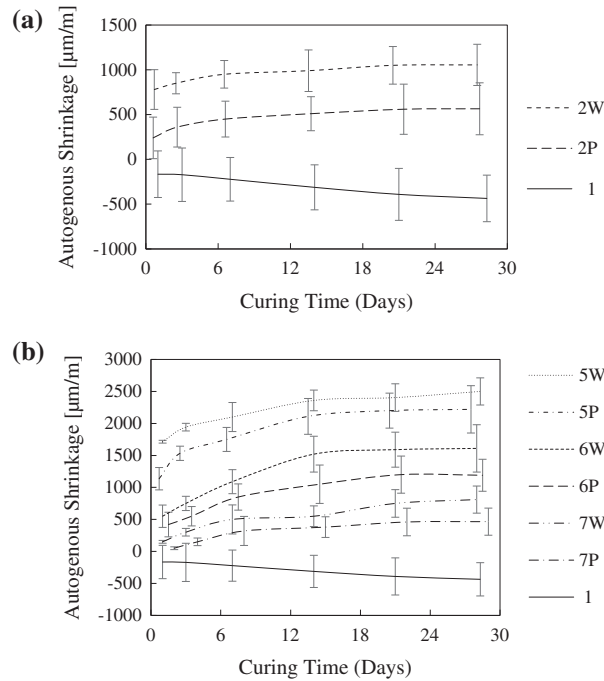


Figure 4. Autogenous shrinkage. (a) Mixes with LWA as the carrier. (b) Mixes with RHA as the carrier.

It should be mentioned that in addition to LWA, other materials such as saturated superabsorbent polymer particles have been used as a water supply to provide extra water for hydration reactions; [49] however, RHA presoaked in water was not previously used for internal curing purposes.

Water/RHA was not selected to be less than 20 wt.% because even with this percentage, the mix had a very low workability, and it was difficult to cast in molds. RHA has a high specific surface area (50–100 m^2/g [29]); thus, RHA particles that are in partially saturated or SSD condition may absorb mix water and lower the workability of the mortar. It is therefore not recommended to use a water/RHA ratio of less than 20 wt.% unless additives like superplasticizers are used to reach the desired workability.

3.3. Total shrinkage

In the total shrinkage mechanism, since the specimens are kept at room conditions, all three shrinkage mechanisms (chemical, autogenous, and drying) take place simultaneously. Therefore, the length of the specimens is reduced because of the hydration reaction, the inward meniscus forces in the pores, and water evaporation. Since the ASTM standard declares that the shrinkage values should not be prefixed with a minus sign, the absolute value of the results is presented. For Mix 1, hydration reactions took place over time and the water content decreased; therefore, the shrinkage increased. The rate of the shrinkage was higher in the first 14 days because the main part of the reaction and water evaporation takes place in the first two weeks after mixing (Figure 5(a)).

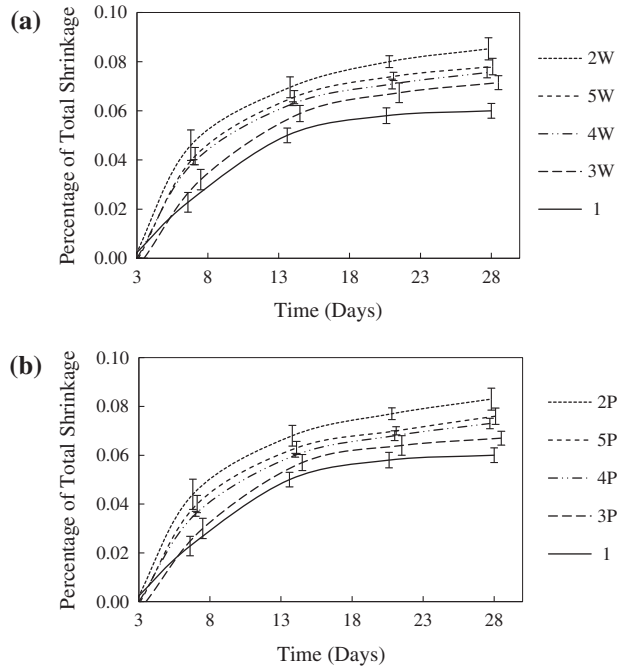


Figure 5. Total shrinkage. (a) Mixes with carrier presoaked in water. (b) Mixes with carrier presoaked in PCM.

For Mix 2W, where a portion of the sand was replaced by LWA, total shrinkage increased (Figure 5(a)). It is established in some studies that the lower restraint provided by LWA can lead to increased total shrinkage compared with mixes containing only sand.[50] This also shows that additional water provided by LWA, which mitigates autogenous shrinkage, may not be effective in reducing total shrinkage because the extra water may evaporate over time.

The same trend can be observed for the mixes to which RHA presoaked in water was added (Figure 5(a)). A portion of cement was replaced by RHA in these mixes and therefore less C-S-H, the primary binding phase in cementitious binders, was produced during hydration reactions. It is possible that the lower strength of RHA compared to the stronger phase of C-S-H provided less restraint against shrinkage and therefore the total shrinkage increased.

As was mentioned earlier, if RHA is burned at a high temperature and is ground to extremely fine powder in the range of the cement particle size (5–45 μm), it shows pozzolanic behavior and enhances compressive strength.[35,36] Here, the utilized RHA was burned at 650 $^{\circ}\text{C}$, and was not ground into fine powder since it was meant to be used as the PCM carrier and grinding would lead to a reduced volume of pores in each particle.

Considering the standard deviations of Mixes 3W, 4W, and 5W, it can be concluded that, since extra water in the media will evaporate over time, presoaking RHA in more water does not make a difference in the level of total shrinkage in the long term. For the mixes in which the carrier was presoaked in PCM, the results had the same trend; incorporating LWA and RHA in the mix increased the total shrinkage and the amount of presoaked PCM did not make a meaningful difference.

The same pattern was observed when the carriers were presoaked in PCM. Incorporating LWA and RHA in the mixes increases the total shrinkage of the mortar because of the foresaid reasons, and presoaking PCM instead of water in the carriers does not change the pattern of the shrinkage. The standard deviation of Mixes 3P, 4P, and 5P suggests that amount of presoaked PCM does not have a meaningful effect of the final shrinkage (Figure 5(b)).

3.4. Semi-adiabatic calorimetry

The hydration reaction between cement and water is an exothermic reaction. Incorporation of LWA and RHA presoaked in PCM decreased the magnitude, and delayed the onset of, the peak temperature (Figure 6(a)). For Mix 1, the control, the peak temperature reached 58.2 °C and occurred at 13 h 30 min;

however, for Mix 2P, the peak temperature reached 55.7 °C and was delayed by 30 min. The PCM that is added to the matrix could act as a retardant by coating cement particles, hampering the transport of water into those particles, and thus reducing the rate and degree of hydration.[14] The results of semi-adiabatic calorimetry in another study showed that incorporating of 1, 3, and 5 vol.% PCM in a mortar reduces the peak temperature by 9, 12, and 15%, respectively, and delays reaching peak temperature by 15, 18, and 22%, respectively.[22]

This shows that using LWA as the PCM carrier can prevent PCM from interfering with the hydration reaction. However, the small reduction in the peak temperature and the short delay are attributed to the effect of PCM that was stuck on the surface of LWA particles and/or leaked out the LWA pores. The results of another study showed that if LWA is used

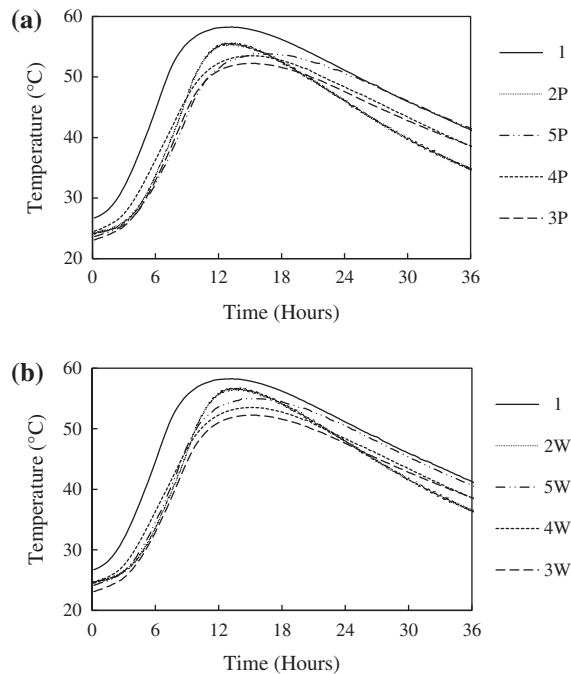


Figure 6. Semi-adiabatic calorimetry. (a) Mixes with carrier presoaked in PCM. (b) Mixes with carrier presoaked in water.

as a PCM carrier and the amount of pre-soaked PCM was equal to the capacity of LWA, there will be a very small reduction and delay in reaching the peak temperature.[28]

The same phenomenon was observed in mixes where RHA was the carrier and 20 wt.% of PCM was pre-soaked in that (Mix 5P). However, a larger decrease and a longer delay were observed when more PCM was used in Mix 4P with 40 wt.% and Mix 3P with 80 wt.% of PCM pre-soaked in RHA, respectively. This suggests that a portion of PCM leaked out of the RHA and that, similar to the LWA, RHA cannot completely contain PCM inside its porous structure. It should be added that in general, the mixes with RHA had a lower peak temperature compared to the mixes with LWA as a carrier because of the lower cement content in those mixes (Figure 6(a)).

Similar results were obtained when LWA and RHA were pre-soaked in water (Figure 6(b)). For Mix 2W, there was about 3% reduction in the peak temperature. Since a portion of water leaks out of the carrier, incorporating LWA and RHA pre-soaked in water increases water content of the mix. Water has a larger heat capacity than cement, sand, or LWA; a mix will therefore reach a reduced peak temperature as the water absorbs energy. Also, for a fixed volume, larger w/c means less cement per unit volume, and thus less heat generation. These results match those of other studies where it was shown that incorporating LWA pre-soaked in water into the cementitious materials lowers the peak temperature and delays that because of the larger heat capacity of water.[51] Also, for mixes with RHA as the carrier (Mixes 3W, 4W, and 5W), the peak temperature was decreased and delayed which shows the w/c ratio had been increased; this suggests that the pre-soaked water has leaked out of the RHA (Figure 6(b)).

3.5. Isothermal calorimetry

Isothermal calorimetry tests were conducted on all the mixes to better understand the effect of incorporating LWA and RHA pre-soaked in PCM and water on the hydration reaction between cement and water. For Mix 1, the control, the heat flow reached to 0.0047 W/(g of cement) after 4 h 15 min (Figure 7(a)). This primary peak is the result of the hydration of Alite (tricalcium silicate). The hydration of Alite is a fast reaction that releases a large amount of heat over a short period of time and controls the set time and the initial strength of the mortar. There is a secondary peak with a magnitude of 0.0041 W/(g of cement) at the age of 6 h 50 min. This peak is the result of the hydration of Belite (dicalcium silicate), which is a slow reaction that releases a relatively small amount of heat at a longer time and adds strength to the mortar over long time periods. Alite and Belite account for more than 70 wt.% of OPC and thus the hydration of them governs the major properties of a cementitious system. Therefore, there is not a visible third peak corresponding to the hydration of other phases in the isothermal calorimetry graphs. It should be mentioned that since recording the actual data took place after about 45-min equilibrium period, the peaks corresponding to the reaction of phases such as Aluminate (tricalcium aluminate) and/or Ferrite (tetracalcium aluminoferrite) are also not visible.

For Mix 2P, the primary peak had a magnitude of 0.0044 W/(g of cement) and took place after 4 h 20 min. The secondary peak had a magnitude of 0.0037 W/(g of cement) and took place after 7 h 20 min (Figure 7(a)). This means that the primary peak was decreased by 7% and was delayed by 4%, and the secondary peak was decreased by 10% and was delayed by 7%. These results match with another

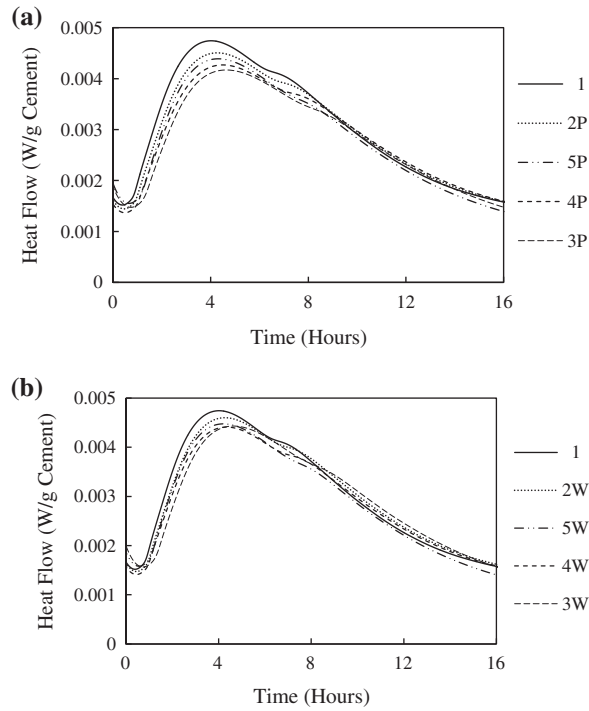


Figure 7. Isothermal calorimetry. (a) Mixes with carrier presoaked in PCM 6. (b) Mixes with carrier presoaked in water.

study where the peak and magnitude of the heat flow were reduced and delayed by 16 and 12%, respectively, where LWA presoaked in PCM was incorporated in the mix.[14] This reduction and delay were attributed the effect of PCM to decrease the production of reaction products, which leads to generation of less heat.

Similar results can be obtained when RHA is used as the PCM carrier. For Mix 5P with 20 wt.% of PCM presoaked in RHA, the decrease and delay in the heat flow peak are almost the same as Mix 2P. Unlike semi-adiabatic calorimetry, the results of this test were normalized by the mass of cement available in the mix; thus, the peak heat flows of the mixes with RHA as the carrier were not affected by the lower cement content in the mix. This suggests that the absorption capacity of RHA is about 20 wt.%. How-

ever, more accurate experiments are required to better estimate the RHA absorption capacity. For Mixes 4P and 3P, with 40 and 80 wt.% of PCM presoaked in RHA, respectively, a larger decrease and longer delay in both primary and secondary heat flow peaks were observed (Figure 7(a)).

Almost the same results were obtained when LWA and RHA were presoaked in water (Figure 7(b)). By incorporating LWA presoaked in water in the mortar, Mix 2W, there is a small reduction in the peak heat flow and a slight retarding effect. LWA releases water to the mix which increases the w/c of the mortar. Water has a larger heat capacity than other components in the mix and thus the heat capacity of the mortar that has pre-wet LWA increases. This reduces the peak of the heat flow.[51] For Mixes 4W and 3P, where more water is

presoaked in RHA, the reduction in the peak of heat flow and the delay in that are more.

These results are in contrast with the results presented in another study.[52] Their results showed that the peak of heat flow was diminished and slightly delayed for the mixtures with lower water content. They argued that since the space available for the growth of hydration products is smaller, the hydration is diminished and retarded for the systems with lower water content.

3.6. Compressive strength

The compressive strength of Mix 1 increased over the period of 28 days; however, the rate of increase diminished over time. The compressive strength increased by 20% (from 33 to 39.5 MPa) between days 3 and 7 after mixing, but increased by only 16% (from 39.5 to 45.7 MPa) between days 7 and 28 after mixing. This is because the main part of hydration of major phases such as Alite, Belite, and Aluminate take place during the first few days and the rate decreases over time (Figure 8).

Mix 2W had a lower strength than Mix 1 because LWA has a lower compressive strength than sand. It should be

mentioned that since the samples were kept in the curing room with controlled temperature and 100% humidity, they remained fully saturated and did not require internal curing; thus, the incorporation of LWA presoaked in water did not increase the compressive strength of Mix 2W when compared to the control mix. Samples stored in a dry environment might have displayed different behaviors.

In mixes incorporating LWA presoaked in PCM, a second parameter could decrease the compressive strength, which is the leakage of PCM out of the LWA structure. This PCM not only diminished the hydration reaction, but also it covered the sand and LWA particles and reduced the bonding strength between the binder and the aggregate particles. The compressive strength of Mix 2P is thus lower than that of Mix 2W.

Other studies have shown that the lower strength of LWA compared to sand and the PCM covering the surface of sand particles reducing the connection force between sand particles and the cement paste bulk are the reasons that diminished the compressive strength of a mortar with LWA presoaked in PCM.[14,53] A study showed that incorporation of PCM decreases the compressive strength of concrete; however, it

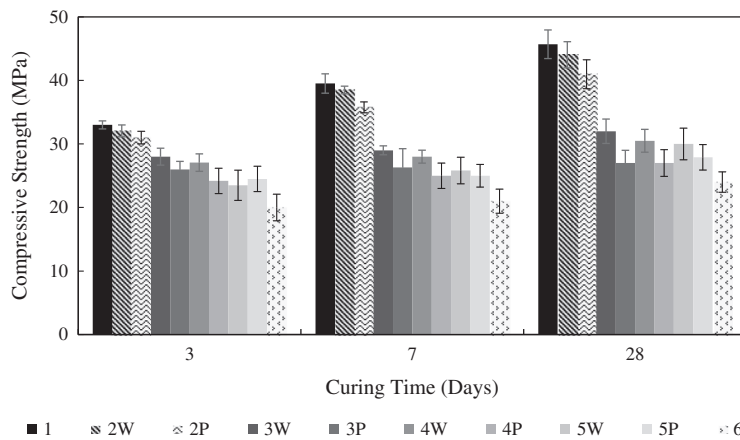


Figure 8. Compressive strength.

remains within the range appropriate for most construction purposes.[54]

For all of the mixes with RHA as the PCM carrier, the compressive strength was drastically decreased. As a portion of cement was replaced by RHA, the cement content was decreased and there was a less creation of the rigid phase of C–S–H. If RHA is burned at a high temperature and ground to extremely fine powder, it shows pozzolanic behavior and enhances the compressive strength.[35,36] But the utilized RHA was burned at 650 °C and was not ground into fine powder since it was meant to be used as the PCM carrier and grinding would lead to a reduced volume of pores in each particle. Further, the RHA presoaked in water exceeded the absorption capacity of RHA and thus the water entered the bulk cement paste, resulting in an increase in water content of Mix 3W and Mix 4W. Finally, the RHA presoaked in PCM exceeded the absorption capacity of RHA and thus entered the bulk cement paste and interfered with hydration reaction. It may also have covered the surface of sand particles and reduced the connective forces between them and the bulk cement paste (Mixes 3P and 4P).

Comparing the results of Mixes 3W, 4W, and 5W with Mixes 3P, 4P, and 5P shows that the compressive strength of the mixes that have PCM presoaked in RHA is relatively lower than the compressive strength of the mixes that have water presoaked in RHA. Also, the results suggest that since the incorporation of RHA decreases the compressive strength of the mortar, it should be used as PCM carrier only when a high compressive strength is not demanded.

For Mix 6, where the PCM was directly added to the mortar, the compressive strength was drastically decreased, which is attributed to the interference of the PCM with the hydration reaction and reduction in the connection force between

sand particles and the cement paste bulk.[5,27] Also, since the density of the utilized PCM as an oil was less than any other ingredient in the media, i.e. sand, cement, and water, the PCM accumulated on the top of the mortar as a layer of wax and made the mixing process harder and more time-consuming. Even after molding, there was a relatively thick layer of PCM stuck on the top of the mix. This shows that incorporation of PCM directly to the mortar causes significant problems during material preparation. Regarding these two observations, adding PCM to the mortar without using a carrier was not considered as a mixing option; thus, other experiments were not conducted on this mix.

3.7. XRD and FTIR analysis

XRD diffractograms of Mix 1 (the control) show a peak at $23^{\circ}-2\theta$ indicative of calcite and/or hydrotalcite, a well-defined peak at $27^{\circ}-2\theta$ indicative of aragonite, a hump centered around $28.5^{\circ}-2\theta$ indicative of calcite and/or C–S–H, a wide hump centered around $46^{\circ}-2\theta$ indicative of calcite, a peak at $51^{\circ}-2\theta$ indicative of C–S–H, and a hump centered around $60^{\circ}-2\theta$ indicative of calcite and/or hydrotalcite (Figure 9). C–S–H has a generally amorphous structure; thus, the broad humps at $27^{\circ}-2\theta$ and $50^{\circ}-2\theta$ are attributed to its structure.[55,56] XRD results elsewhere also show well-defined peaks at $23^{\circ}-2\theta$ and $27^{\circ}-2\theta$ for concrete.[57]

The FTIR spectrum of this mix shows broad peaks around 3400 cm^{-1} indicating water, a broad peak centered around 1300 cm^{-1} that could indicate C–O bonds, a peak at 980 cm^{-1} indicating Si–O and/or Al–O stretching vibrations, and a weak peak around 760 cm^{-1} likely to indicate C–O bending vibrations (Figure 9).

Similar XRD and FTIR results can be observed for the mixes with LWA and

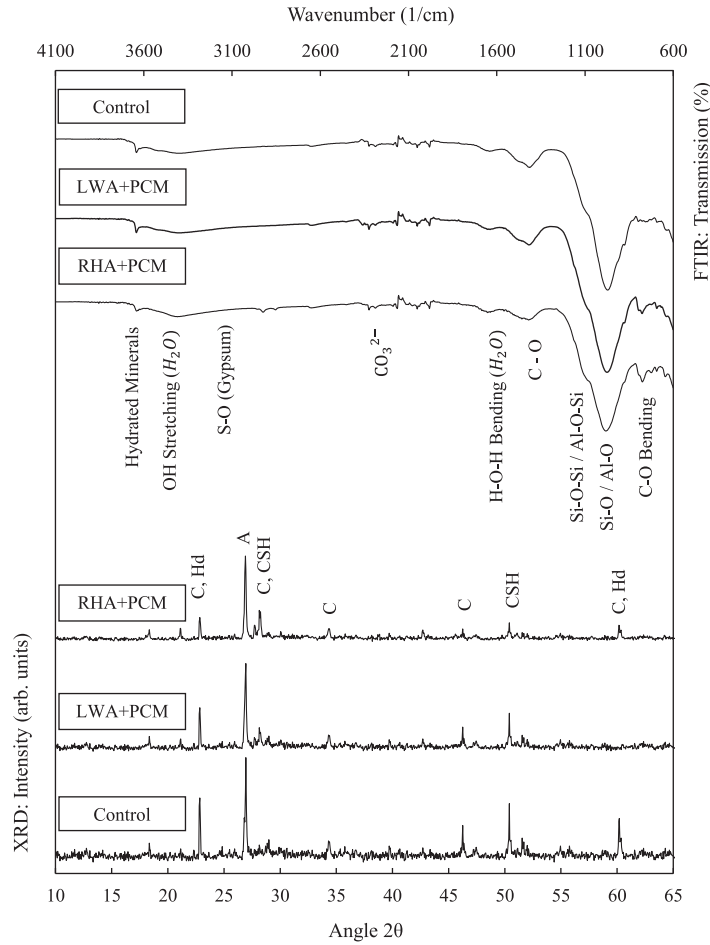


Figure 9. XRD diffractograms and FTIR spectra of raw materials used in Mix 1. Notes: C = Calcite, A = Aragonite, Hd = Hydrotalcite, CSH = Calcium Silicate Hydrate (C–S–H), and Al = alumina.

RHA presoaked in PCM, which show incorporation of PCM in the media does not drastically change the crystal structure or chemical composition of the binding phase. These results imply that the reduced strength and heat evolution observed in mixes containing PCM are therefore due to microstructural alterations, such as at the sand/cement interface, or chemical effects, such as reducing the overall reactivity of the system and not the production of alternative phases.

3.8. SEM observation of ITZ

The ITZ is one of the important zones that affects different physical and mechanical properties of concrete. Aggregate particles are several orders of magnitude larger than cement particles. This difference in size disrupts the packing of the cement grains close to the aggregate surface. This phenomenon is called the ‘wall’ effect and causes the closest zone to the aggregate have smaller cement particles and higher porosity.[58–60]

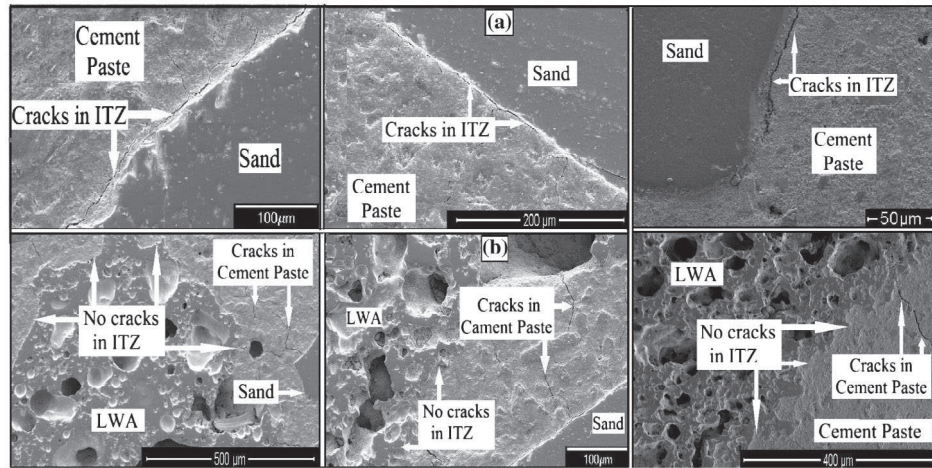


Figure 10. SEM imaging of mortar. (a) Cracks in the ITZ of sand. (b) No cracks in the ITZ of LWA.

Because of this relatively high porosity, ITZ is weaker in strength than the paste that is further away from the aggregate particle and thus, this zone has been considered the weak link of concrete. Therefore, any cracking in the concrete has been noticed to initiate in the immediate area around the aggregates.[61,62]

LWA has a porous structure, whereas there is no porosity in the structure of sand (Figure 1(a)). Because of this, sand particles disrupt the packing of the cement grains, leading to a porous ITZ. Therefore, microcracks were initiated in the weak ITZ of sand (Figure 10(a)). In contrast to sand, LWA particles do not disrupt the packing of the cement grains. The surface of LWA particles contains pores with different sizes. The size of the pores is bigger than the size of cement particles, thus allowing these particles to pass through the LWA surface and enter the pores' volume along with the water.[63] Therefore, the LWA particles do not disturb the size distribution of cement particles closest to their surface, and thus the 'wall' effect does not take place. Therefore, the ITZ of LWA had a porosity and strength comparable to porosity and strength of the bulk cement

paste; thus, no extra cracks were generated on the closest layer to the LWA particles (Figure 10(b)).

It should be mentioned that while the size of the sand and LWA particles was on the order of some mm, their ITZ was in the order of some μm . The size of RHA particles was in the size of some μm ; thus, even if they cause 'wall' effect for cement particles, a much more advanced and accurate SEM machine than the one that was available would be required to capture their ITZ.

4. Conclusion and future work

The ability of LWA and RHA to incorporate PCMs in cementitious materials was investigated. The results show that because of their porosity, LWA and RHA can absorb and keep PCMs inside their structure; however, they release a portion of PCM into the bulk cement paste. Incorporation of LWA presoaked in PCM in the mortar decreases compressive strength; however, it remains within the range appropriate for most construction purposes. When RHA is utilized as the carrier, the compressive strength is drastically reduced; therefore, it should be used

as the carrier agent when high compressive strengths are not demanded. The results also show that the incorporation of LWA and RHA presoaked in PCM does not lead to a significant change in the chemical composition or the creation of new phases in the mortar; and regarding compatibility with the cementitious media, they can be used as PCM carrier agents.

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Note

1. Certain commercial equipments, 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, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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