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Los Angeles

**Microencapsulated Phase Change Composite Materials
for Energy Efficient Buildings**

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Philosophy in Mechanical Engineering

by

Alexander Thiele

2016

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ABSTRACT OF THE DISSERTATION

Microencapsulated Phase Change Composite Materials for Energy Efficient Buildings

by

Alexander Thiele

Doctor of Philosophy in Mechanical Engineering

University of California, Los Angeles, 2016

Professor Laurent G. Pilon, Co-Chair

Professor Gaurav Sant, Co-Chair

This study aims to elucidate how phase change material (PCM)-composite materials can be leveraged to reduce the energy consumption of buildings and to provide cost savings to ratepayers. Phase change materials (PCMs) can store thermal energy in the form of latent heat when subjected to temperatures exceeding their melting point by undergoing a phase transition from solid to liquid state. Reversibly, PCMs can release this thermal energy when the system temperature falls below their solidification point. The goal in implementing composite PCM walls is to significantly reduce and time-shift the maximum thermal load on the building in order to reduce and smooth out the electricity demand for heating and cooling. This Ph.D. thesis aims to develop a set of thermal design methods and tools for exploring the use of PCM-composite building envelopes and for providing design rules for their practical implementation.

First, detailed numerical simulations were used to show that the effective thermal conductivity of core-shell-matrix composites depended only on the volume fraction and thermal conductivity of the constituent materials. The effective medium approximation reported by Felske (2004) was in very good agreement with numerical predictions of the effective thermal conductivity. Second, a carefully validated transient thermal model was used to simulate microencapsulated PCM-composite walls subjected to diurnal or annual outdoor tempera-

ture and solar radiation flux. It was established that adding microencapsulated PCM to concrete walls both substantially reduced and delayed the thermal load on the building. Several design rules were established, most notably, (i) increasing the volume fraction of microencapsulated PCM within the wall increases the energy savings but at the potential expense of mechanical properties [1], (ii) the phase change temperature leading to the maximum energy and cost savings should equal the desired indoor temperature regardless of the climate conditions, (iii) microencapsulated PCM-concrete walls have the best energetic performance in climates where the outdoor temperature oscillates around the desired indoor temperature, (iv) microencapsulated PCM offers the largest energy and cost savings when embedded in South- and West-facing walls and during the summer months in San Francisco and Los Angeles, CA.

Third, a novel experimental method was developed to rapidly quantitatively characterize the thermal performance and potential energy savings of composite materials containing phase change materials (PCM) based on a figure of merit termed the energy indicator (EI). The method featured (i) commonly used specimen geometry, (ii) straightforward experimental implementation, and (iii) sensitivity to relevant design parameters including PCM volume fraction, enthalpy of phase change, composite effective thermal conductivity, and specimen dimensions.

Finally, the widely-used admittance method was extended to account for the effects of phase change on the thermal load passing through PCM-composite building walls subjected to realistic outdoor temperature and solar radiation flux. The speed and simplicity of the admittance method could facilitate the design and evaluation of the energy benefits of PCM-composite walls through user-friendly design software for a wide range of users.

The dissertation of Alexander Thiele is approved.

Adrienne Lavine

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University of California, Los Angeles

2016

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NOMENCLATURE

a	length of cubic unit cell, μm
A	parameter in Equation (3.4)
A, B	parameters used in Equation (7.6)
A_c	cross-sectional area, m^2
$AFUE$	annual fuel utilization efficiency
A_k	area of wall with orientation “k”, m^2
B	parameter in Equation (3.4)
$c_{p,j}$	specific heat of phase “j” in the composite structure, $\text{J/kg}\cdot\text{K}$
C_D	centroidal distance between two proximal capsules, μm
C_T, C_H, C_C	total, heating, and cooling cost, \$
d_i	specimen diameter, mm
d_o	outer cylindrical mold diameter, mm
D	diameter, μm
E_r	relative energy reduction, %
f	decrement factor
h_i, h_o	indoor and outdoor convective heat transfer coefficient, $\text{W/m}^2\cdot\text{K}$
h_{sf}	latent heat of fusion, J/kg
H	enthalpy, J
$H_H(q_L''), H_C(q_L'')$	heating and cooling heaviside step functions
k	thermal conductivity, $\text{W/m}\cdot\text{K}$
k_j	thermal conductivity of phase “j” in the composite structure, $\text{W/m}\cdot\text{K}$
L	unit cell length or wall layer thickness, μm or mm
$m_{i,j}$	i^{th} element of layer j 's transmission matrix [Equation (7.10)]
M_i	i^{th} element of the overall transmission matrix [Equation (7.8)]
$\mathbf{n}$	normal unit vector
N	number of unit cells or parameter used to determine f_S in Equation (7.17)
p	number of spherical capsules in a unit cell

Q	energy, J
Q''	energy flux, J/m ²
q_s''	solar irradiation, W/m ²
q_x'', q_y'', q_z''	heat flux along the x -, y -, and z -directions, W/m ²
$\bar{q}_x''$	area-averaged heat flux along the x -direction, W/m ²
r	radius, μm
$\mathbf{r}$	position vector $\mathbf{r} = \langle x, y, z \rangle$
R_E	electricity rate, \$/kWh
R_G	gas rate, \$/J
S_T, S_H, S_C	total, heating, and cooling cost savings, \$
$SEER$	seasonal energy efficiency ratio, BTU/Wh
t	time, s
t_{max}	time of maximum heat flux through composite wall, hours
$t_{max,m}$	time of maximum heat flux through pure concrete wall, hours
t_s	thickness of capsule shell, <i>i.e.</i> $t_s = (D_s - D_c)/2$, μm
T	temperature, K or °C
T_o, T_L	temperature at $x = 0$ and $x = L$, K
$T_{in}, T_\infty, T_{sky}$	indoor, ambient, and sky temperatures, °C
T_{max}, T_{min}	maximum and minimum outdoor temperatures, °C
T_{sa}	sol-air temperature, °C
$\bar{T}_{sa}$	daily-averaged sol-air temperature, °C
$\bar{T}_z$	daily-averaged temperature at the center of a wall layer containing PCM, °C
U	overall heat transfer coefficient, W/(m ² ·K)
V	volume, m ³
x_{PCM}	distance between the inner wall surface and the center of the PCM-layer, m
Greek symbols	
α	thermal diffusivity, m ² /s
α_s	surface solar absorptivity
β	parameter in Equation (3.9)

δ	ratio of shell diameter to core diameter, $\delta = D_s/D_c$
δ_ϕ	incremental PCM volume fraction
ΔT_{pc}	phase change temperature window, °C
ΔT_n	amplitude of temperature oscillation at a location “n”, °C
Δx	minimum mesh size, μm
ϵ	surface emissivity
ϕ_i	time lag “i” where i = AM, MW, or S, h
ϕ_j	volume fraction of phase “j” in the composite structure
$\phi_{c/s}$	volume fraction of core to shell in a microcapsule, $\phi_{c/s} = \phi_c/(\phi_c + \phi_s)$
ϕ_{c+s}	volume fraction of capsules in the composite structure, $\phi_{c+s} = \phi_c + \phi_s$
ϕ_{max}	volume fraction of closely-packed capsules
γ	factor used in Equation (7.33)
ρ_j	density of phase “j” in the composite structure, kg/m^3
σ	Stefan-Boltzmann constant, $\text{W}/\text{m}^2 \cdot \text{K}^4$
τ_d	time delay, i.e. $\tau_d = t_{max} - t_{max,m}$, hours
Θ_N, Θ_D	numerator and denominator of the Felske model [Equation (3.3)]

Subscripts

AM	refers to admittance method
c	refers to core material
$c + s$	refers to core-shell particle
cr	refers to the critical thermal conductivity ratios
eff	refers to effective properties
E	refers to East
f	refers to final conditions
i	refers to initial conditions
ins	refers to insulation
j	refers to constituent material “j”
l	refers to PCM liquid phase
L	refers to values at $x = L$

<i>MW</i>	refers to Mackey and Wright
<i>m</i>	refers to matrix
<i>max</i>	refers to maximum value of variable
<i>min</i>	refers to minimum value of variable
<i>N</i>	refers to North
<i>o</i>	refers to values at $x = 0$
<i>opt</i>	refers to optimum values
<i>pb</i>	refers to plaster board
<i>pc</i>	refers to phase change
<i>s</i>	refers to PCM solid phase or shell
<i>S</i>	refers to South or Surface
<i>t</i>	refers to total quantities
<i>W</i>	refers to West

CHAPTER 1

Introduction

1.1 Building energy consumption

In 2009, building operation was responsible for about 30% of greenhouse gas emission and accounted for about 40% of primary energy consumption globally [12]. Furthermore, greenhouse gas emission from the building sector is expected to grow in the next decades as a result of rapid economic growth [13]. Thus, the United Nations Environment Programme (UNEP) suggested that governments prioritize the building sector in their strategies to curtail climate change in their respective countries by reducing greenhouse gas emission and improving building energy efficiency [12].

Similar statistics hold for the United States. In 2011, building operation accounted for 41% of total US primary energy consumption with 46% consumed by commercial and 54% by residential buildings [14]. About 30 and 43% of this energy was consumed for space heating and air conditioning in commercial and residential buildings, respectively [14]. Therefore, reducing the energy required for heating and cooling would substantially improve building energy efficiency.

On the other hand, energy consumption by the building sector in California was below the national average in 2012, accounting for 26% of total state energy consumption [15]. This can be attributed to the mild climate and to aggressive energy efficiency policies set by the state government [3]. In fact, California had the third smallest energy consumption per capita in the U.S. in 2012 [15]. Figures 1.1a and 1.1b show the relative energy consumption by end use for commercial buildings in 2002 and for residential buildings in 2006 in California, respectively. They illustrate that space heating and cooling accounted for approximately 17

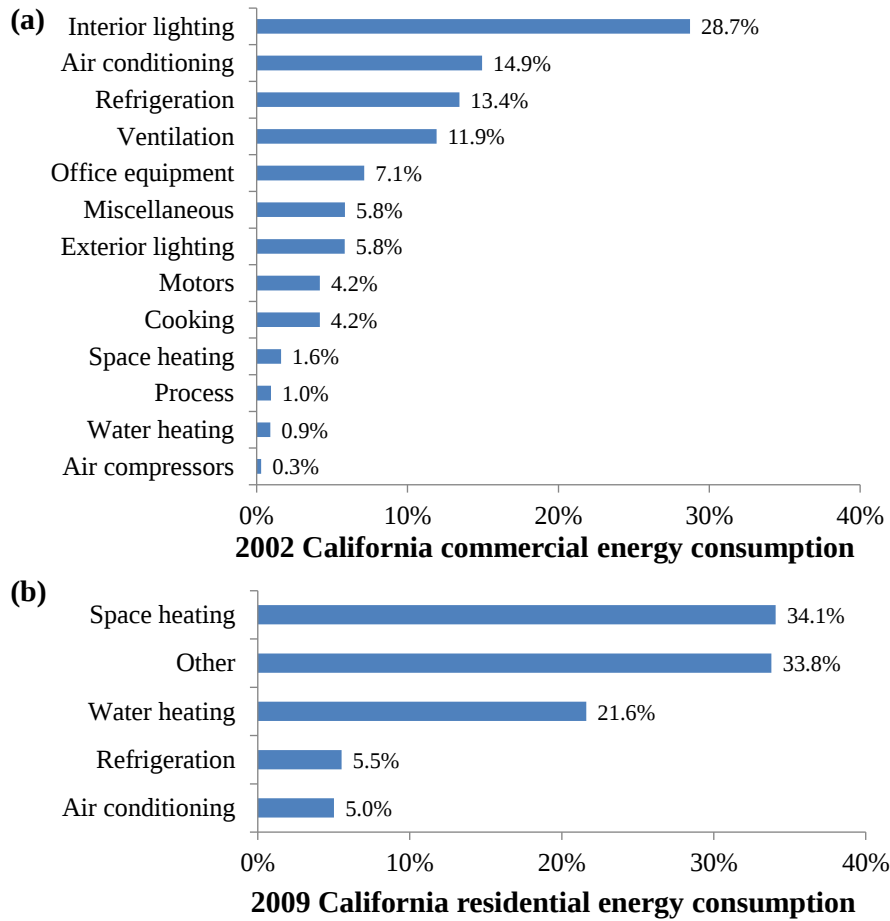


Figure 1.1: (a) Commercial and (b) residential energy consumption by end use in California in 2002 and 2009, respectively [2,3].

and 40% of primary energy consumption by commercial and residential buildings in 2002 and in 2009, respectively [2,3].

1.2 California climates and energy landscape

1.2.1 California climate zones

Energy requirements for space heating and cooling in buildings vary regionally based on climate. California has been divided into 16 climate zones based on numerous factors such as energy use and climate characteristics [16]. Figure 1.2a shows a map illustrating the different California climate zones defined by the California Energy Commission (CEC) and

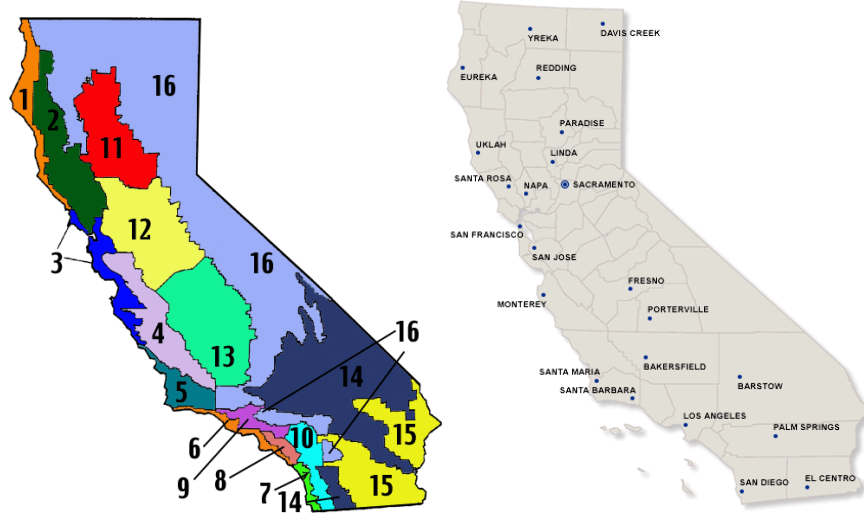


Figure 1.2: Map of the 16 California climate zones and of the major cities.

a map of the major cities for geographic reference. The climate map was used to establish zone-specific energy budgets which designate the maximum amount of energy that a building in each zone is expected to consume annually. This enables more informed decision-making around urban development and expansion of the energy infrastructure. Additionally, by using representative weather datasets, simulations can be performed to evaluate zone-specific building energy efficiency strategies [16].

The Energy Design Tools Group in the Department of Architecture and Urban Design at UCLA developed the Climate Consultant software [17]. It organizes climate data, such as outdoor temperature, solar irradiation, psychrometric data, and wind speed and direction, into graphical representations that can assist users in developing climate-specific energy efficiency strategies. In addition, Climate Consultant can translate EnergyPlus weather (EPW) files, available from the U.S. Department of Energy website [18] for thousands of weather stations around the world, into usable datasets.

1.2.2 Peak electricity demand and time of use pricing

Electricity demand follows a reliable diurnal variation. It is minimal at night time and increases to a peak that typically occurs in the late afternoon [19]. Furthermore, electricity

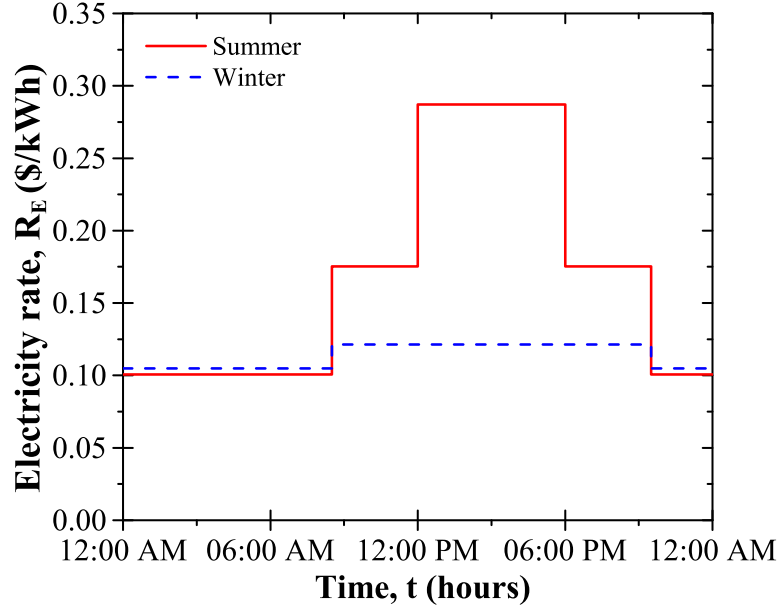


Figure 1.3: TOU electricity rate schedule for a typical summer and winter day.

demand is often substantially larger during the summer, due to the fact that air conditioning systems consume large amounts of electricity [19]. Electric grid operators satisfy demand throughout most of the year using baseload plants. However, they rely on peaker plants during large demand periods such as summer afternoons to avoid grid damage and blackouts. Peaker plants are substantially more costly to operate and typically run on fossil fuels. In fact, the cost of generating electricity can be as much as ten times larger during peak hours than during night time [19].

To encourage ratepayers to reduce peak-hour electricity consumption, California utilities such as Pacific Gas and Electric (PG&E) and the Los Angeles Department of Water and Power (LADWP) have adopted time of use (TOU) electricity rate schedules for their residential and commercial customers. Figure 1.3 plots the electricity rate as a function of time throughout a summer and winter day under a TOU schedule. Time of use rate schedules divide the day into peak, partial-peak, and off-peak time periods and into peak and off-peak periods during the summer and winter, respectively, each with a different electricity price. Such a rate schedule incentivizes customers to curtail their electricity consumption during peak hours by charging them a higher rate during that time. By adjusting their power con-

sumption habits, ratepayers can save money while reducing the need for the costly operation of peaker plants.

1.3 Zero net energy

To curb the energy consumption of the building sector, the 2008 California long term energy efficiency strategic plan established two major objectives: (1) all new residential buildings should be zero net energy (ZNE) by 2020 and (2) all new commercial buildings by 2030 [20]. This plan was developed by the California Public Utilities Commission (CPUC) in collaboration with several California investor owned utilities (IOU): Pacific Gas and Electric (PG&E), Southern California Edison Company (SCE), Southern California Gas Company (SCG), and San Diego Gas & Electric (SDG&E). The ZNE goals are expected to support California’s greenhouse gas reduction goals by (i) accelerating the adoption of greater energy efficiency in buildings, (ii) promoting distributed renewable energy generation, and (iii) driving job growth in the clean energy sector [21]. However, there has been debate regarding what metric or combination of metrics should be used to classify ZNE buildings [21].

Table 1.1 describes four metrics that have been suggested for the evaluation of ZNE buildings: site energy, source energy, cost, and emissions [22].

The ZNE site definition is both intuitive and easy to measure at the building under consideration and has thus been used in nationwide studies of ZNE buildings [23]. However, it fails to distinguish between the comparative advantages and disadvantages of different forms of on-site energy consumption such as gas and electricity. More specifically, it neglects differences between the fuels used to generate the electricity as well as differences in the distribution processes for electricity and gas. For example, a unit (e.g., J) of electrical energy is given the same value as an energy unit of gas on-site even though electricity is more valuable than gas at the generation source [22]. On the other hand, the ZNE source definition employs site-to-source energy conversion factors to relate the value of energy on-site to its value at the off-site generation source [24]. These factors account for the energy associated with extraction, processing, and transportation of a fuel prior to consumption or

Table 1.1: Summary of ZNE metrics.

Metric	Description
ZNE site energy	Building produces at least as much energy as it consumes annually accounted for at the site of consumption.
ZNE source energy	Building produces at least as much energy as it consumes annually accounted for at the source of energy production.
ZNE cost	The ratepayer either receives net payment from the utility or has a zero net electricity cost annually.
ZNE emissions	Building produces at least as much emissions-free renewable energy as it consumes from emission-generating sources.

distribution, greenhouse gas emission due to combustion, and transmission and distribution losses [24]. For example, with an energy conversion factor of three, a unit of electrical energy produced from solar panels on site will offset three times that amount of energy at the off-site generation source [24]. Energy conversion factors are complicated to define and vary widely with generation fuel, geographic region, and time of day [24]. As a result, a ZNE source building is difficult to evaluate, but the metric provides a more rigorous indication of a building’s ecological footprint than the ZNE site definition.

The ZNE cost definition is very appealing to ratepayers. However, electricity cost is largely dependent on government subsidies and incentives and on utility rates and policies which can vary dramatically over time [22]. As a result, a ZNE cost building may not necessarily reduce energy use or greenhouse gas emissions, which are the primary objectives of a ZNE building [21]. Additionally, without financial contribution from the ratepayer, the utilities would incur the large fixed cost of maintaining the energy infrastructure and would thus have little incentive to support this ZNE definition.

Lastly, the ZNE emissions definition effectively accounts for the difference in greenhouse gas emissions between different electricity generation methods. Similar to the ZNE source definition, complicated conversion factors are necessary to determine the emissions associated

with electricity from the grid. This definition complicates the comparison of ZNE buildings in different regions. For example, a building in a region supplied by hydroelectricity or nuclear power generation would have a substantially smaller on-site generation requirement to achieve ZNE emissions than one in a region supplied by a coal power plant.

The time-dependent valuation (TDV) of energy refers to a methodology similar to that described for TOU electricity pricing. By considering TDV, on-site solar electricity generation would have higher value during peak hours than during off-peak hours. This has been suggested as an additional consideration to the aforementioned ZNE definitions [21].

Regardless of the chosen metric, a ZNE building should first achieve high energy efficiency in design and operation and should then meet its remaining energy needs with on-site renewable energy generation [22]. In some cases, high energy efficiency may be achieved but local renewable energy resources may be limited. In favor of meeting the California ZNE objectives, it has been suggested that policy makers adopt a ZNE equivalency definition by which a highly efficient building without renewable generation capability may be recognized as ZNE [21].

It is important to note that the ZNE objectives are not mandatory. In fact, satisfaction of these goals is contingent upon both technical feasibility and cost-effectiveness [21]. The IOUs have suggested a general strategic path to ZNE buildings consisting of six steps: (1) minimize building loads, (2) optimize system efficiency based on equipment efficiency and use, (3) use the highest efficiency appliances, (4) optimize building operations to better meet occupant and energy efficiency needs, (5) improve occupant interactions with the building, and as a last step (6) employ renewable power generation wherever it is feasible [21]. These steps do not require completion in any particular order. Each represents an important area for progress toward the goal of satisfying the desired ZNE metric(s).

1.4 Energy efficient building envelopes

One strategy to minimize building loads involves using building envelope materials that control the heat flow into and out of buildings. Thermally massive materials, such as concrete,

have large heat capacity which allows them to store thermal energy and release it at a later time [25, 26]. This results in both a reduction and time delay of the thermal load on the building. On the other hand, materials with large thermal resistance, such as insulation, have very small thermal conductivities and can reduce the thermal load on the building [25]. However, walls with high thermal resistance may run the risk of surface condensation, which can contribute to microbial growth [25]. Furthermore, it has been suggested that increasing the thermal resistance of a building wall may decrease the benefit from using high thermal mass materials [26]. Therefore, both the thermal mass and thermal resistance must be considered carefully when designing building envelope materials.

Composite cementitious materials containing microencapsulated phase change materials (PCM) have also been suggested as a way to increase the buildings' thermal inertia and thus their energy efficiency [27–29]. PCM are distinguished from traditionally thermally massive materials, as they store energy in the form of latent heat by reversibly changing phase between solid and liquid instead of storing energy as sensible heat. One advantage of latent over sensible heat storage is the relatively large energy storage capacity per unit volume [5, 8]. The goal in implementing composite PCM walls is to significantly reduce and time shift the maximum thermal load on the building in order to reduce and smooth out the electricity demand for heating and cooling. This could help ratepayers take advantage of TOU electricity rate schedules while reducing the ecological footprint of buildings towards achieving ZNE [5, 30–33].

1.5 Objectives and scope

The overall goal of this study is to elucidate how PCM-composite building envelopes can be leveraged to reduce the energy consumption of buildings for space heating and cooling and to provide cost savings to ratepayers. The specific objectives are as follows:

1. To develop thermal design methods and tools for exploring the use of PCM-composite materials in smart multifunctional building envelopes.

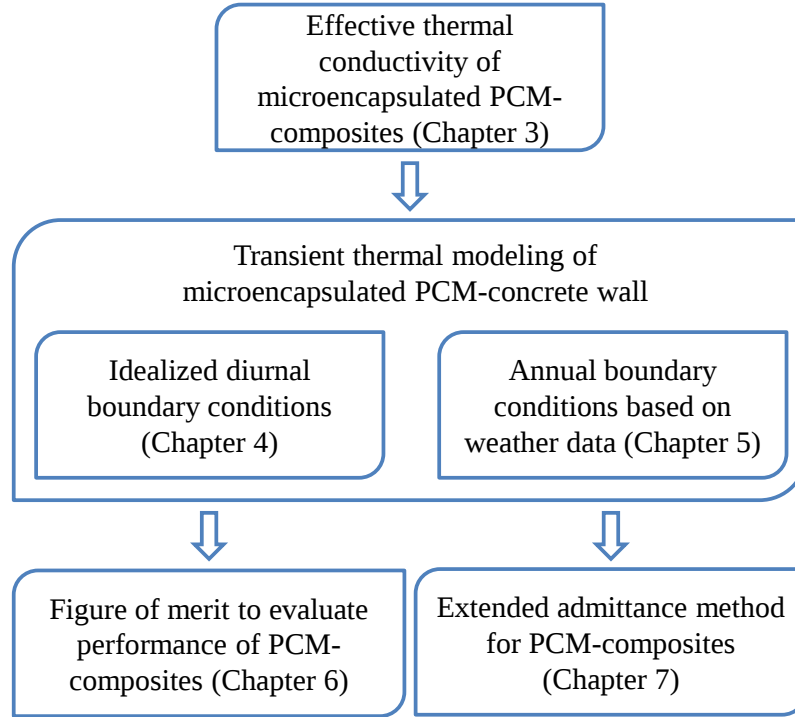


Figure 1.4: Flowchart describing the projects corresponding to each chapter of this thesis.

2. To assess the potential energy and cost savings of a building made with PCM-composites in selected California climates.
3. To provide design rules for the practical implementation of PCM-composite building walls.

Figure 1.4 illustrates the progression of projects corresponding to the primary chapters of this thesis. Chapter 2 begins with a review of the types of PCM and their use in building materials. Chapter 3 [34] presents detailed numerical simulations predicting the effective thermal conductivity of spherical monodisperse and polydisperse core-shell particles ordered or randomly distributed in a continuous matrix. Chapter 4 [35] assesses the daily energy savings potential of a concrete wall containing microencapsulated PCM wall under idealized diurnal temperature variations based on a carefully validated transient thermal model. Chapter 5 [36] evaluates the annual energy and cost savings potential of adding microencapsulated PCM to an average single family home located in either San Francisco or Los Angeles using actual weather data. Chapter 6 [37] describes a simple experimental method supported

by numerical simulations and a figure of merit to characterize the energy performance of microencapsulated PCM-composite building materials. Chapter 7 presents an extension of the widely-used admittance method to evaluate the thermal load through single and multilayer microencapsulated PCM-composite building envelopes. Lastly, chapter 8 summarizes the main contributions of this thesis and presents recommendations for future work.

CHAPTER 2

Background

2.1 Phase change materials

Phase change materials (PCM) transitioning between solid and liquid states near room temperature have been used to enhance the thermal storage capacity of traditional building materials [6, 9]. They store thermal energy in the form of latent heat when subjected to temperatures in excess of their melting point. Reversibly, PCM can release the thermal energy previously stored when the system temperature drops below their melting point.

2.1.1 Classification

PCM can be divided into three categories: organic, inorganic, and eutectic [6]. Organic PCM consist mainly of paraffins and fatty acids. Paraffins are straight-chain hydrocarbons with the general chemical formula C_nH_{2n+2} and are a by-product of oil refining [38]. They can be categorized based on purity as technical ($\sim 95\%$ pure) or laboratory grade ($>99\%$ pure). However cost considerations limit commercial use to technical grade paraffins [5, 6, 39]. Inorganic PCM are typically either salt hydrates or metallics [6]. Lastly, eutectics are mixtures of two or more PCM and can be any combination of organic and inorganic constituents [6]. Table 2.1 summarizes the advantages and disadvantages of organic and inorganic PCM [4–10].

Table 2.1: Characteristics of organic and inorganic PCM [4–10].

Organic	Inorganic
Advantages	
1. Wide phase change temperature selection	1. Wide phase change temperature selection
2. No supercooling	2. High latent heat of fusion
3. No phase segregation	3. Narrow phase change temperature window
4. Low thermal conductivity	4. Non-flammable
5. Stable	5. Low cost relative to organic compounds
6. Non-reactive, non-corrosive	
7. Non-toxic	
8. Recyclable	
Disadvantages	
1. Low volumetric latent heat of fusion	1. Supercooling
2. Flammable	2. Phase segregation
3. Relatively low latent heat of fusion	3. High volume change during transition
	4. Degradation after many cycles
	5. High thermal conductivity
	6. Corrosive

2.1.2 Thermophysical properties

Numerous reviews have summarized the thermophysical properties of commercial and laboratory grade PCM [4–11, 40–45]. Figure 2.1 compares the phase change temperature and latent heat of fusion for common types of PCM [4]. In general, paraffin has a small latent heat of fusion compared to inorganic materials, such as salt hydrates, but their phase change temperatures are within the desired temperature range for building applications.

Many of the aforementioned reviews reported only the phase change temperature and latent heat of fusion. In fact, the density, specific heat, and thermal conductivity of most phase change materials were not reported in the literature. We recently compiled a complete database of the thermophysical properties of PCM from the literature that can be found online [46]. It reports properties such as phase change temperature, latent heat of fusion,

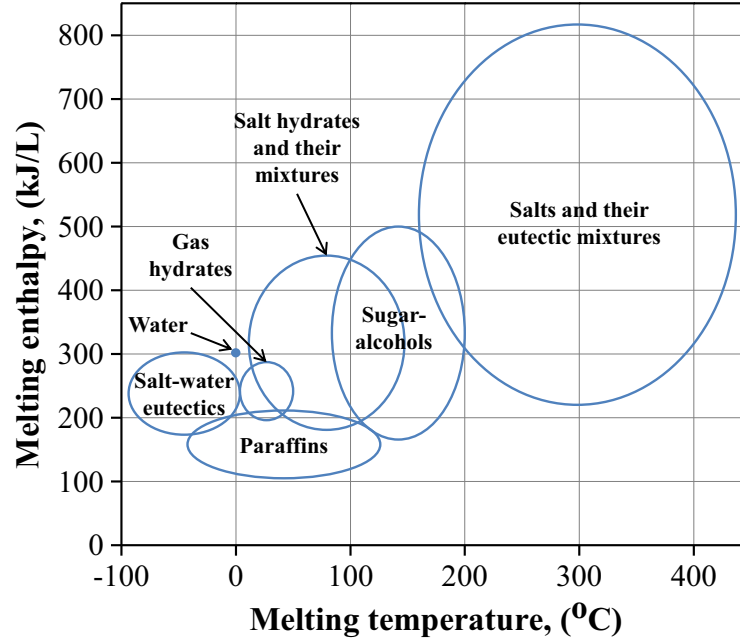


Figure 2.1: Comparison of the phase change temperature and latent heat of fusion for several types of PCM (reproduced based on Baetens et al. [4]).

thermal conductivity, density, and specific heat for a large number of commercially available PCM and also for laboratory grade PCM reported in the literature [4–11, 40–45].

2.1.3 PCM-composite building materials

The use of composite building materials containing PCM has been reviewed extensively [4, 6–9, 11, 29, 47, 48] and need not be repeated. The forms of PCM composite walls that have received the most attention include wallboard (i.e., plasterboard or drywall), shape stabilized PCM (SSPCM) board, and PCM-concrete composites, as well as masonry blocks and alternative containers made of PVC or aluminum foil [6, 8, 11]. Most experimental studies have reported that adding PCM to building walls reduced the amplitude of wall surface and/or room temperature oscillations and time-shifted the temperature [8].

Table 2.2 shows a set of desirable thermophysical, kinetic, chemical, and economic traits of PCM that have been identified for building applications [4, 6, 7, 10, 11]. In summary, the ideal PCM for building applications is one that offers (i) large latent and sensible thermal energy storage capacity, (ii) reliable and robust ability to store and release latent thermal energy

Table 2.2: Desirable PCM characteristics for building applications [4, 6, 7, 10, 11].

Thermophysical properties
1. Phase change temperature within desired operating range
2. Large volumetric latent heat of fusion
3. Large volumetric heat capacity
4. Small phase change-induced volume changes
5. No phase segregation
6. Small vapor pressure at operating temperature
Kinetic properties
1. High nucleation rate to avoid supercooling of the liquid phase
2. High crystal growth rate so the system can meet heat recovery demands
Chemical properties
1. Complete and reversible freeze/melt cycles
2. Long and robust cycle lifetime
3. Stable
4. Non-toxic, non-flammable, and non-corrosive
Economic properties
1. Low cost
2. Large scale availability

through complete phase change cycles at building operating temperatures, (iii) compatibility with the built environment, and (iv) economic viability. In Table 2.2, phase segregation refers to non-uniform phase change within the PCM volume, leading to the formation of coexisting solid and liquid regions. It can occur by one of two mechanisms: (i) the outer boundaries of a PCM melt or freeze while the rest of the volume remains in a solid or liquid state or (ii) the constituents of an impure PCM separate and change phase incongruently. It has been suggested that PCM for building applications should have high thermal conductivity to promote complete melting and avoid phase segregation [6, 10, 11]. However, this may be counterproductive, as it would also increase the effective thermal conductivity of the building wall, thus reducing the thermal resistance and increasing heat transfer through the wall.

Methods of adding PCM into building materials generally fall into four categories: (i) di-

rect incorporation, (ii) immersion, (iii) macroencapsulation, and (iv) microencapsulation [11]. Direct incorporation consists of adding PCM to supporting materials, such as wallboard or concrete, during the production process. The immersion method involves dipping a finished porous building material into melted PCM. Major drawbacks of these two methods include the lack of a barrier to protect the PCM against leakage during melting and against chemical reactions with the matrix material [8, 9]. To address this issue, macroencapsulation of PCM in containers such as bags, tubes, or panels has been proposed before incorporating the encapsulated PCM into composite walls [11, 47]. However, macroencapsulation suffers from a high temperature differential between the encapsulated PCM core and the boundary which can lead to incomplete melting or solidification of the PCM [11, 47, 49]. This can be addressed by containing PCM in microscopic capsules with thin walls and diameter ranging from 1 μm to 1 mm [45, 49]. The microencapsulated PCM can easily be added to a building material such as concrete during production as long as the shell material is compatible with the supporting material [11, 47, 49].

Several authors have used the immersion technique to impregnate ordinary wallboard (i.e., plasterboard or drywall) with PCM [50, 51]. Scalat et al. [50] impregnated wallboard with 28.9 wt.% of a combination of butyl stearate and butyl palmitate PCM. They constructed indoor test rooms with and without PCM wallboard to evaluate the heat load shifting capability of the PCM. The heating and cooling cycles in the room with PCM-impregnated wallboard lasted at least 2 hours longer than in the room with ordinary wallboard. Athienitis [51] conducted experiments on a full scale outdoor test room lined with wallboard impregnated with about 25 wt.% of butyl stearate. A 1 ft² piece of wall was cut out and replaced with ordinary wallboard for comparison. The test room was exposed to winter weather conditions in Montreal, Canada. Over a given day, the amplitude of surface temperature variation was about 7°C smaller for the PCM wallboard. These measurements were compared to numerical predictions with an average absolute error of 0.25°C. However, that incorporating PCM in materials via immersion eventually leads to leakage [11, 52]. To address this issue, Borreguero et al. [53] formed wallboards with up to 7.5 wt.% of microencapsulated PCM instead of impregnating. Their experimental setup consisted of a

wallboard sample insulated on all four lateral faces to simulate one dimensional heat flow. A cyclic temperature profile was imposed at one face and the resulting temperature variation was measured at the adjacent face with thermocouples. Over a given cycle, the amplitude of temperature variation measured at the face adjacent to the controlled temperature decreased by about 2.6°C when adding microencapsulated PCM to the wallboard.

Shape stabilized PCM (SSPCM) boards have been proposed as an alternative latent heat storage material to composite PCM/wallboards [54–57]. They are fabricated by adding molten PCM to a melted supporting material such as high density polyethylene (HDPE) and extruding the mixture into a slab [56]. Inaba and Tu [54] and Sari [56] used HDPE to form SSPCM boards containing up to 74 and 77 wt.% paraffin wax, respectively, with no PCM leakage. Xiao et al. [55] fabricated SSPCM board using styrene butadiene styrene (SBS) that contained up to 80 wt.% paraffin wax. A commercial SSPCM called Energain developed by DuPont de Nemours, consisted of 60 wt.% paraffin wax stabilized in a copolymer and laminated with aluminum.

Concrete is an appealing construction material thanks to its inherently large thermal inertia. In fact, concrete has a significantly larger volumetric heat capacity than gypsum wallboard due to its higher density [29]. However, PCM-concrete composites have been experimentally studied much less extensively than PCM-wallboards and shape stabilized PCM (SSPCM) boards [8, 9]. Hunger et al. [58] studied the effect of adding microencapsulated PCM to self-compacting concrete on the effective thermal and mechanical properties of the composite. They found that the compressive strength of their specific mixture decreased by 13% for every additional mass percentage of PCM. The effective thermal conductivity of the composite also decreased with the addition of PCM. They concluded that composite concrete with a PCM content of 3 wt.% and a compressive strength of 35 N/mm² was acceptable for most building applications. Cabeza et al. [27] constructed outdoor enclosures made with plain concrete and with concrete containing 5 wt.% microencapsulated PCM. The enclosures were exposed to weather conditions in Lleida, Spain and temperatures were measured at the inner wall surfaces during week-long tests during the late summer. The PCM concrete enclosure featured a 3°C decrease in the amplitude of indoor temperature oscillations and

a 2 hour shift in the maximum indoor temperature compared with its counterpart made of plain concrete.

2.2 Simulating phase change in single phase systems

Analytical solutions of solid-liquid phase change heat transfer problems are only available for homogeneous systems with simple geometries and boundary conditions [28, 59, 60]. As a result, numerical methods have been devised to model heat transfer during solid-liquid phase change including (i) the enthalpy method, (ii) the heat capacity method, (iii) the temperature transforming model, and (iv) the heat source method [59]. The advantages, disadvantages, and limitations of each method have been reviewed by Al-Saadi and Zhai [59]. The enthalpy method [60–64] and heat capacity method [61, 62, 65, 66] are the two most commonly used numerical methods [28].

The enthalpy method consists of solving the transient heat conduction equation expressed in terms of temperature and enthalpy $H(T)$ as [61],

$$\frac{\partial \rho H(T)}{\partial t} = \nabla(k \nabla T) \quad (2.1)$$

where ρ and k are the density and thermal conductivity of the PCM, respectively. The enthalpy function $H(T)$ represents the total energy of the material including sensible and latent forms of energy. The enthalpy of a PCM can be determined as a continuous function of temperature by using differential scanning calorimetry (DSC) measurements [67]. Alternatively, a piecewise enthalpy function $H(T)$ may be defined in terms of the latent heat of fusion h_{sf} and the phase change temperature window ΔT_{pc} [60, 63, 64].

Moreover, the heat capacity method consists of solving the transient heat conduction equation expressed in terms of temperature and specific heat $c_p(T)$ as [61, 62, 65, 66],

$$\rho c_p(T) \frac{\partial T}{\partial t} = \nabla(k \nabla T) \quad (2.2)$$

To account for the latent heat stored during phase transition, the specific heat is defined as

a piecewise function of temperature given by [62],

$$c_{p,c}(T) = \begin{cases} c_{p,c,s} & \text{for } T < T_{pc} - \Delta T_{pc}/2 \\ c_{p,c,s} + \frac{h_{sf}}{\Delta T_{pc}} & \text{for } T_{pc} - \Delta T_{pc}/2 \leq T \leq T_{pc} + \Delta T_{pc}/2 \\ c_{p,c,l} & \text{for } T > T_{pc} + \Delta T_{pc}/2 \end{cases} \quad (2.3)$$

where $c_{p,c,s}$ and $c_{p,c,l}$ are the specific heats of the solid and liquid phase, respectively. Here, h_{sf} , T_{pc} , and ΔT_{pc} are the latent heat of fusion, the phase change temperature, and the temperature windows, respectively.

Lamberg et al. [62] experimentally studied heat transfer through a homogeneous paraffin PCM block contained in a rectangular aluminum enclosure. The PCM temperature was measured using thermocouples placed at various locations in the enclosure. The authors compared the measured local temperatures to numerical predictions obtained by implementing both the enthalpy and the heat capacity methods. They concluded that both numerical methods provided a “*good estimation*” of melting and freezing processes but that the heat capacity method agreed more closely with experimental data.

2.3 Simulation tools for energy efficiency of buildings

EnergyPlus is a comprehensive whole building energy simulation program that engineers, architects, and researchers use to model both energy consumption (e.g., HVAC, lighting, and plug and process loads) and water use in buildings. EnergyPlus is notable for its breadth but also for its versatility. It is free, open-source, and cross-platform; it can be run using Windows, Mac, and Linux operating systems. The program allows for the refinement or extension of analysis capability through the development of new modules. Alternatively, TRNSYS and ESP-r are modular open-source software that can be used to simulate building energy consumption.

Building envelopes embedded with PCMs have been incorporated as a material option within EnergyPlus [68–70], TRNSYS [71], and ESP-r [66]. Such software was designed primarily for use by experienced researchers and engineers. On the other hand, PCMExpress

[72] was developed to enable users with limited experience in thermal science and building modeling to evaluate the energy and economic benefits of PCM-composite materials. All of the above-mentioned software rely upon computationally intensive finite element methods when considering materials with temperature-dependent thermal properties such as those embedded with PCM [68]. This could limit the use of such software to personal computers.

Alternatively, the home energy efficient design (HEED) software was developed by the Environmental Design Tools Group at UCLA [73] for users with limited engineering expertise. HEED employs the admittance and total equivalent temperature difference/time-averaging (TETD-TA) methods to assess the thermal load through building walls rather than finite element methods [74]. This software allows users to evaluate a building's energy performance and to compare the effects of design changes on that performance. First, the user specifies the type, size, number of stories, and location of the building they would like to analyze. HEED then generates a corresponding building design that exactly meets the current California energy code as well as a design that is roughly 30% more energy efficient. Design parameters such as the floor plan, window type, wall construction, or on-site electricity generation may then be adjusted manually. Using EPW files as in the Climate Consultant software, HEED calculates the performance of the building over a whole year or over any given 12 day period. Building designs may be compared via three metrics: the Site Energy Use Intensity (SUI), the CO₂ production, and the passive performance. The SUI represents the BTU equivalent of all fuel and electricity used on site, while the passive performance describes the number of hours that the building operates with no heating or cooling. Fuel and electricity expenditures are also reported over the period under consideration. Rate information for several California utilities is available within HEED but the user may also manually input rate data.

HEED was validated against both Standard 140 and HERS BESTEST and passed nearly 100% of the validation test cases [73]. It was created according to building simulation software guidelines set by the CEC in the Alternative Calculation Method (ACM) [75]. This manual specifies how a baseline building should be designed based on building codes and numerous design parameters such as building type, climate, window areas and locations, and wall construction.

The same UCLA team is currently developing the software OPAQUE, a design tool that can enable users to understand the thermal performance of different composite wall designs. Wall assemblies may be created using innovative materials such as microencapsulated PCM-composites as well as conventional building materials. OPAQUE will allow users to evaluate the potential energy savings associated with incorporating PCM-composite materials into building envelopes. It will play an important role in communicating the benefits of using PCM-composites to homeowners and designers.

OPAQUE relies upon the widely-used admittance method [76] to evaluate the thermal load through composite building envelopes subjected to a sinusoidal outdoor temperature. The software requires the thermal conductivity k , density ρ , and specific heat c_p of each constituent wall material and also the wall design geometry as input parameters. It then evaluates the thermal behavior of the composite wall by determining two parameters known as the decrement factor f_{AM} and time lag ϕ_{AM} . By designing composite walls with large time lag and small decrement factor, the amplitude of indoor temperature oscillations can be reduced, thus increasing the thermal comfort of the occupants [77].

CHAPTER 3

Effective Thermal Conductivity of Three-Component Composites Containing Spherical Capsules

This chapter presents detailed numerical simulations predicting the effective thermal conductivity of spherical monodisperse and polydisperse core-shell particles ordered or randomly distributed in a continuous matrix. It aims (1) to rigorously predict the effective thermal conductivity of three-component core-shell composite materials, (2) to identify the material design parameters controlling the thermal conductivity, (3) to validate effective medium approximations previously proposed in the literature, and (4) to derive design rules for composite walls.

3.1 Background

Numerous models have been derived to predict the effective thermal conductivity of two-component composites as reviewed by Progelhof et al. [78], for example. Comparatively, few models exist for three-component composites [79–89]. Several models were developed for liquid and gas phases in a porous solid matrix such as building materials or soil [85, 86]. Other models require prior knowledge of the temperature gradients in each component of the composite to determine the effective thermal conductivity [81, 82]. The most practical models provide explicit analytical expressions for the effective thermal conductivity of three-component composites based on the constituent thermal conductivities and on the geometric parameters of the composite structure such as core and shell diameters and/or volume fractions.

Lichtenecker [88] proposed an ad hoc expression for the electrical permittivity of a com-

posite consisting of any number of randomly mixed components [90]. Woodside and Messmer [90], among others, have applied this model to the effective thermal conductivity of three-component composites expressed as [88, 90, 91],

$$k_{eff} = k_c^{\phi_c} k_s^{\phi_s} k_m^{\phi_m} \quad (3.1)$$

where k_c , k_s , and k_m are the thermal conductivities of the core, shell, and matrix materials, respectively. Similarly, ϕ_c , ϕ_s , and $\phi_m = 1 - \phi_c - \phi_s$, are the volume fractions of the core, shell, and matrix materials, respectively. Woodside and Messmer [90] referred to Equation (3.1) as a “geometric mean” and noted that it corresponds to the arithmetic mean of the logarithms of the constituent thermal conductivities. Zakri et al. [91] analytically derived Lichtenecker’s [88] model [Equation (3.1)] for the effective electrical permittivity of three-component composites. They concluded that Equation (3.1) is “*physically founded*,” despite criticism from Reynolds and Hough [92] who suggested that the model “*lacked a theoretical basis*.” Note that Equation (3.1) predicts that k_{eff} vanishes if the thermal conductivity of either the core or the shell vanishes. This is obviously not the case since heat conduction could still take place through the continuous matrix material.

Brailsford and Major [87] developed a model for the effective thermal conductivity of monodisperse homogeneous particles randomly distributed in a continuous matrix. This two-component model was equivalent to the Maxwell-Garnett model for electrical conductivity [93]. Brailsford and Major [87] extended the two-component model to account for monodisperse homogeneous particles made of two different materials randomly distributed in a continuous matrix. Then, the effective thermal conductivity of three-component media was given by [87],

$$k_{eff} = \frac{k_m \phi_m + k_c \phi_c \frac{3k_m}{(2k_m + k_c)} + k_s \phi_s \frac{3k_m}{(2k_m + k_s)}}{\phi_m + \phi_c \frac{3k_m}{(2k_m + k_c)} + \phi_s \frac{3k_m}{(2k_m + k_s)}} \quad (3.2)$$

Model predictions for two-component media agreed well with experimental data for the effective thermal conductivity of solid glass spheres surrounded by air or water [87]. However, experimental validation was not reported for three-component composite materials.

Felske [89] derived a model, using the self-consistent field approximation [94], to predict the effective thermal conductivity of monodisperse spherical capsules randomly distributed in a continuous matrix. This effort was motivated by the need to estimate the effective thermal conductivity of syntactic foam insulation. The geometry considered in the derivation consisted of a spherical volume of matrix material containing a concentric core-shell particle with volume fractions representative of the overall composite. The model accounted for contact resistance at the shell-matrix interface. An exact series solution of the heat conduction equation was obtained for the temperature distribution in each phase. In absence of contact resistance, the model can be expressed as [89],

$$k_{eff} = \frac{\Theta_N}{\Theta_D} k_m \quad (3.3)$$

Here, the numerator Θ_N and denominator Θ_D are expressed as [89],

$$\begin{aligned} \Theta_N &= 2(1 - \phi_{c+s})A + (1 + 2\phi_{c+s})B, \\ \text{and } \Theta_D &= (2 + \phi_{c+s})A + (1 - \phi_{c+s})B \end{aligned} \quad (3.4)$$

where the parameters A and B are given by [89],

$$\begin{aligned} A &= \left(1 + \frac{2}{\phi_{c/s}}\right) - \left(1 - \frac{1}{\phi_{c/s}}\right) \frac{k_c}{k_s}, \\ \text{and } B &= \left(2 + \frac{1}{\phi_{c/s}}\right) \frac{k_c}{k_m} - 2 \left(1 - \frac{1}{\phi_{c/s}}\right) \frac{k_s}{k_m} \end{aligned} \quad (3.5)$$

Here, ϕ_{c+s} is the volume fraction of the composite occupied by the capsule and $\phi_{c/s}$ is the volume fraction of the core with respect to the capsule. They are expressed as $\phi_{c+s} = (D_s/D_m)^3$ and $\phi_{c/s} = (D_c/D_s)^3$ where D_c , D_s , and D_m are the diameters of the core, shell, and matrix domains, respectively. The volume fraction of core-shell capsules ϕ_{c+s} can be written as $\phi_{c+s} = \phi_c + \phi_s$. Pal [80] noted that the Felske model [89] “*generally describes thermal conductivity data well when the core-shell volume fraction ϕ_{c+s} is less than about 0.2,*” but no evidence was provided to demonstrate this claim.

Park et al. [79] also developed a model predicting the effective thermal conductivity of monodisperse spherical capsules randomly distributed in a continuous matrix based on a two-step approach. First, the effective thermal conductivity of the two-component core-shell

capsule denoted by k_{c+s} was modeled based on the core and shell thermal conductivities and on the volume fraction of core with respect to the core-shell composite $\phi_{c/s}$. It was based on a modified Eshelby effective medium approximation (EMA) [95, 96] and expressed as [79],

$$k_{c+s} = \frac{2(1 - \phi_{c/s})k_s + (1 + 2\phi_{c/s})k_c}{(2 + \phi_{c/s})k_s + (1 - \phi_{c/s})k_c}k_s. \quad (3.6)$$

The effective thermal conductivity k_{eff} of the three-component composite was then expressed based on the core-shell effective thermal conductivity k_{c+s} , the matrix thermal conductivity k_m , and the core-shell volume fraction ϕ_{c+s} as [79],

$$k_{eff} = \frac{2(1 - \phi_{c+s})k_m + (1 + 2\phi_{c+s})k_{c+s}}{(2 + \phi_{c+s})k_m + (1 - \phi_{c+s})k_{c+s}}k_m. \quad (3.7)$$

After careful consideration, combining Equations (3.6) and (3.7) led to the Felske model [89] given by Equations (3.3) to (3.5).

Pal [80] developed an implicit model to predict the effective thermal conductivity of three-component composites of monodisperse spherical capsules randomly distributed in a continuous matrix. This model was derived using the differential effective medium approach [97]. The resulting model was an implicit function of the volume fraction of capsules expressed as [80],

$$\left(\frac{k_{eff}}{k_m}\right)^{1/3} \left(\frac{\beta - 1}{\beta - k_{eff}/k_m}\right) = \left(1 - \frac{\phi_{c+s}}{\phi_{c+s,max}}\right) \quad (3.8)$$

where $\phi_{c+s,max}$ is the maximum capsule volume fraction for a given packing arrangement and β was expressed as [80],

$$\beta = \frac{(2 + \delta^3) \frac{k_c}{k_m} - 2(1 - \delta^3) \frac{k_s}{k_m}}{(1 + 2\delta^3) - (1 - \delta^3) \frac{k_c}{k_s}} \quad (3.9)$$

where δ is the shell to core diameter ratio, i.e., $\delta = D_s/D_c$ or $\delta^3 = \phi_{c/s}^{-1}$. The model accounted for the upper limit of the capsule volume fraction $\phi_{c+s,max}$ corresponding to close packing. Predictions by Equations (3.8) and (3.9) were reported to agree well with experimental data for thirteen different samples of two-phase media for “reasonable values” of $\phi_{c+s,max}$ [80]. However, $\phi_{c+s,max}$ was taken as 0.7, 0.85, or 1 which seems arbitrary and large. Indeed, the maximum volume fraction reaches 0.74 for face-centered cubic packing and 0.6 for randomly

distributed monodisperse solid spheres [98]. Note that in the case of composite building materials with PCM, the capsule volume fraction is typically much smaller than the packing limit, as large volume fractions could compromise the mechanical strength of the wall [29].

Overall, several EMAs have been proposed in the literature for the effective thermal conductivity of three-component composite materials consisting of monodisperse capsules in a continuous matrix. However, these models are significantly different from one another and their validation against experimental data has been limited mainly to two-component media. Therefore, it remains unclear which one of these models is the most appropriate and accurate. In addition, to the best of our knowledge, no study has rigorously investigated the effects of the capsules' spatial and size distributions on the effective thermal conductivity of three-component composites.

The aim of this study is to predict and to identify the dominant parameters controlling the effective thermal conductivity of three-component composite materials. To do so, detailed “numerical experiments” were performed to investigate the effects of (1) core and shell dimensions and volume fractions, (2) spatial distribution of the capsules, (3) size distribution of the capsules, and (4) core, shell, and matrix thermal conductivities. The results were compared with the previously reviewed EMAs to identify the most appropriate one and its range of validity.

3.2 Analysis

3.2.1 Schematics

The present study examined various composite representative volumes consisting of different packing arrangements of monodisperse and polydisperse spherical capsules distributed in a continuous matrix. Figure 3.1 shows three-component unit cells with (a) simple, (b) body-centered, and (c) face-centered cubic packing arrangements along with the associated Cartesian coordinate system. The inner core and outer shell diameters were given by D_c and D_s , respectively with shell thickness $t_s = (D_s - D_c)/2$, and the length of the unit cell was

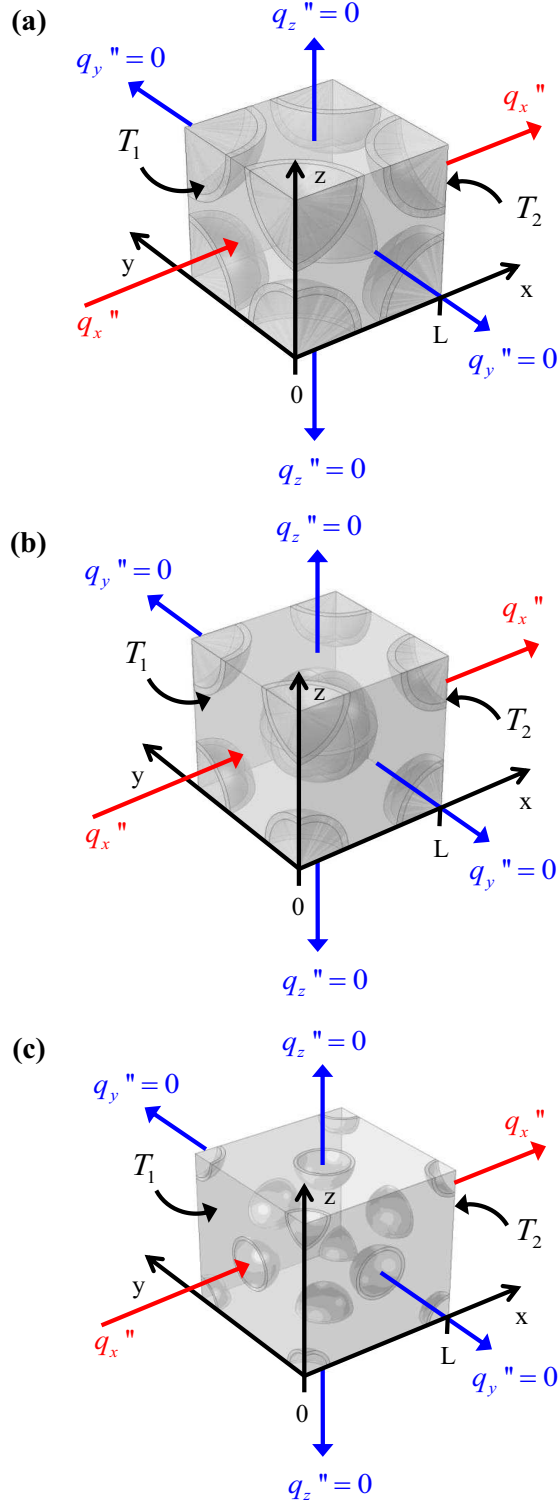


Figure 3.1: Schematic and computational domain of a single unit cell consisting of capsules distributed in a continuous matrix with (a) simple, (b) body-centered, and (c) face-centered cubic packing arrangement. Core and shell diameters and unit cell length corresponding to core and shell volume fractions ϕ_c and ϕ_s were denoted by D_c , D_s , and L , respectively.

denoted by L . For any packing arrangement of monodisperse capsules, the core and shell volume fractions ϕ_c and ϕ_s were expressed as,

$$\phi_c = \frac{p\pi D_c^3}{6L^3} \quad \text{and} \quad \phi_s = \frac{p\pi (D_s^3 - D_c^3)}{6L^3} \quad (3.10)$$

where p is the number of spherical capsules per unit cell. It was equal to 1, 2, and 4 for simple, body-centered, or face-centered cubic arrangements, respectively.

To study the effects of the capsule's size and spatial distributions in detail, a microstructural stochastic packing algorithm was implemented [99]. This algorithm considered a size distribution corresponding to an average outer shell diameter D_s of 18 μm with 10th and 95th percentile diameters equal to 9 μm and 33 μm , respectively, and a shell thickness t_s of 1 μm . It placed spherical capsules in a 3D representative volume of arbitrary size until the desired core phase volume fraction was achieved. Microstructural generation and packing was performed such that the minimum centroidal distance C_D between two proximal capsules was always greater than the sum of their radii r_1 and r_2 , i.e., $C_D > r_1 + r_2$. The packing algorithm placed capsules at random locations in the volume in accordance with two packing rules: (1) the size and number of capsules maintained the desired size distribution and (2) the desired core phase volume fraction was achieved within 0.5%. Figure 3.2 shows examples of computational volumes consisting of 38 to 61 monodisperse or polydisperse capsules randomly distributed in a continuous matrix. Figures 3.2a to 3.2d correspond to cases 3, 6, 9, and 10 summarized in Table 3.1, respectively.

3.2.2 Assumptions

To make the problem mathematically tractable, the following assumptions were made: (1) steady-state heat conduction prevailed. (2) All materials were isotropic and had constant properties. (3) There was no heat generation. (4) Interfacial contact resistance was neglected, and (5) phase change and natural convection in the core phase were absent. This last assumption stemmed from the fact that even if microcapsules were filled with liquid (e.g., molten PCM) the Rayleigh number would be small.

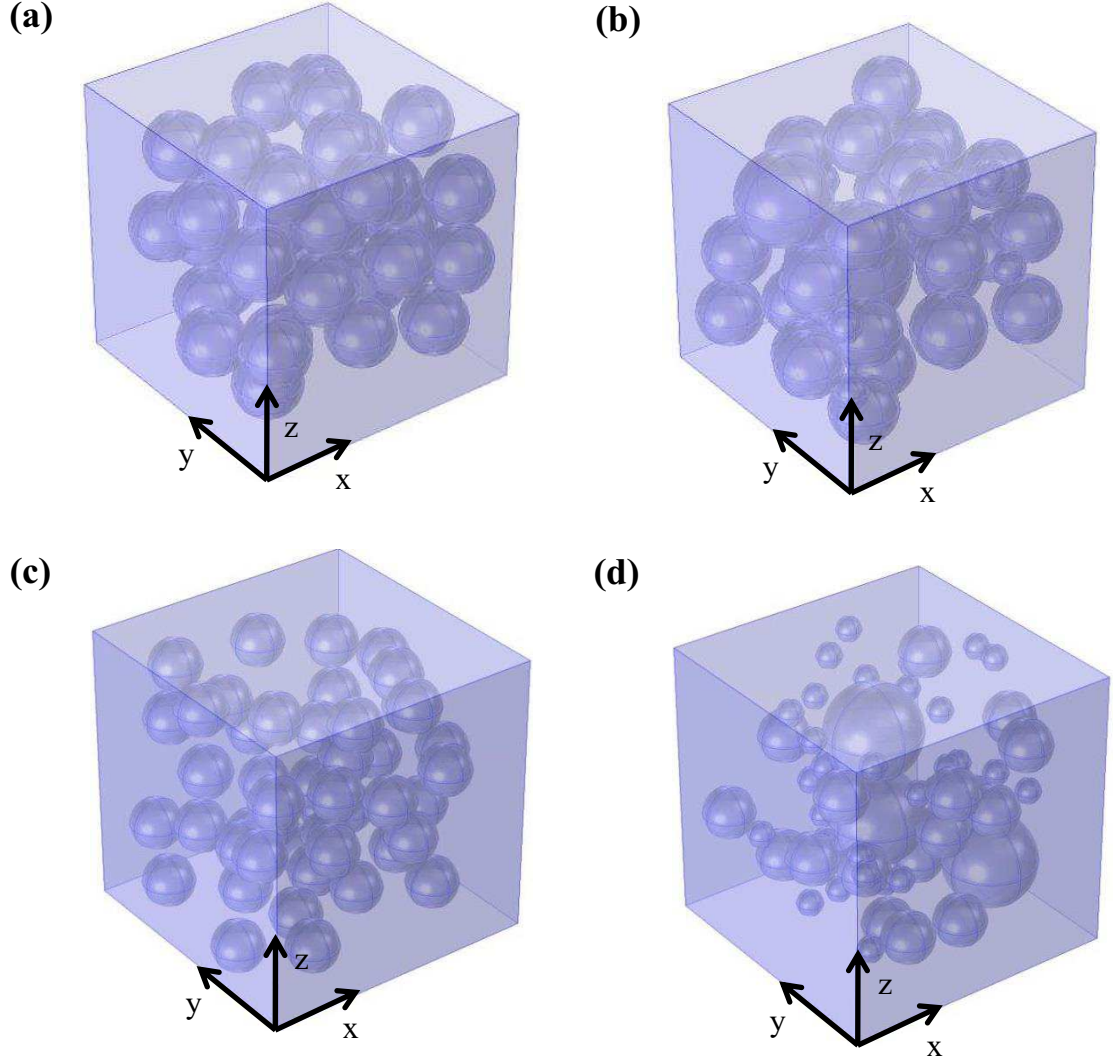


Figure 3.2: Computational cells containing monodisperse capsules with (a) $p = 39$, $L = 75 \mu\text{m}$, $\phi_c = 0.198$, and $\phi_s = 0.041$, and (c) $p = 49$, $L = 100 \mu\text{m}$, $\phi_c = 0.105$, and $\phi_s = 0.045$, as well as polydisperse capsules with (b) $p = 38$, $L = 75 \mu\text{m}$, $\phi_c = 0.197$, and $\phi_s = 0.075$, and (d) $p = 61$, $L = 100 \mu\text{m}$, $\phi_c = 0.095$, and $\phi_s = 0.035$.

3.2.3 Governing equations and boundary conditions

Under the above assumptions, the local temperatures in the core, shell, and matrix denoted by T_c , T_s , and T_m were governed by the steady-state heat diffusion equation in each domain, given by,

$$\nabla^2 T_c = 0, \quad \nabla^2 T_s = 0, \quad \text{and} \quad \nabla^2 T_m = 0. \quad (3.11)$$

These equations were coupled through the boundary conditions. Heat conduction took place mainly in the x -direction of the unit cell or representative cube (Figures 3.1 or 3.2) by imposing the temperature on the faces of the cube located at $x = 0$ and $x = L$ such that for $0 \leq y \leq L$ and $0 \leq z \leq L$,

$$T(0, y, z) = T_o \quad \text{and} \quad T(L, y, z) = T_L. \quad (3.12)$$

By virtue of symmetry, the heat flux through the four lateral faces vanished, i.e.,

$$q_y''(x, 0, z) = q_y''(x, L, z) = 0 \quad \text{and} \quad q_z''(x, y, 0) = q_z''(x, y, L) = 0 \quad (3.13)$$

where $q_y''(x, y, z)$ and $q_z''(x, y, z)$ are the heat fluxes along the y - and z -axes, respectively. They are given by Fourier's law, i.e., $q_y'' = -k\partial T/\partial y$ and $q_z'' = -k\partial T/\partial z$. The boundary temperatures on the faces $x = 0$ and $x = L$ were taken as $T_o = 294$ K and $T_L = 292$ K. Coupling between the temperatures of the different domains was achieved by imposing continuous heat flux across their interfaces, i.e.,

$$-k_m \frac{\partial T_m}{\partial \mathbf{n}} \Big|_{m/s} = -k_s \frac{\partial T_s}{\partial \mathbf{n}} \Big|_{m/s} \quad \text{and} \quad -k_s \frac{\partial T_s}{\partial \mathbf{n}} \Big|_{s/c} = -k_c \frac{\partial T_c}{\partial \mathbf{n}} \Big|_{s/c} \quad (3.14)$$

where $\mathbf{n}$ is the unit normal vector at any given point on the matrix/shell and shell/core interfaces, designated by subscript m/s and s/c , respectively.

3.2.4 Data processing

Based on Fourier's law, the effective thermal conductivity of the core-shell composite medium was computed from the imposed temperature difference along the x -direction, the domain

length L , and the area-averaged heat flux $\bar{q}_x''$ along the x -direction according to,

$$k_{eff} = -\frac{\bar{q}_x'' L}{T_L - T_o} \quad \text{where} \quad \bar{q}_x''(x) = \frac{1}{A_c} \iint q_x''(x, y, z) dydz. \quad (3.15)$$

Here, A_c is the cross-sectional area of the computational domain perpendicular to the x -axis. Due to the heterogeneous nature of the composite medium the heat flux was not uniform over a given cross-section perpendicular to the x -axis. However, it was systematically verified that the area-averaged heat flux $\bar{q}_x''(x)$ was the same at any cross-section between $x = 0$ and $x = L$.

3.2.5 Method of solution

The governing Equation (3.11) along with the boundary conditions given by Equations (3.12) to (3.14) were solved using finite element methods. The numerical convergence criteria was defined such that the maximum relative difference in the predicted local area-averaged heat flux $\bar{q}_x''(x)$ was less than 0.5% when reducing the mesh size by a factor of 2. Converged solutions were obtained by imposing the minimum mesh size to be $\Delta x = (D_s - D_c)/4$ and the maximum growth rate to be 1.5. The number of finite elements needed to obtain a converged solution ranged from 12,873 to 1,451,237 depending on the size of the computational cell and on the core and shell dimensions.

In order to validate the computational tool, a unit cell containing capsules with face-centered cubic packing arrangement was simulated with the same boundary conditions given by Equations (3.12) to (3.14) but assuming $k_s = k_c = k_m$. As expected, the predicted area-averaged heat flux at $x = L$ fell within 0.5% of Fourier's law given by $\bar{q}_x''(x) = k_m(T_o - T_L)/L$ for $L = 20.3 \mu\text{m}$, $k_m = 0.4 \text{ W/m}\cdot\text{K}$, $T_o = 294 \text{ K}$, and $T_L = 292 \text{ K}$. Note also that the area-averaged heat flux $\bar{q}_x''(x)$ was the same at any cross-section along the x -direction.

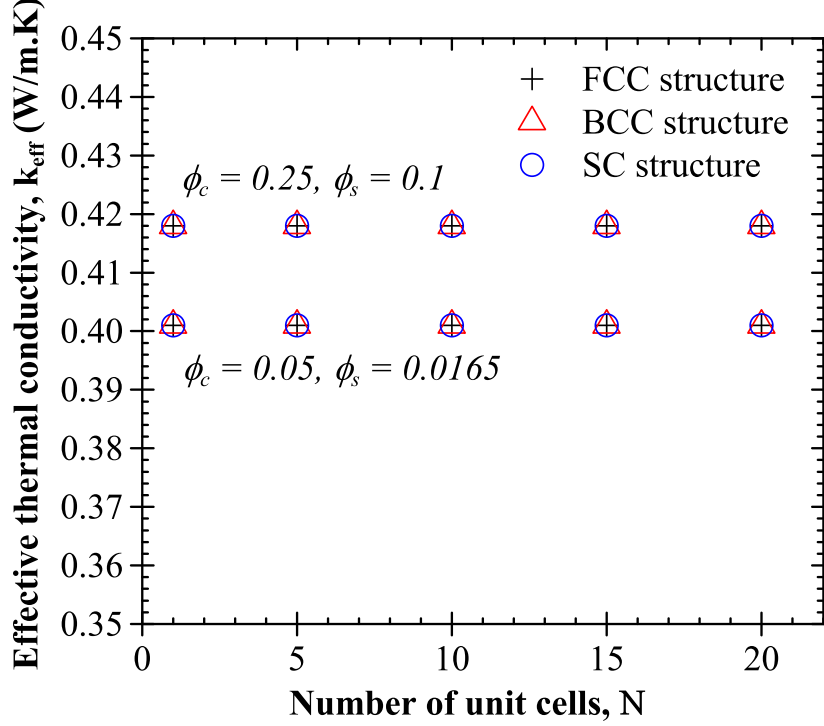


Figure 3.3: Effective thermal conductivity for linear arrays of N unit cells with two different combinations of volume fractions ϕ_c and ϕ_s and packing arrangements SC, BCC, and FCC. Core, shell, and matrix thermal conductivities were $k_c = 0.21$ W/m·K, $k_s = 1.3$ W/m·K, and $k_m = 0.4$ W/m·K, respectively.

3.3 Results and discussion

3.3.1 Effect of capsule dimensions and packing arrangement

Figure 3.3 shows the effective thermal conductivity k_{eff} for domains comprised of 1 to 20 stacked unit cells for simple, body-centered, and face-centered cubic packing arrangements (Figure 3.1). Two sets of volume fractions were considered: (i) $\phi_c = 0.25$ and $\phi_s = 0.1$ and (ii) $\phi_c = 0.05$ and $\phi_s = 0.0165$. The diameters D_c and D_s and the unit cell length L were adjusted with each packing arrangement to achieve the desired volume fractions. The core, shell, and matrix thermal conductivities were taken to be $k_c = 0.21$ W/m·K [65], $k_s = 1.3$ W/m·K [100], and $k_m = 0.4$ W/m·K [61], respectively. These values correspond to paraffin wax PCM in silica shells embedded in cement. Figure 3.3 establishes that k_{eff} was independent (i) of the number of stacked unit cells, as expected from symmetry considerations, and (ii) of the choice of packing arrangement. The same conclusions were reached for different volume

fractions. Therefore, a single unit cell with a face-centered cubic packing arrangement will be considered in the remainder of this study as representative of any composite media consisting of ordered monodisperse capsules.

Figure 3.4 shows the effective thermal conductivity k_{eff} of a composite containing monodisperse capsules as a function of (a) the core volume fraction ϕ_c ranging from 0.0 to 0.55 for a constant shell volume fraction of $\phi_s = 0.025$ and (b) the shell volume fraction ϕ_s ranging from 0.0 to 0.55 for a constant core volume fraction of $\phi_c = 0.05$. The desired volume fractions were imposed by either adjusting the relevant diameter (D_c or D_s) while holding the unit cell length L constant or by adjusting the unit cell length L and holding the relevant diameter constant. Here also, the core, shell, and matrix thermal conductivities were taken as $k_c = 0.21$ W/m·K, $k_s = 1.3$ W/m·K, and $k_m = 0.4$ W/m·K, respectively. Figures 3.4a and 3.4b establish that k_{eff} depended only on ϕ_c and ϕ_s and not on the individual geometric parameters D_c , D_s , and L .

Overall, this section demonstrated that the effective thermal conductivity of a composite material containing monodisperse capsules was a function only of five parameters namely, the volume fractions ϕ_c and ϕ_s and the constituent material thermal conductivities k_c , k_s , and k_m , i.e., $k_{eff} = k_{eff}(\phi_c, \phi_s, k_c, k_s, k_m)$.

3.3.2 Effect of core and shell volume fractions

For any packing arrangement of monodisperse spherical capsules the term $\phi_{c/s}$ used in Equations (3.5) and (3.6) can be written in terms of ϕ_c and ϕ_s so that,

$$\frac{1}{\phi_{c/s}} = 1 + \frac{\phi_s}{\phi_c}. \quad (3.16)$$

Then, the Felske model [89], given by Equation (3.3) can be written in terms of ϕ_c and ϕ_s as,

$$k_{eff} = \frac{2k_m(1 - \phi_c - \phi_s) \left(3 + 2\frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_s} \right) + (1 + 2\phi_c + 2\phi_s) \left[\left(3 + \frac{\phi_s}{\phi_c} \right) k_c + 2\frac{\phi_s k_s}{\phi_c} \right]}{(2 + \phi_c + \phi_s) \left(3 + 2\frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_s} \right) + (1 - \phi_c - \phi_s) \left[\left(3 + \frac{\phi_s}{\phi_c} \right) \frac{k_c}{k_m} + 2\frac{\phi_s k_s}{\phi_c k_m} \right]} \quad (3.17)$$

Similar operation can also be performed for the models proposed by Park [79] and Pal [80].

Thus, the EMAs previously reviewed satisfy the relationship $k_{eff} = k_{eff}(\phi_c, \phi_s, k_c, k_s, k_m)$.

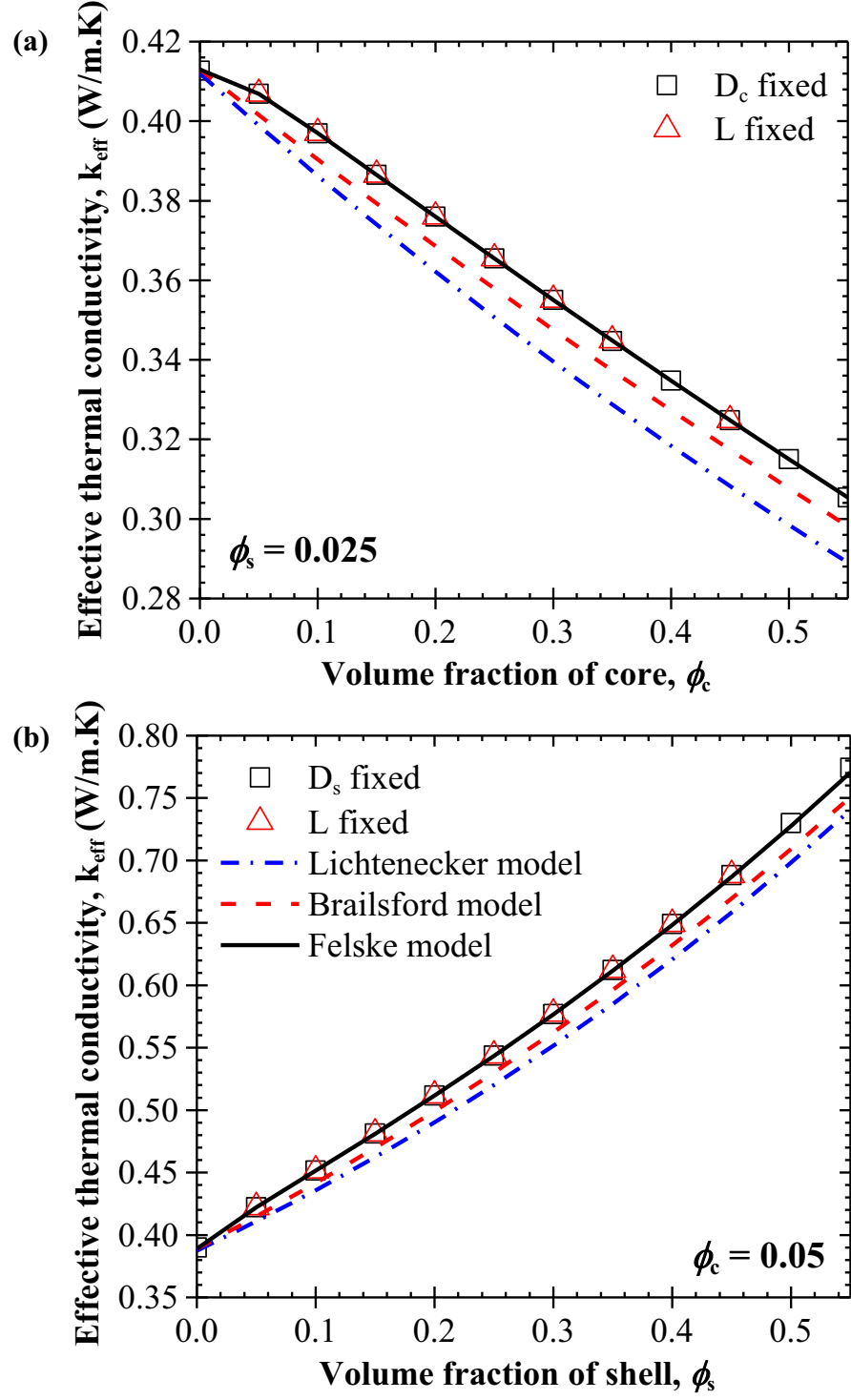


Figure 3.4: Effective thermal conductivity for (a) different values of ϕ_c with $\phi_s = 0.025$ and (b) different values of ϕ_s with $\phi_c = 0.05$. The volume fractions were varied by adjusting either the diameter or unit cell length. Here, $k_c = 0.21$ W/m.K, $k_s = 1.3$ W/m.K, and $k_m = 0.4$ W/m.K. Predictions by the Lichtenecker, Brailsford, and Felske models are also shown.

However, it remains unclear which one best predicts the effective thermal conductivity retrieved from detailed numerical simulations based on Equation (5.9).

Figure 3.4 compares the effective thermal conductivity k_{eff} of a composite containing monodisperse capsules retrieved numerically with that predicted by the Lichtenecker [88], Brailsford [87], and Felske [89] models given respectively by Equations (3.1), (3.2), and (3.17) as a function of (a) the core volume fraction ϕ_c for $\phi_s = 0.025$ and (b) the shell volume fraction ϕ_s for $\phi_c = 0.05$. Here also, $k_c = 0.21$ W/m·K, $k_s = 1.3$ W/m·K, and $k_m = 0.4$ W/m·K, respectively. Figures 3.4a and 3.4b indicate that k_{eff} decreased as ϕ_c increased and increased as ϕ_s increased, for the values of k_c , k_s , and k_m considered. More importantly, they indicate that predictions by the Felske model [Equation (3.17)] fell within 0.5% of numerical predictions, i.e., within numerical uncertainty. The other models underpredicted k_{eff} by 2.4% to 5.4% for the values of ϕ_c , ϕ_s , k_c , k_s , and k_m considered. These relative errors are expected to increase as the thermal conductivity mismatch between the three phases increases.

3.3.3 Effect of constituent thermal conductivities

Figure 3.5 plots the effective thermal conductivity k_{eff} of a composite material containing monodisperse capsules as a function of matrix thermal conductivity k_m ranging from 1 to 50 W/m·K for volume fractions $\phi_c = 0.2$ and $\phi_s = 0.145$ and two combinations of core and shell thermal conductivities, namely, (i) $k_c = 5$ W/m·K and $k_s = 10$ W/m·K and (ii) $k_c = 10$ W/m·K and $k_s = 30$ W/m·K. This study demonstrated that predictions of k_{eff} by the Felske model [Equation (3.17)] fell within 0.3% of the numerical predictions for k_m up to 500 W/m·K (see supplementary material). On the other hand, predictions by the Brailsford model [Equation (3.2)] and the Lichtenecker model [Equation (3.1)] underpredicted k_{eff} by up to 3% and 60%, respectively. The discrepancies between these model's predictions and numerical simulations increased with increasing k_m .

Figure 3.6 plots the effective thermal conductivity k_{eff} of a composite containing monodisperse capsules as a function of the core thermal conductivity k_c ranging from 1 to 500 W/m·K

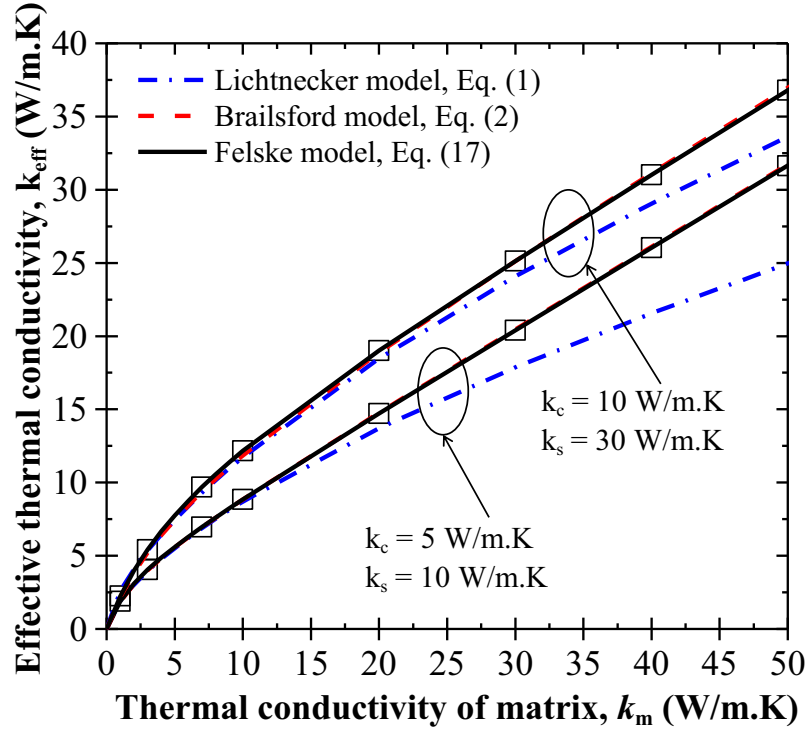


Figure 3.5: Effective thermal conductivity k_{eff} of core-shell composite as a function of the thermal conductivity of the continuous phase k_m obtained numerically and predicted by the Lichtenecker, Brailsford, and Felske models given by Equations (3.1), (3.2), and (3.17), respectively. The volume fractions of core and shell were $\phi_c = 0.2$ and $\phi_s = 0.145$.

for volume fractions $\phi_c = 0.2$ and $\phi_s = 0.145$ and two combinations of matrix and shell thermal conductivities, namely, (i) $k_m = 5 \text{ W/m}\cdot\text{K}$ and $k_s = 10 \text{ W/m}\cdot\text{K}$ and (ii) $k_m = 10 \text{ W/m}\cdot\text{K}$ and $k_s = 30 \text{ W/m}\cdot\text{K}$. Figure 3.6 demonstrates that predictions by the Felske model [Equation (3.17)] fell within 0.2% of the numerical predictions while the other models deviated by more than 10% for the values of k_m and k_s considered. Figure 3.6 also indicates that k_{eff} asymptotically reached a plateau as k_c increased. This can be attributed to the fact that as k_c becomes much greater than k_s and k_m , the temperature gradient throughout the core material vanishes. Then, the core provides negligible thermal resistance to heat conduction through the composite medium and thus does not affect k_{eff} . From a mathematical point of view, for $k_c \gg k_s$ and $k_c \gg k_m$, Equation (3.17) simplifies to

$$k_{eff} = \frac{2(1 - \phi_c - \phi_s) \frac{\phi_s k_m}{\phi_c k_s} + (1 + 2\phi_c + 2\phi_s) \left(3 + \frac{\phi_s}{\phi_c}\right)}{(2 + \phi_c + \phi_s) \frac{\phi_s}{\phi_c k_s} + (1 - \phi_c - \phi_s) \left(3 + \frac{\phi_s}{\phi_c}\right) \frac{1}{k_m}}. \quad (3.18)$$

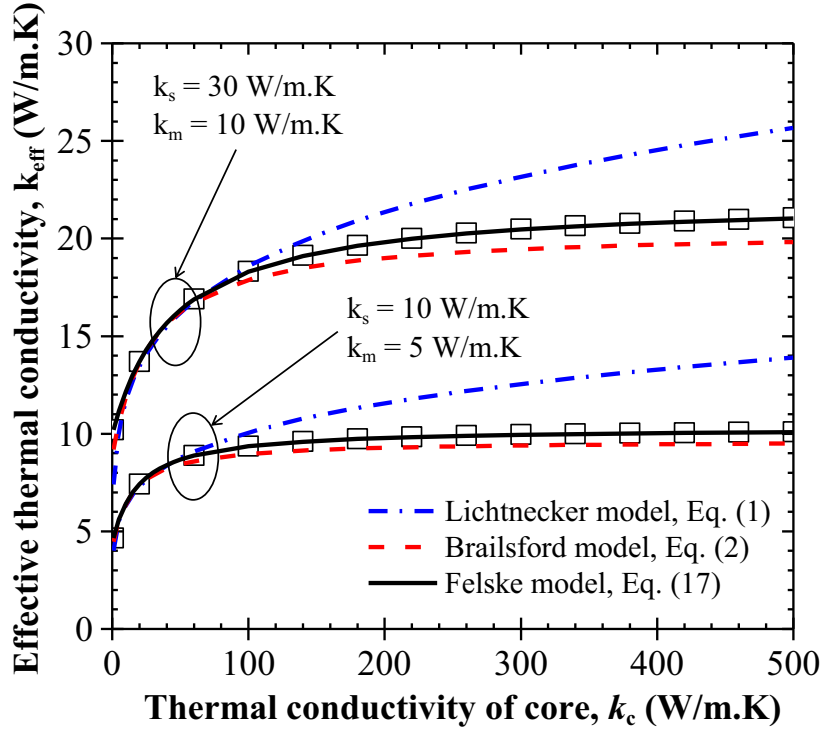


Figure 3.6: Effective thermal conductivity k_{eff} of core-shell composite as a function of the thermal conductivity of the core phase k_c obtained numerically and predicted by the Lichtenecker, Brailsford, and Felske models given by Equations (3.1), (3.2), and (3.17), respectively. The volume fractions of core and shell were $\phi_c = 0.2$ and $\phi_s = 0.145$.

Similarly, Figure 3.7 plots the effective thermal conductivity k_{eff} of a composite material containing monodisperse capsules as a function of shell thermal conductivity k_s ranging from 1 to 500 W/m·K for volume fractions $\phi_c = 0.2$ and $\phi_s = 0.145$ and two combinations of core and matrix thermal conductivities, namely, (i) $k_c = 5$ W/m·K and $k_m = 10$ W/m·K and (ii) $k_c = 10$ W/m·K and $k_m = 30$ W/m·K. Here also, the Felske model [Equation (3.17)] agreed very well with the numerical predictions while the other models deviated by more than 33% for the values of k_c and k_m considered. For $k_s \gg k_c$ and $k_s \gg k_m$, k_{eff} asymptotically converged to a function independent not only of k_s but also of k_c given by,

$$k_{eff} = \frac{(1 + 2\phi_c + 2\phi_s)}{(1 - \phi_c - \phi_s)} k_m. \quad (3.19)$$

In this case, k_s did not contribute to k_{eff} because the shell thermal resistance was negligible compared with that of the matrix. In addition, heat can be transferred through the capsule via two paths: through the shell and the core, or along the shell around the core. When

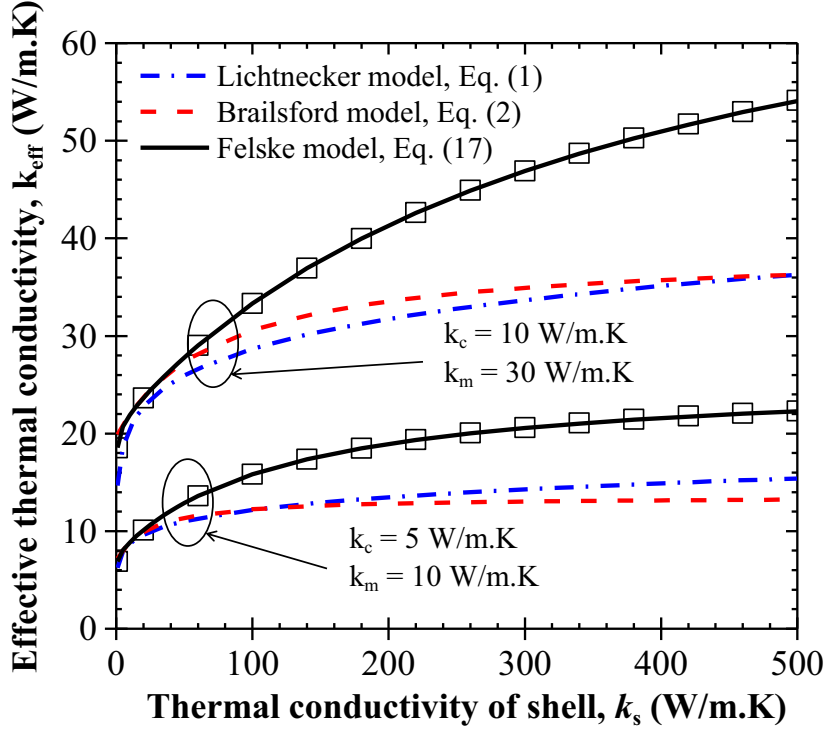


Figure 3.7: Effective thermal conductivity k_{eff} of core-shell composite as a function of the thermal conductivity of the shell phase k_s obtained numerically and predicted by the Lichtenecker, Brailsford, and Felske models given by Equations (3.1), (3.2), and (3.17), respectively. The volume fractions of core and shell were $\phi_c = 0.2$ and $\phi_s = 0.145$.

$k_s \gg k_c$ and $k_s \gg k_m$, the latter path provided the least resistance to heat transfer. Then, the highly conducting shell thermally “short-circuited” the core and k_c did not affect k_{eff} . As a result, k_{eff} was only a function of k_m .

Finally, Figures 3.5 to 3.7 show that the Felske model [Equation (3.17)] predicted the effective thermal conductivity of composites containing monodisperse capsules within the estimated numerical uncertainty for all volume fractions ϕ_c and ϕ_s considered and for a wide range of thermal conductivities k_s , k_c , and k_m . It remains to be shown whether this model is also valid for polydisperse and/or randomly distributed capsules.

3.3.4 Effect of capsule spatial and size distributions

Ten composite structures consisting of monodisperse and polydisperse microcapsules randomly distributed in a continuous matrix were generated as described previously. The num-

ber of capsules p in the computational domain ranged from 19 to 61 and the thickness of the shells was taken as $t_s = 1 \mu\text{m}$. Table 3.1 summarizes the different values of p , L , ϕ_c , ϕ_s , k_c , k_s , and k_m considered in each case. It also compares the numerically predicted effective thermal conductivity k_{eff} of these composite microstructures to that predicted by the Felske model [Equation (3.17)]. Cases 1 and 2 indicate that the numerically predicted k_{eff} was the same for composites with monodisperse or polydisperse capsules for the same values of ϕ_c , ϕ_s , k_c , k_s , and k_m . Table 3.1 also shows that k_{eff} predicted by the Felske model [Equation (3.17)] fell within 0.25% of numerical predictions for a wide range of constituent thermal conductivities k_c , k_s , and k_m and volume fractions ϕ_c and ϕ_s .

In summary, these results established that the effective thermal conductivity of three-component composites consisting of capsules distributed in a continuous matrix was independent of capsule size distribution and of their spatial distribution. In all cases, the Felske model [Equation (3.17)] predicted the effective thermal conductivity within numerical uncertainty.

Table 3.1: Numerical and analytical predictions of the effective thermal conductivity of composites consisting of monodisperse or polydisperse capsules randomly distributed in a continuous matrix. The average outer diameter and thickness of the shell are $D_{s,avg} = 18 \mu\text{m}$ and $t_s = 1 \mu\text{m}$, respectively for all cases.

			Input			Numerical					Eq. (3.17)
	Size distribution	p	L (μm)	ϕ_c	ϕ_s	k_c (W/m·K)	k_s (W/m·K)	k_m (W/m·K)	k_{eff} (W/m·K)	k_{eff} (W/m·K)	% difference
1	Monodisperse	19	75	0.097	0.041	0.21	1.3	0.4	0.41	0.41	0.02
2	Polydisperse	22	75	0.095	0.041	0.21	1.3	0.4	0.41	0.41	0.02
3	Monodisperse	39	75	0.198	0.084	0.21	1.3	0.4	0.42	0.42	0.01
4	Monodisperse	39	75	0.198	0.084	10	100	30	30.17	30.17	0.00
5	Monodisperse	39	75	0.198	0.084	100	10	30	33.41	33.42	0.03
6	Polydisperse	38	75	0.197	0.075	0.21	1.3	0.4	0.41	0.41	0.11
7	Polydisperse	38	75	0.197	0.075	10	100	30	29.68	29.72	0.14
8	Polydisperse	38	75	0.197	0.075	100	10	30	33.85	33.78	0.22
9	Monodisperse	49	100	0.105	0.045	10	20	50	42.83	42.89	0.14
10	Polydisperse	61	100	0.095	0.035	50	10	20	21.30	21.28	0.10

3.3.5 Critical condition for effective thermal conductivity

As previously mentioned, encapsulated PCM can be used to reduce and delay the thermal load in concrete buildings. However, the addition of PCM microcapsules should not increase the effective thermal conductivity k_{eff} of the composite wall meant to provide not only large thermal mass but also act as thermal insulation [29]. Based on Equation (3.17), the critical core to matrix thermal conductivity ratio above which k_{eff} becomes larger than k_m can be written as,

$$\left(\frac{k_c}{k_m}\right)_{cr} = \frac{2\left(\frac{k_s}{k_m} - 1\right) - 3\frac{\phi_c}{\phi_s}}{\frac{k_m}{k_s} - 1 - 3\frac{\phi_c}{\phi_s}}. \quad (3.20)$$

This expression can be used as a thermal design rule for core-shell composite materials with monodisperse or polydisperse and ordered or randomly distributed capsules.

Figure 3.8 plots the critical core to matrix thermal conductivity ratio $(k_c/k_m)_{cr}$ given by Equation (3.20) as a function of the shell to matrix thermal conductivity ratio k_s/k_m . Four combinations of core and shell volume fractions were used, namely, (i) $\phi_c = 0.4$ and $\phi_s = 0.191$, (ii) $\phi_c = 0.2$ and $\phi_s = 0.124$, (iii) $\phi_c = 0.1$ and $\phi_s = 0.082$, and (iv) $\phi_c = 0.05$ and $\phi_s = 0.054$. All curves passed through the same point $(1, 1)$ corresponding to $k_c = k_s = k_m = k_{eff}$. Each design curve represents the ensemble of conditions for which $k_{eff} = k_m$. The area under the curve correspond to the desirable conditions for which k_{eff} is smaller than k_m .

3.3.6 Comparison with experimental data

Several studies have experimentally measured the effective thermal conductivity of three-component core-shell composite materials [101–106]. Liang and Li [101] measured the effective thermal conductivity of polydisperse hollow glass microspheres randomly distributed in a polypropylene matrix. These measurements were then compared with numerical predictions using finite element methods [102]. Surprisingly, the measured effective thermal conductivity was larger than that of the individual constituent materials which cast doubt on the data. Other studies reported the effective thermal conductivity of three-component composites but

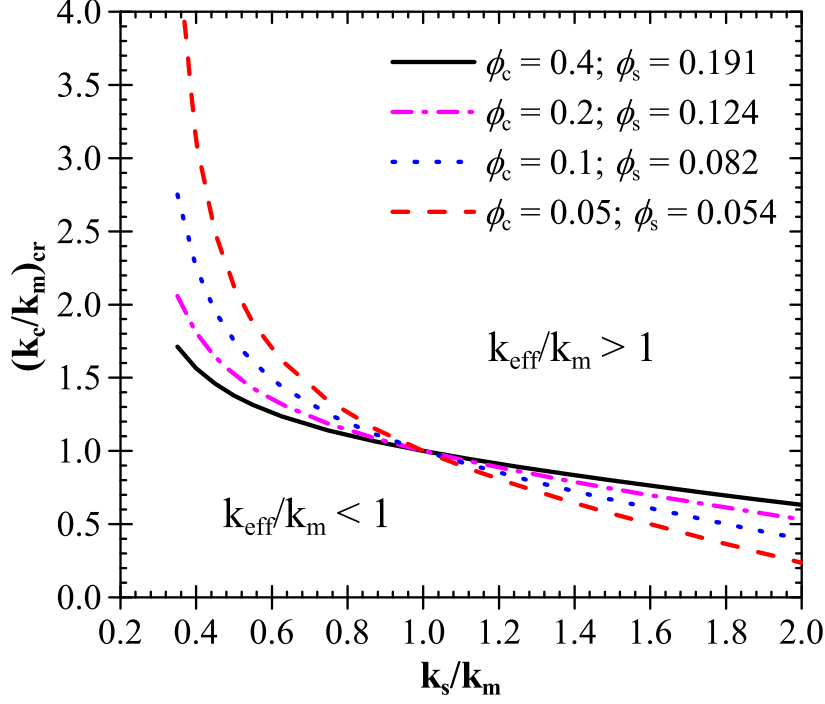


Figure 3.8: Critical core and shell conductivity ratios $(k_c/k_m)_{cr}$ and (k_s/k_m) (a) for different values of matrix thermal conductivity k_m with $\phi_c = 0.4$ and $\phi_s = 0.191$ and (b) for core and shell volume fractions ϕ_c and ϕ_s .

did not report the thermal conductivities of the constituents and/or the relevant geometric parameters such as the shell and/or the core volume fractions [103–106]. However, these parameters are necessary in order to accurately validate numerical predictions and effective medium approximations. In addition, contact resistance between the different phases may affect the experimental measurements. This effect was considered in the general case of the Felske model [89].

3.4 Conclusion

This study established that the effective thermal conductivity was independent of the capsules' spatial distribution and size distribution. The effective thermal conductivity was found to depend solely on the core and shell volume fractions and on the core, shell, and matrix thermal conductivities. The Felske model [Equation (3.17)] predicted the effective thermal

conductivity of the composite material within numerical uncertainty for the wide range of parameters considered. This model was used to identify conditions under which the effective thermal conductivity k_{eff} of the composite materials remained smaller than that of the matrix material. This thermal design rule will be useful in developing PCM-composite materials for energy efficient buildings.

CHAPTER 4

Diurnal Thermal Analysis of Microencapsulated PCM-Concrete Composite Walls

This chapter aims to evaluate the benefits of adding PCM to concrete used in building envelopes to reduce energy consumption and costs to ratepayers. Diurnal transient numerical simulations were performed on microencapsulated PCM-composite walls subjected to sinusoidal outdoor temperature and solar radiation heat flux. Rules were established to guide the design PCM composite walls in various climates and to take advantage of time-of-use electricity pricing.

4.1 Background

Zhou et al. [107] numerically simulated a room with one south-facing exterior wall and three interior walls. The multilayer ceiling and walls had either a mixed PCM-gypsum or a shape-stabilized PCM (SSPCM) composite layer at the inner surface. Time-dependent outdoor temperature and solar irradiation were imposed on the exterior wall to reflect a typical winter week in Beijing, China. The authors modeled phase change using the enthalpy method and studied the effect of phase change temperature T_{pc} and temperature window ΔT_{pc} on the indoor temperature. The amplitude of the temperature oscillations was found to decrease with decreasing phase change temperature window ΔT_{pc} . It could be reduced by as much as 46% and 56% for mixed PCM-gypsum and SSPCM layers, respectively, compared with a plain gypsum board layer. They also found that the optimal phase change temperature T_{pc} to minimize the amplitude of the indoor temperature oscillations was 21°C for both mixed PCM-gypsum and for SSPCM layers. In another study, Zhou et al. [108] simulated the same

room with multilayer ceiling and walls containing a SSPCM composite layer on a different winter week in Beijing, China. Once again, the amplitude of temperature oscillations was minimized for a phase change temperature T_{pc} of 20°C, which was within the range of indoor comfort temperature.

Diaconu and Cruceru [109] conducted a numerical study of a room with multilayer exterior walls consisting of an insulation layer between two PCM wallboards. Time-dependent temperature and solar irradiation were imposed at the outer surface of the walls to reflect yearly averaged annual weather conditions in Bechar, Algeria. Each PCM-wallboard layer was assumed to be homogeneous with some arbitrarily chosen effective thermal properties. The enthalpy method was used to simulate phase change. The cooling/heating load on the room was determined by performing an energy balance on the indoor space. The authors evaluated the effects of phase change temperature T_{pc} and temperature window ΔT_{pc} in each PCM layer on the total annual heating and cooling energy reduction and on the reduction of the peak heating and cooling loads. Unlike Zhou et al. [107], they found that the phase change temperature window had very little effect on the heating and cooling energy reductions. However, they also found that the annual total and maximum cooling loads were minimized when the phase change temperature within the inner layer was within the range of indoor comfort temperature.

Mathieu-Potvin and Gosselin [110] conducted a numerical study of south-facing multilayer exterior walls consisting of a plane-parallel PCM layer sandwiched between two insulation layers. First, the effects of the position and phase change temperature of the PCM layer on the annual energy flux through the wall subjected to sinusoidal outdoor temperature oscillations were studied. The annual energy flux was minimized when the PCM layer was positioned near the center of the wall and the phase change temperature was close to the indoor temperature. Second, a genetic algorithm was used to optimize a 20-layer wall to minimize the annual thermal energy flux through the wall subjected either to sinusoidal outdoor temperature boundary conditions or to outdoor temperature and solar irradiation based on real weather data corresponding to Orlando, FL and Quebec City, Canada. Each layer was 0.5 cm thick and was made of concrete, insulation, or pure PCM with one of six

possible phase change temperatures. For the wall subjected to sinusoidal outdoor temperature, the optimal design for Quebec City, Canada did not include a PCM layer. The authors postulated that this was because the indoor temperature was not within the range of outdoor temperature variation. However, the optimal design included a PCM layer when the wall was subjected to realistic outdoor temperature and solar irradiation boundary conditions, even though the indoor temperature was not within the range of outdoor temperature variation for most of the year. The authors concluded that realistic outdoor temperature and solar irradiation conditions must be considered in order to determine the energy saving potential of a PCM composite wall.

Overall, the literature reported contradictory conclusions about the effects of phase change temperature window ΔT_{pc} on the time-dependent thermal load through multilayer walls containing PCM. In addition, to the best of our knowledge, no study has simulated microencapsulated PCMs uniformly distributed in concrete while rigorously accounting for the thermal effects of the PCM, shell, and matrix materials. The aim of the present study is (1) to develop a simple, efficient, and accurate thermal model of microencapsulated PCM-concrete composite walls and (2) to investigate the impact of adding microencapsulated PCMs to concrete walls on the thermal load of buildings. The effects of four design parameters, namely, the PCM volume fraction, latent heat of fusion, phase change temperature and temperature window on the reduction and delay of thermal load were evaluated, along with the effect of the outdoor temperature oscillations.

4.2 Analysis

4.2.1 Schematic

Figure 4.1a shows a single unit cell containing core-shell particles arranged in a face-centered cubic (FCC) packing. The corresponding core and shell volume fractions ϕ_c and ϕ_s are respectively expressed as,

$$\phi_c = \frac{2\pi D_c^3}{3a^3} \quad \text{and} \quad \phi_s = \frac{2\pi (D_s^3 - D_c^3)}{3a^3} \quad (4.1)$$

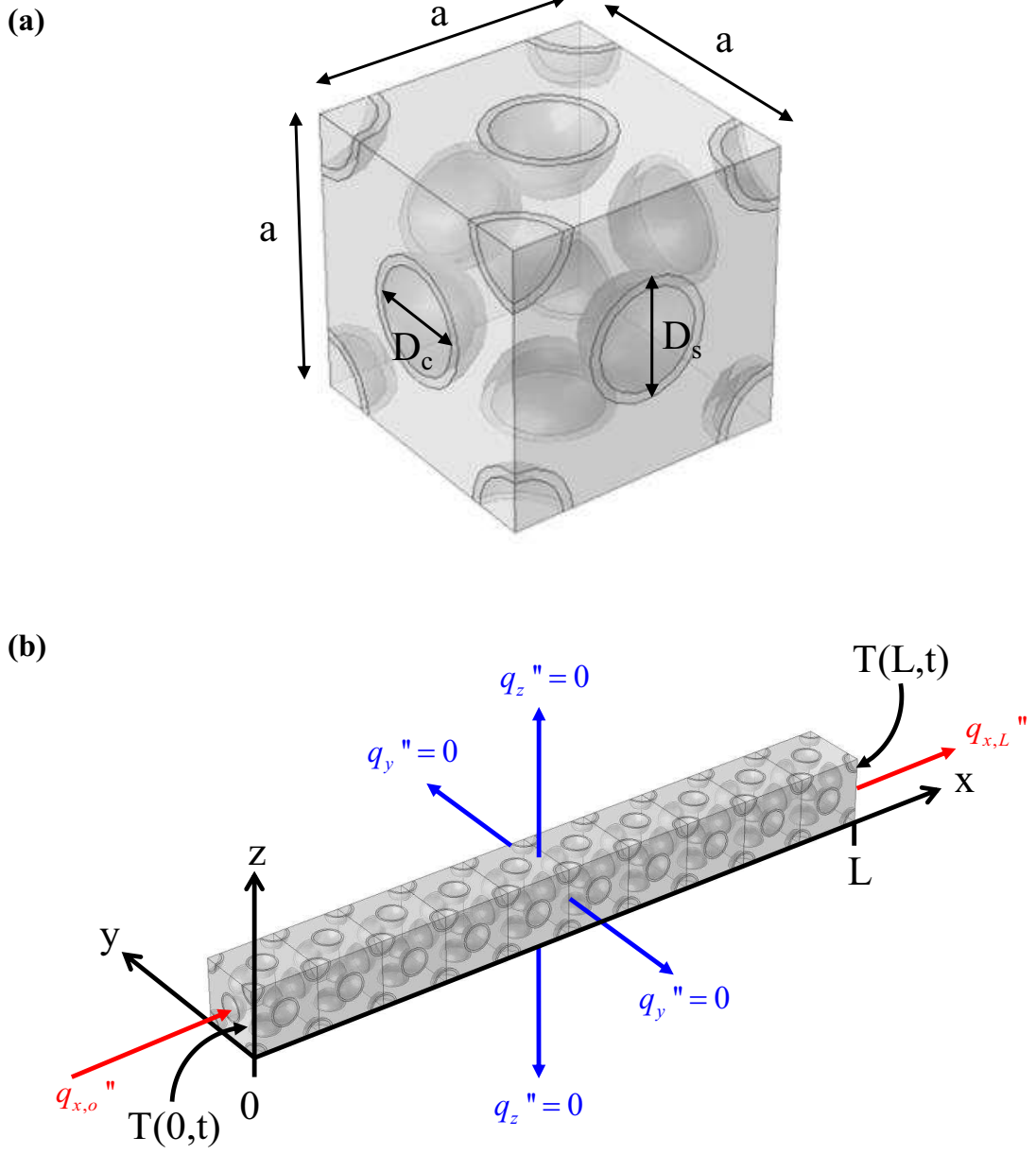


Figure 4.1: (a) Schematic of a single unit cell containing core-shell capsules with a face-centered cubic packing arrangement and (b) schematic and coordinate system of a heterogeneous composite of length L made up of aligned unit cells. Core and shell diameters and unit cell length corresponding to core and shell volume fractions ϕ_c and ϕ_s were denoted by D_c , D_s , and a , respectively.

where a is the length of the unit cell while D_c and D_s are the inner core and outer shell diameters, respectively. The unit cell width a was arbitrarily taken to be $25\text{ }\mu\text{m}$ for all cases considered. Throughout this study, ϕ_s was arbitrarily imposed to be 8% and D_c and D_s were adjusted based on the desired PCM volume fraction ϕ_c . The volume fraction of core with respect to shell material $\phi_{c/s} = (D_c/D_s)^3$ ranged from about 55 to 86%. Note that, in a recent study [34], we showed that the packing arrangement and the polydispersity of the microcapsules had no effect on the effective thermal conductivity of the composite wall. In other words, the situation depicted in Figure 4.1a is also representative of the practical situation of randomly distributed and polydisperse microcapsules in concrete [34]. Figure 4.1b illustrates a heterogeneous slab of a three-component composite material consisting of aligned unit cells of monodisperse microcapsules filled with PCM and embedded in a concrete matrix in an FCC packing arrangement. It also shows the associated coordinate system and the boundary conditions used to validate the effective homogeneous model. The overall thickness of this composite slab was denoted by L .

4.2.2 Assumptions

To make the problem mathematically tractable, the following assumptions were made: (1) all materials were isotropic and had constant properties except for the temperature-dependent specific heat of the PCM given by Equation (2.3). (2) The specific heat of the PCM was the same for solid and liquid phases, i.e., $c_{p,c,s} = c_{p,c,l}$. (3) Interfacial contact resistances between the concrete, the shell, and the PCM were negligible. (4) Natural convection in the molten microencapsulated PCM was absent based on the fact that the Rayleigh number was very small, and (5) there was no heat generation in the wall.

4.2.3 Heterogeneous wall simulations

4.2.3.1 Governing equations

Under the above assumptions, the local temperatures in the PCM, shell, and concrete at time t and location $\mathbf{r} = \langle x, y, z \rangle$ within the heterogeneous composite material denoted by

$T_c(\mathbf{r}, t)$, $T_s(\mathbf{r}, t)$, and $T_m(\mathbf{r}, t)$ were governed by the transient heat conduction equation in each domain, given by,

$$\frac{\partial T_c}{\partial t} = \alpha_c(T_c) \nabla^2 T_c, \quad \frac{\partial T_s}{\partial t} = \alpha_s \nabla^2 T_s, \quad \text{and} \quad \frac{\partial T_m}{\partial t} = \alpha_m \nabla^2 T_m \quad (4.2)$$

where $\alpha_j = k_j / \rho_j c_{p,j}$ is the thermal diffusivity of constituent j , where subscripts “c,” “s,” and “m” refer to the core, the shell, and the matrix, respectively. Here, the heat capacity method was used to solve for the local temperature $T_c(\mathbf{r}, t)$.

4.2.3.2 Boundary conditions

These transient three-dimensional (3D) energy conservation equations were solved in the PCM, the shell, and the concrete domains. The initial temperature was assumed to be uniform throughout the composite material and equal to T_i , i.e.,

$$T(x, y, z, 0) = T_i. \quad (4.3)$$

At time $t = 0$, the temperature was imposed on the faces of the slab located at $x = 0$ and $x = L$ so that the overall heat transfer took place along the x -direction (Figure 4.1b), i.e.,

$$T(0, y, z, t) = T(0, t) \quad \text{and} \quad T(L, y, z, t) = T(L, t) \quad (4.4)$$

where $T(0, t)$ and $T(L, t)$ were taken as constant and equal to T_o and T_L , respectively.

By virtue of symmetry, the heat flux through the four lateral faces vanished, i.e.,

$$q_y''(x, 0, z, t) = q_y''(x, a, z, t) = 0 \quad \text{and} \quad q_z''(x, y, 0, t) = q_z''(x, y, a, t) = 0 \quad (4.5)$$

where $q_y''(x, y, z, t)$ and $q_z''(x, y, z, t)$ are the heat fluxes at location (x, y, z) along the y - and z -axes and given by Fourier's law, i.e., $q_y'' = -k \partial T / \partial y$ and $q_z'' = -k \partial T / \partial z$, respectively.

Coupling between the temperatures in the different domains of the heterogeneous composite was achieved by imposing continuous heat flux boundary conditions across their interfaces, i.e.,

$$-k_m \frac{\partial T_m}{\partial \mathbf{n}} \Big|_{m/s} = -k_s \frac{\partial T_s}{\partial \mathbf{n}} \Big|_{m/s} \quad \text{and} \quad -k_s \frac{\partial T_s}{\partial \mathbf{n}} \Big|_{s/c} = -k_c \frac{\partial T_c}{\partial \mathbf{n}} \Big|_{s/c} \quad (4.6)$$

Table 4.1: Density ρ , specific heat capacity c_p , and thermal conductivity k of PCM, high density polyethylene (HDPE), and concrete.

		ρ	c_p	k	
Material	Subscript	(kg/m ³)	(J/kg·K)	(W/m·K)	Ref.
PCM	c	860	2590	0.21	[111]
HDPE	s	930	2250	0.49	[112]
Concrete	m	2300	880	1.4	[113]

where k_m , k_s , and k_c are the thermal conductivities of the matrix, shell, and core, respectively, and $\mathbf{n}$ is the unit normal vector at any given point on the concrete/shell and shell/PCM interfaces, designated by m/s and s/c , respectively.

4.2.3.3 Constitutive relationships

Table 7.1 summarizes the thermophysical properties of the different materials used in this study. The density, thermal conductivity, and specific heat of the PCM, shell, and matrix corresponded to those of a commercial organic PCM PureTemp 20 by Entropy Solution Inc. (Plymouth, MN) [111], high density polyethylene (HDPE) [112], and concrete [113], respectively. Here, the PCM specific heat $c_{p,c}(T_c)$ was given by Equation (2.3). The phase change temperature T_{pc} and temperature window ΔT_{pc} as well as the latent heat of fusion h_{sf} of the PCM were treated as parameters.

Due to the heterogeneous nature of the composite and to the differences in the thermal properties of the core, shell, and matrix, the heat flux was not necessarily uniform over a given cross-section perpendicular to the x -axis. Thus, the area-averaged heat flux $\bar{q}_x''$ along the x -direction was defined as,

$$\bar{q}_x''(x, t) = \frac{1}{A_c} \iint q_x''(x, y, z, t) dydz \quad (4.7)$$

where A_c is the cross-sectional area of the computational domain perpendicular to the x -axis.

4.2.4 Homogeneous wall simulations

4.2.4.1 Governing equation

The temperature T in the homogeneous material equivalent to the heterogeneous wall of identical dimensions is governed by

$$\frac{\partial T}{\partial t} = \alpha_{eff}(T) \nabla^2 T \quad (4.8)$$

where $\alpha_{eff}(T) = k_{eff}/(\rho c_p)_{eff}(T)$ is the effective thermal diffusivity. Note that $\alpha_{eff}(T)$ is a function of the local temperature T since it accounts for the temperature-dependent specific heat of the PCM. However, a consistent model for the effective volumetric heat capacity $(\rho c_p)_{eff}$ and the effective thermal conductivity k_{eff} of the composite wall needs to be specified.

4.2.4.2 Effective thermal properties

To approximate the heterogeneous composite by a homogeneous medium with some effective thermal properties, it is necessary to define its effective volumetric heat capacity $(\rho c_p)_{eff}$ and its effective thermal conductivity k_{eff} . First, from thermodynamic considerations, the volumetric heat capacity of any material (ρc_p) is related to its enthalpy H according to [114],

$$\rho c_p V = \frac{\partial H}{\partial T} \quad (4.9)$$

where V is the volume of the material. Equation (4.9) applies not only to single phase systems but also to a three-component composite wall of total volume $V_t = V_c + V_s + V_m$ where V_c , V_s , and V_m are the overall volumes occupied by the core, shell, and matrix, respectively. The corresponding total enthalpy H_t (in J) is the sum of the enthalpies of each constituent, i.e., $H_t = H_c + H_s + H_m$. Thus, the effective volumetric heat capacity can be expressed as,

$$(\rho c_p)_{eff}(T) = \frac{1}{V_t} \frac{\partial H_t}{\partial T} = \phi_c (\rho c_p)_c(T) + \phi_s (\rho c_p)_s + (1 - \phi_c - \phi_s) (\rho c_p)_m \quad (4.10)$$

where $\phi_c = V_c/V_t$ and $\phi_s = V_s/V_t$ are the volume fractions of the core and shell materials, while $(\rho c_p)_c$, $(\rho c_p)_s$, and $(\rho c_p)_m$ are the volumetric heat capacities of the core, shell, and

matrix materials, respectively. By substituting $c_{p,c}(T)$ given by Equation (2.3) into Equation (4.10), $(\rho c_p)_{eff}(T)$ can be expressed as,

$$(\rho c_p)_{eff}(T) = \begin{cases} (\rho c_p)_{eff,s} & \text{for } T < T_{pc} - \Delta T_{pc}/2 \\ (\rho c_p)_{eff,s} + \phi_c \frac{\rho_c h_{sf}}{\Delta T_{pc}} & \text{for } T_{pc} - \Delta T_{pc}/2 \leq T \leq T_{pc} + \Delta T_{pc}/2 \\ (\rho c_p)_{eff,l} & \text{for } T > T_{pc} + \Delta T_{pc}/2 \end{cases} \quad (4.11)$$

where $(\rho c_p)_{eff,s}$ is the effective volumetric heat capacity of the PCM-concrete composite wall with unmelted PCM given by $(\rho c_p)_{eff,s} = \phi_c (\rho c_p)_{c,s} + \phi_s (\rho c_p)_s + (1 - \phi_c - \phi_s) (\rho c_p)_m$. Here, it was assumed to be equal to the effective volumetric heat capacity of the composite with fully melted PCM, i.e., $(\rho c_p)_{eff,s} = (\rho c_p)_{eff,l}$.

Moreover, Felske [89] used the self-consistent field approximation [94] to derive an effective medium approximation (EMA) to predict the effective thermal conductivity k_{eff} of monodisperse spherical capsules randomly distributed in a continuous matrix given by,

$$k_{eff} = \frac{2k_m (1 - \phi_c - \phi_s) \left(3 + 2\frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_s} \right) + (1 + 2\phi_c + 2\phi_s) \left[\left(3 + \frac{\phi_s}{\phi_c} \right) k_c + 2\frac{\phi_s k_s}{\phi_c} \right]}{(2 + \phi_c + \phi_s) \left(3 + 2\frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_s} \right) + (1 - \phi_c - \phi_s) \left[\left(3 + \frac{\phi_s}{\phi_c} \right) \frac{k_c}{k_m} + 2\frac{\phi_s k_s}{\phi_c k_m} \right]} \quad (4.12)$$

This expression was validated using detailed numerical simulations of ordered and randomly distributed monodisperse and polydisperse microcapsules [34].

It is important to note that Equations (4.10) through (3.17) indicate that the effective volumetric heat capacity and thermal conductivity depended only on the constitutive phase properties and on their volume fractions. They were independent of the microcapsule spatial arrangement and polydispersity. Thus, from a thermal point of view, FCC packing is representative of any arbitrary packing arrangement, as previously discussed [34].

4.2.4.3 Boundary conditions

Two types of boundary conditions were imposed on the homogeneous wall. First, to demonstrate that the heterogeneous composite can be treated as a homogeneous material with some effective thermal properties, the initial and boundary conditions given by Equations (4.3) and (4.4) were imposed with $T(0, t) = T_o$ and $T(L, t) = T_L$. Second, when simulating

sinusoidal diurnal boundary conditions, convective heat transfer was imposed at the interior wall surface $x = L$ with a constant indoor temperature T_{in} maintained by the HVAC system so that [110],

$$-k_{eff} \frac{\partial T}{\partial x}(L, t) = h_i(T(L, t) - T_{in}) \quad (4.13)$$

where h_i is the indoor mixed convective heat transfer coefficient accounting for both forced and natural convections. Combined convective and radiative heat transfer was imposed at the exterior wall surface given by [109, 110],

$$-k_{eff} \frac{\partial T}{\partial x}(0, t) = h_o[T_\infty(t) - T(0, t)] + \alpha_s q_s''(t) - \epsilon \sigma [T(0, t)^4 - T_{sky}^4] \quad (4.14)$$

where h_o is the outdoor convective heat transfer coefficient, T_{sky} represents the average sky temperature, α_s and ϵ are the total hemispherical absorptivity and emissivity of the outdoor wall surface, respectively, and σ is the Stefan-Boltzmann constant, i.e., $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$. The ambient outdoor temperature $T_\infty(t)$ was imposed as a sinusoidal function of time t (in s) expressed as,

$$T_\infty(t) = \frac{T_{max} + T_{min}}{2} + \frac{T_{max} - T_{min}}{2} \sin\left(\frac{\pi}{43200}t - \frac{2\pi}{3}\right) \quad (4.15)$$

where T_{max} and T_{min} are the maximum and minimum outdoor temperatures during a day, respectively. A phase shift of $2\pi/3$ placed the peak outdoor temperature T_{max} at 2:00 pm, as the daily maximum occurred between 1:00 pm and 3:00 pm for more than 80% of the year in California climate zone 9 (Los Angeles, CA) based on weather data [17]. Similarly, the solar irradiation $q_s''(t)$ as a function of time t (in s) was imposed as,

$$q_s''(t) = \begin{cases} 0 & \text{for } 6 : 00 \text{ pm} \leq t \leq 6 : 00 \text{ am} \\ q_{s,max}'' \cos\left(\frac{\pi}{43200}t - \pi\right) & \text{for } 6 : 00 \text{ am} \leq t \leq 6 : 00 \text{ pm} \end{cases} \quad (4.16)$$

where $q_{s,max}''$ is the maximum daily solar irradiation (in W/m^2). Here, the maximum daily solar irradiation $q_{s,max}''$ was taken as 535 W/m^2 and occurred at 12:00 pm corresponding to the average daily maximum value and time throughout the year in California climate zone 9 [17].

4.2.4.4 Constitutive relationships

The indoor heat transfer coefficient h_i was taken to be $8 \text{ W/m}^2\cdot\text{K}$. This value was consistent with experimental measurements for mixed forced and natural convection on a vertical wall reported by Awbi and Hatton [115]. The outdoor heat transfer coefficient h_o was taken as $20 \text{ W/m}^2\cdot\text{K}$, based on previous numerical simulations of walls exposed to outdoor weather conditions [116, 117]. The total hemispherical solar absorptivity α_s and surface emissivity ϵ of the outer wall were taken as 0.26 and 0.9, respectively corresponding to typical values for white paint [113]. Finally, an average sky temperature T_{sky} of 2°C was used [113]. Four outdoor temperature conditions were considered with minimum and maximum outdoor temperatures T_{min} and T_{max} set at (i) 20 and 40°C , (ii) 10 and 30°C , (iii) 0 and 30°C , or (iv) 5 and 35°C , respectively. Table 7.1 summarizes the properties corresponding to PureTemp 20 PCM microencapsulated in HDPE and dispersed in concrete. The resulting effective volumetric heat capacity $(\rho c_p(T))_{eff}$ increased and the effective thermal conductivity k_{eff} decreased nearly linearly with increasing PCM volume fraction ϕ_c from 0.0 to 0.5 and $\phi_s = 0.08$ (see supplementary material). Thus, both the thermal resistance and the sensible heat storage capacity of the composite wall increased with the addition of PCM.

4.2.5 Performance metrics

Many numerical studies considering building materials containing PCMs reported either the inside surface temperature of the wall and/or the average indoor temperature [66, 107, 118]. It has been suggested that reducing the fluctuation of these temperatures enhances the thermal comfort of occupants within a room [66, 107]. However, they do not directly contribute in determining energy or cost savings. In the present study, the relative energy reduction and the time delay of the maximum thermal load were used to evaluate the performance of PCM composite walls with respect to plain concrete walls. First, the relative energy reduction E_r was defined as the relative difference between the daily energy fluxes (in J/m^2) through the

plain concrete wall $Q''_{L,m}$ and through the PCM-concrete composite wall Q''_L expressed as,

$$E_r = \frac{Q''_{L,m} - Q''_L}{Q''_{L,m}} \quad (4.17)$$

where the energy fluxes $Q''_{L,m}$ and Q''_L were respectively expressed as,

$$Q''_{L,m} = \int_0^{24 \text{ h}} |q''_{L,m}(t)| dt \quad \text{and} \quad Q''_L = \int_0^{24 \text{ h}} |q''_L(t)| dt. \quad (4.18)$$

Here, $q''_{L,m}$ and q''_L are the conductive heat fluxes (in W/m²) at the inner wall located at $x = L$ for plain concrete walls and for PCM-concrete composite walls, respectively. They are given by Fourier's law as,

$$q''_{L,m}(t) = -k_m \frac{\partial T_m}{\partial x}(L, t) \quad \text{and} \quad q''_L(t) = -k_{eff} \frac{\partial T}{\partial x}(L, t). \quad (4.19)$$

The absolute values of $q''_{L,m}$ and q''_L were considered to account for the fact that there is an energy cost associated with maintaining the indoor temperature at T_{in} , regardless of the direction of the heat flux across the wall. The relative energy reduction E_r describes the reduction in the daily thermal energy added or removed from the room per unit surface area of wall achieved by adding microencapsulated PCM to the concrete wall.

The second performance metric considered was the time delay τ_d of the maximum inner wall heat flux defined as $\tau_d = t_{max} - t_{max,m}$ where t_{max} and $t_{max,m}$ are the times at which $q''_L(t)$, for the PCM-concrete composite wall, and $q''_{L,m}(t)$, for the plain concrete wall, reached their respective maximum value during the day. The time delay is an important metric when a building is located in a place, such as California, where TOU electricity rate schedules are used by utility companies. In these cases, the time delay of the heat flux may shift the peak cooling load to a time of day with lower electricity rates, thus resulting in cost savings for the ratepayer.

4.2.6 Method of solution

The governing Equations (4.2) and (4.8) along with the initial and boundary conditions given by Equations (4.3) to (4.6), (4.13), and (4.14) were solved using finite element methods on unstructured grids. In cases with varying outdoor boundary temperatures, simulations were

run for 3 days and temperature and heat flux predictions for the third day were considered. By then, the diurnal heat flux had reached periodic steady-state and the maximum relative difference in the inner wall heat flux was less than 1% when extending the simulation period by one day. Numerical convergence was considered to be achieved if the maximum relative difference in the predicted local heat flux $q''_x(x, t)$ was less than 0.5% when reducing the mesh size or time step by a factor of 2. In practice, converged solutions were obtained by imposing the minimum mesh size and maximum growth rate to be $\Delta x = (D_s - D_c)/6$ and 1.5, respectively. The number of finite elements needed to obtain a converged solution ranged from 3289 to 786,985 depending on the size of the computational cell and on the core and shell dimensions.

4.2.7 Validation

In order to validate the computational tool, heat conduction through a two-dimensional $0.1 \times 0.2 \text{ m}^2$ rectangular paraffin slab heated at constant temperature on one side and thermally insulated on the other. This slab, undergoing partial solid-liquid phase transition was simulated following the study by Ogoh and Groulx [65]. The predicted transient temperature profiles agreed well with the exact solution for the one-dimensional Stefan problem derived by Alexiades [119]. The results were also consistent with those of Ogoh and Groulx [65] and support their conclusion that conduction through a material during phase change can be modeled numerically using the heat capacity method.

4.3 Results and discussion

4.3.1 Heterogeneous vs. homogeneous wall

In this section, we consider the slab of heterogeneous composite material shown in Figure 4.1b with thickness $L = 1 \text{ mm}$ subjected to a step boundary condition given by Equations (4.3) and (4.4). The initial temperature T_i and inner surface temperature $T(L, t) = T_L$ were equal and arbitrarily chosen to be 20°C , and the outer surface temperature $T(0, t) = T_0$ was

taken as 37°C. The composite material consisted of PCM microencapsulated in HDPE shells and distributed in concrete (Table 7.1) and featured PCM volume fractions ϕ_c of 0.05, 0.25, or 0.40 while ϕ_s was constant and equal to 0.08. The corresponding effective volumetric heat capacity $(\rho c_p)_{eff,s}$ of the equivalent homogeneous wall predicted by Equation (4.10) was 2.04, 2.08, and 2.11 MJ/m³·K, respectively. Similarly, the effective thermal conductivity k_{eff} predicted by Equation (4.12) was 1.23, 0.94, and 0.75 W/m·K, respectively. The latent heat of fusion h_{sf} , phase change temperature T_{pc} , and temperature window ΔT_{pc} of the PCM were taken as 180 kJ/kg, 21.5°C, and 3°C, respectively.

Figure 4.2 shows the area-averaged inner surface heat flux $\bar{q}_L''(t) = q_x''(L, t)$ as a function of time for PCM volume fraction ϕ_c of 0.5, 0.25, and 0.4. It also shows the corresponding predictions of the heat flux for the equivalent homogeneous slab with the above mentioned effective thermal properties. In all cases, the average relative difference in the predicted area-averaged inner surface heat flux $\bar{q}_L''(t)$ between the heterogeneous composite slab and the equivalent homogeneous slab was less than 2% at all times when the inner surface heat flux was greater than 5% of its steady-state value. Figure 4.2 also demonstrates that increasing the PCM volume fraction decreased the inner surface heat flux at all times and delayed its steady state. This can be attributed to the fact that adding PCM not only enhanced the latent and sensible thermal mass of the composite material but also its thermal resistance.

Figure 4.3 compares the temperature profiles along the centerline $(x, a/2, a/2)$ of the composite structure of Figure 4.1b at different times predicted for the heterogeneous composite and for the corresponding homogeneous material for (a) $\phi_c = 0.05$ and (b) $\phi_c = 0.40$ under the same conditions as the results shown in Figure 4.2. The relative difference in the local temperature between the heterogeneous composite and the equivalent homogeneous material was less than 1% at all times and locations. Figures 4.3a and 4.3b confirm that the time delay in the temperature evolution increased with increasing PCM volume fraction. They also illustrate that the temperature front progressed faster in the absence of phase change.

Overall, these results demonstrated that the heterogeneous composite can be treated as a homogeneous material with effective volumetric heat capacity $(\rho c_p)_{eff}(T)$ and effective thermal conductivity k_{eff} given by Equations (4.10) through (4.12). Consequently, for the

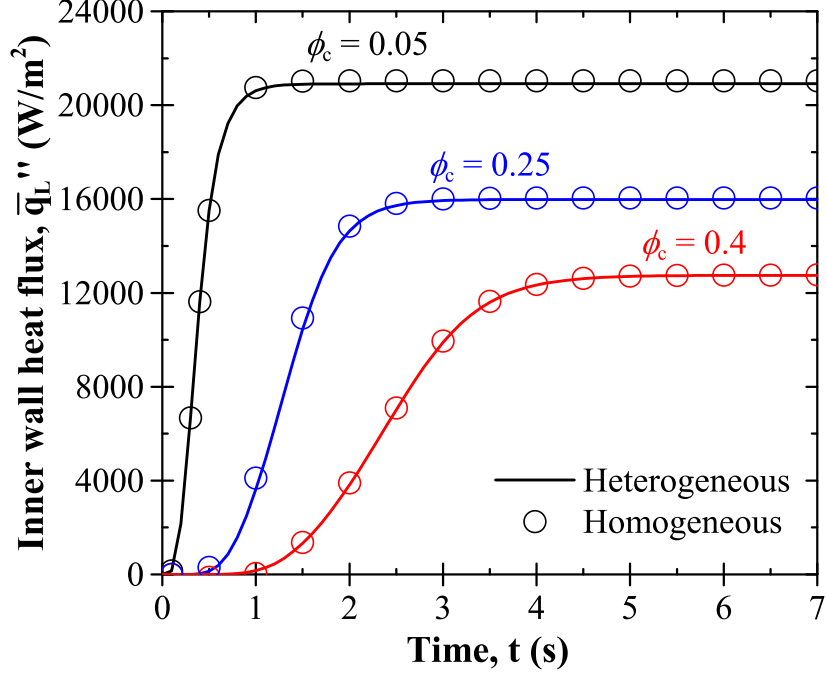


Figure 4.2: Area-averaged inner surface heat flux $\bar{q}_L''$ predicted for the heterogeneous three-phase 1 mm thick slab and the corresponding homogeneous slab with effective thermal properties as a function of time t for $T(0, t) = T_0 = 20^\circ\text{C}$ and $T(L, T) = T_L = 37^\circ\text{C}$. Values of effective volumetric specific heat and effective thermal conductivity were $(\rho c_p)_{eff,s} = 2.04, 2.08,$ and $2.11 \text{ MJ/m}^3\cdot\text{K}$ and $k_{eff} = 1.23, 0.94,$ and $0.75 \text{ W/m}\cdot\text{K}$ corresponding to PCM volume fractions of $\phi_c = 0.05, 0.25,$ and 0.4 , respectively. The phase change properties were taken to be $h_{sf} = 180 \text{ kJ/kg}$, $T_{pc} = 20^\circ\text{C}$, and $\Delta T_{pc} = 3^\circ\text{C}$.

remainder of this study, a PCM-concrete composite wall will be simulated as a homogeneous wall with these effective thermal properties. This will make possible the simulation of walls with realistic thickness L , on the order of tens of centimeters. Simulating a heterogeneous wall of such thickness with PCM microcapsules would be excessively time consuming and would require large computational resources due to the large number of mesh elements required to solve for the local temperature in the PCM and shell of the microcapsules.

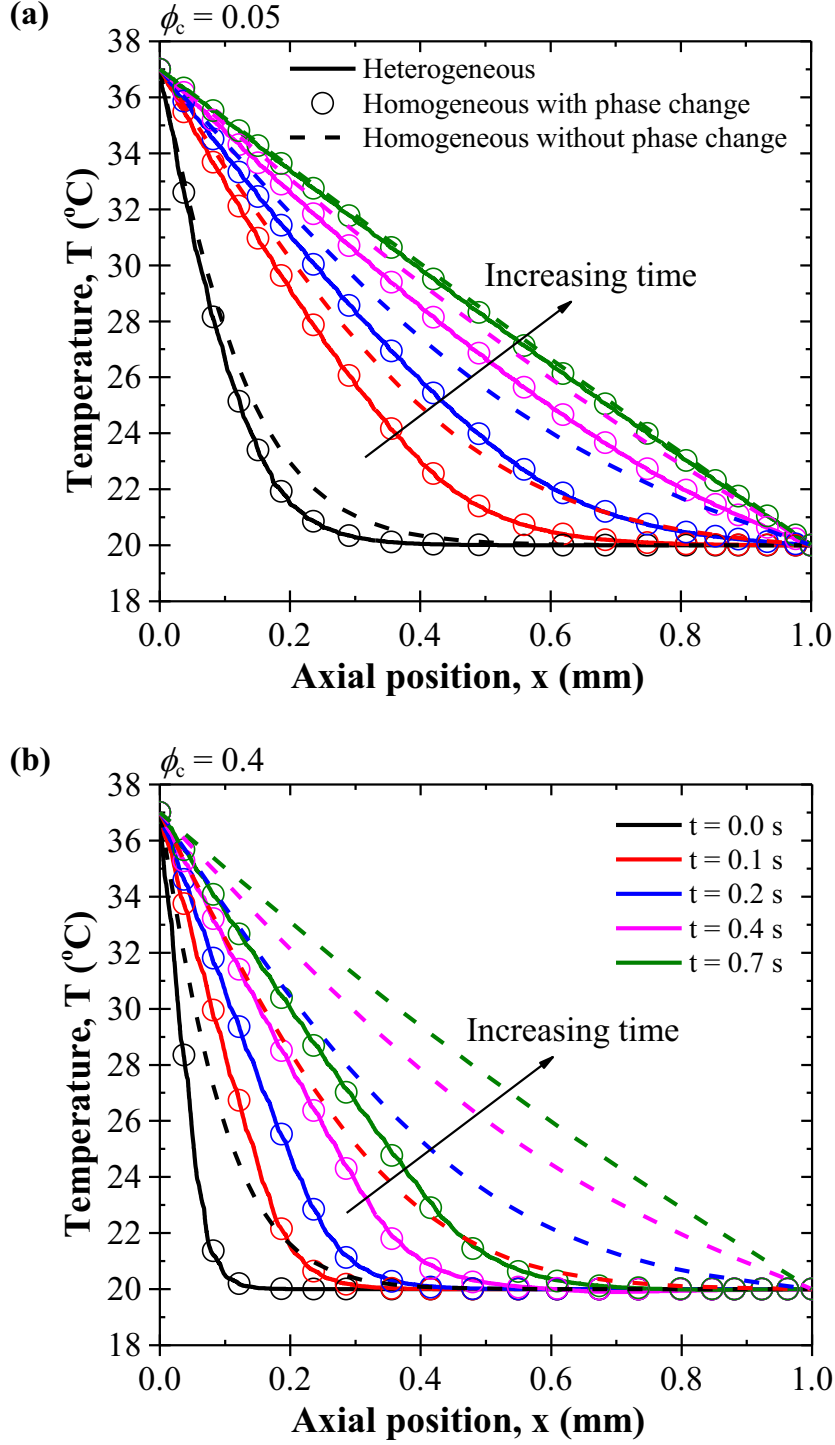


Figure 4.3: Temperature profiles at different times through a 1 mm thick heterogeneous composite slab and its equivalent homogeneous slab with and without phase change for PCM volume fraction of (a) $\phi_c = 0.05$ and (b) $\phi_c = 0.4$, respectively. All boundary conditions and thermal properties were consistent with those specified for Figure 4.2.

4.3.2 Diurnal thermal behavior

4.3.2.1 Effect of PCM volume fraction

This section considered homogeneous walls of thickness $L = 10$ cm subjected to sinusoidal diurnal boundary conditions imposed at the inner and outer wall surfaces as described by Equations (4.13) to (4.16). The latent heat of fusion h_{sf} , phase change temperature T_{pc} , and temperature window ΔT_{pc} were taken as 180 kJ/kg, 20°C, and 3°C, respectively. The outdoor temperature $T_{\infty}(t)$ described by Equation (4.15) oscillated sinusoidally around T_{pc} between $T_{min} = 10^\circ\text{C}$ and $T_{max} = 30^\circ\text{C}$. Figure 4.4a plots the inner wall heat flux as a function of time for PCM volume fractions ϕ_c ranging from 0.0 to 0.5. It demonstrates that increasing the PCM volume fraction significantly reduced the heat transfer through the wall. In fact, a PCM volume fraction ϕ_c of 0.5 reduced the range of variation in the inner wall heat flux by more than 90% compared with plain concrete. Moreover, adding microencapsulated PCM to concrete delayed the peak inner wall heat flux corresponding to the maximum cooling load.

Figure 4.4b plots the relative energy reduction E_r as a function of PCM volume fraction ϕ_c ranging from 0.0 to 0.5. In order to distinguish the contribution of phase change from that of other thermal effects, the PCM specific heat $c_{p,c}$ was imposed to be either constant and equal to $c_{p,c,s}$ or a function of temperature as described by Equation (2.3). Figure 4.4b shows that the relative energy reduction E_r increased substantially with increasing PCM volume fraction. In the absence of phase change, E_r increased linearly with increasing ϕ_c due to the associated increase in thermal resistance and sensible heat storage of the wall, i.e., $k_{eff} < k_m$ and $(\rho c_p)_{eff,s} > (\rho c_p)_m$. The relative energy reduction E_r was notably larger when phase change was accounted for. However, its rise slowed down significantly when the PCM volume fraction ϕ_c exceeded 0.2. In fact, the temperature profile corresponding to $\phi_c = 0.5$ revealed that the temperature within a portion of the wall never exceeded the upper limit of the phase change temperature window $T_{pc} + \Delta T_{pc}/2$ during the day. In other words, the benefit of the latent heat of fusion was not fully realized when the PCM volume fraction exceeded a critical value.

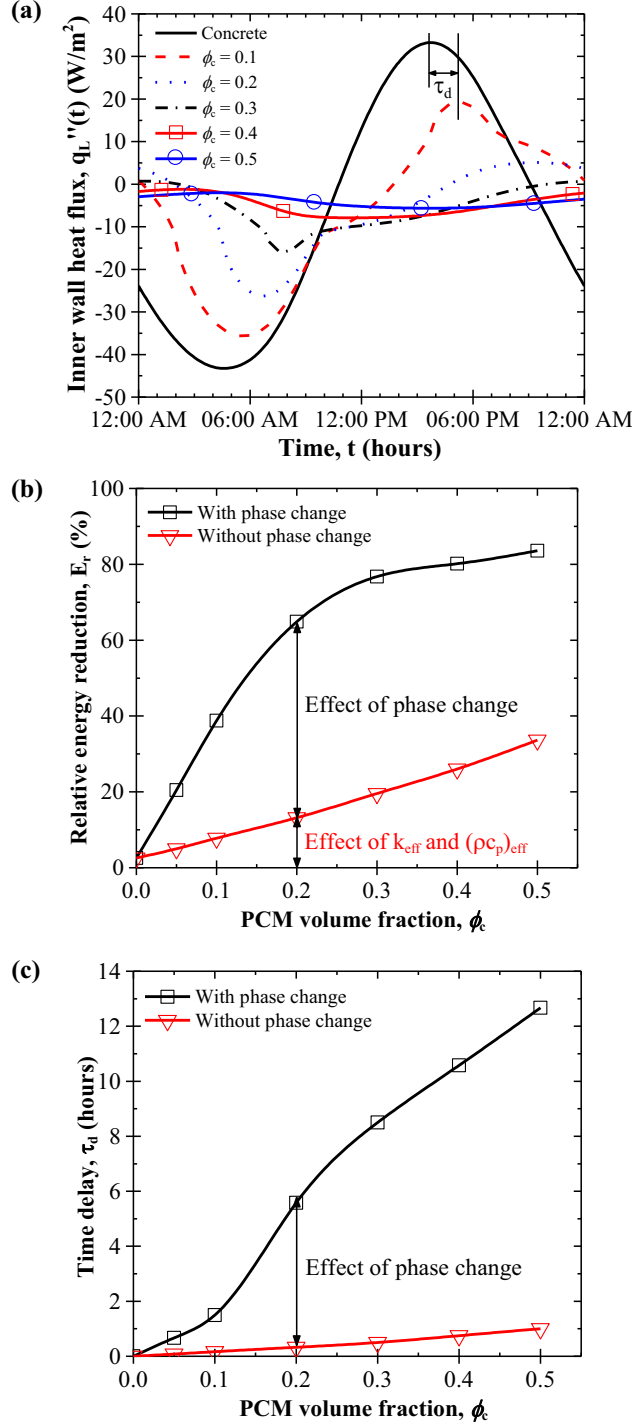


Figure 4.4: (a) Inner heat flux $q_L''(t)$ as a function of time through a 10 cm thick microencapsulated PCM-concrete wall subjected to sinusoidal diurnal boundary conditions with $T_{min} = 10^\circ\text{C}$ and $T_{max} = 30^\circ\text{C}$. (b) Relative energy reduction E_r and (c) time delay τ_d for PCM volume fraction ϕ_c ranging from 0.0 to 0.5. Here, $h_{sf} = 180 \text{ kJ/kg}$, $T_{pc} = 20^\circ\text{C}$, and $\Delta T_{pc} = 3^\circ\text{C}$. The PCM specific heat was either constant and equal to $(\rho c_p)_{eff,s}$ or temperature-dependent as defined by Equation (2.3) to assess the effects of phase change.

Figure 4.4c shows the time delay τ_d in the maximum inner wall heat flux as a function of PCM volume fraction ϕ_c . It indicates that τ_d increased significantly with increasing PCM volume fraction, reaching more than 13 hours for ϕ_c of 0.5. Here also, the contribution of phase change to the time delay was important and dominated over that of other thermal effects.

4.3.2.2 Effect of latent heat of fusion

The inner wall heat flux was computed as a function of time for latent heat of fusion h_{sf} ranging from 100 to 400 kJ/kg, representative of actual PCMs [7, 45, 111]. The volume fraction of PCM ϕ_c , phase change temperature T_{pc} , and temperature window ΔT_{pc} were taken as 0.1, 20°C, and 3°C, respectively. The minimum and maximum outdoor temperatures were $T_{min} = 10^\circ\text{C}$ and $T_{max} = 30^\circ\text{C}$, respectively. The results established that increasing the latent heat of fusion reduced and delayed heat transfer through the wall. In fact, the relative energy reduction E_r increased from 25 to 64% and the time delay τ_d increased from 0.8 to 5.7 hours as h_{sf} increased from 100 to 400 kJ/kg. This trend was consistent with physical intuition based on the fact that increasing the latent heat of fusion enhanced the wall's thermal mass and the amount of energy stored therein.

4.3.2.3 Effect of phase change temperature window

Figures 4.5a through 4.5c plot the inner wall heat flux $q_L''(t)$ as a function of time for phase change temperature window ΔT_{pc} ranging from 1 to 5°C and for average outdoor temperature $(T_{max} + T_{min})/2$ of 10, 20, and 30°C, respectively. The volume fraction of PCM ϕ_c , latent heat of fusion h_{sf} , phase change temperature T_{pc} , and amplitude of the outdoor temperature oscillations $(T_{max} - T_{min})/2$ were taken as 0.1, 180 kJ/kg, 20°C, and 10°C, respectively. Figure 4.5a indicates that, for an average daily outdoor temperature $(T_{max} + T_{min})/2$ of 10°C, changing the phase change temperature window affected only slightly the delay and reduction of heat transfer during the afternoon and evening. The PCM remained solid throughout the wall until the afternoon when the outdoor temperature T_∞ approached the phase change

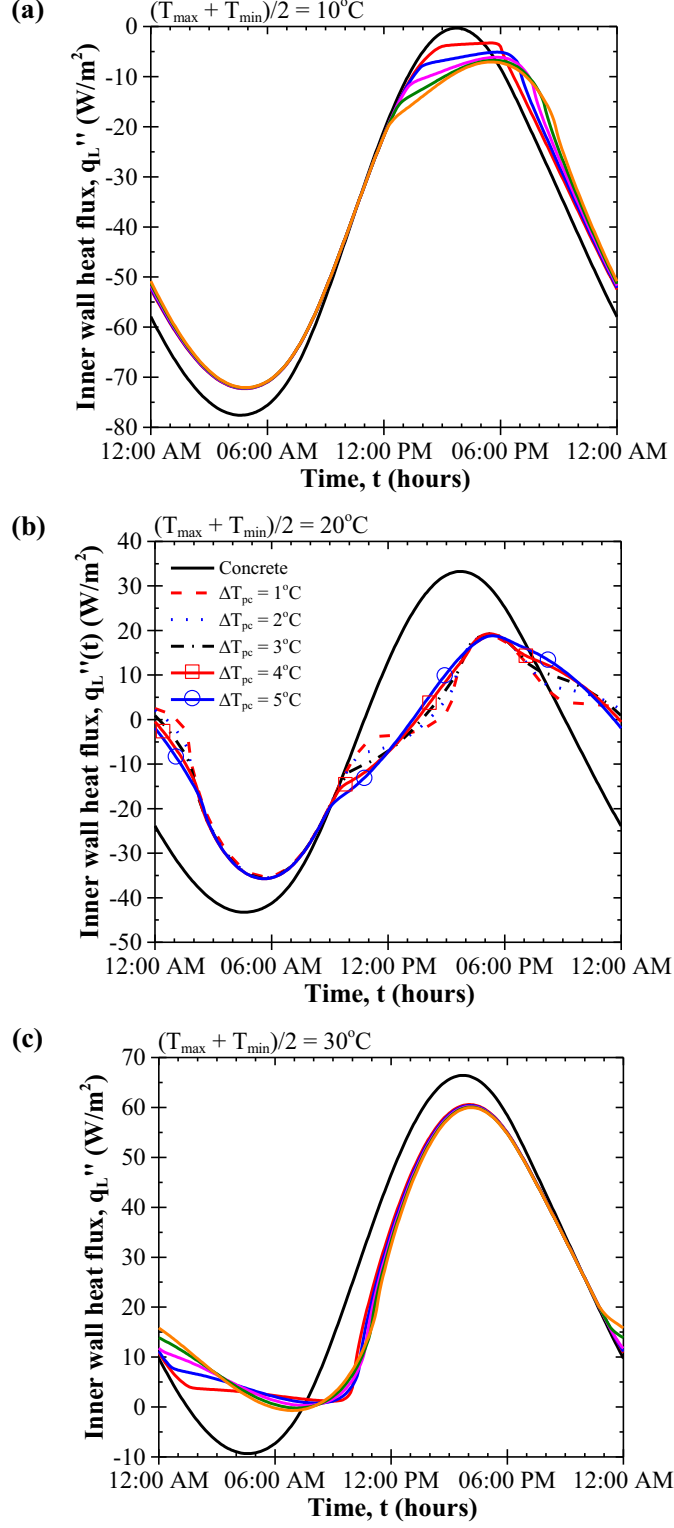


Figure 4.5: Inner heat flux $q_L''(t)$ as a function of time through a 10 cm thick microencapsulated PCM-concrete wall for ΔT_{pc} ranging from 1 to 5°C with minimum and maximum outdoor temperatures T_{min} and T_{max} of (a) 0 and 20°C, (b) 10 and 30°C, and (c) 20 and 40°C. Here, $\phi_c = 0.1$, $h_{sf} = 180$ kJ/kg, and $T_{pc} = 20^\circ\text{C}$.

temperature $T_{pc} = 20^\circ\text{C}$. At this time, the wall experienced partial melting, thus reducing and delaying the heat flux. Figure 4.5b indicates that, for $(T_{max} + T_{min})/2 = 20^\circ\text{C}$, decreasing ΔT_{pc} from 5°C to 1°C flattened the heat flux curves corresponding to a melting period between 9:00 am and 4:00 pm and a freezing period from 6:00 pm to 2:00 am. However, the minimum and maximum values of the wall heat flux were not affected by changes in ΔT_{pc} . Finally, Figure 4.5c illustrates that, for $(T_{max} + T_{min})/2 = 30^\circ\text{C}$, the phase change temperature window had an effect on the delay and reduction in the wall heat flux only during the morning hours. Here, the PCM remained liquid across the wall most of the day except early in the morning when it experienced partial freezing.

Moreover, the phase change temperature window ΔT_{pc} was found to have nearly no effects on the relative energy reduction E_r and on the time delay τ_d . In fact, E_r was strictly independent of ΔT_{pc} when the heat flux was unidirectional during the entire day. Both E_r and τ_d were the largest for $(T_{max} + T_{min})/2$ of 20°C and equal to $\sim 40\%$ and ~ 2 hours, respectively.

4.3.2.4 Effect of phase change temperature

Figures 4.6a through 4.6c plot the inner wall heat flux $q_L''(t)$ as a function of time for different phase change temperature T_{pc} ranging from 10 to 28°C and for average outdoor temperature $(T_{max} + T_{min})/2$ of 10 , 20 , and 30°C , respectively. The volume fraction of PCM ϕ_c , latent heat of fusion h_{sf} , phase change temperature window ΔT_{pc} , and amplitude of the outdoor temperature oscillations $(T_{max} - T_{min})/2$ were taken as 0.1 , 180 kJ/kg , 3°C , and 10°C , respectively. Figures 4.6a through 4.6c indicate that, for given outdoor temperature conditions, increasing the phase change temperature T_{pc} up to a certain value delayed the peak and reduced the amplitude of the heat flux through the microencapsulated PCM-concrete composite wall compared with a plain concrete wall. They suggest that the delay and reduction of the thermal load on the wall may be maximized by choosing the optimum phase change temperature based on outdoor temperature conditions.

Figure 4.7a plots the relative energy reduction E_r as a function of phase change tem-

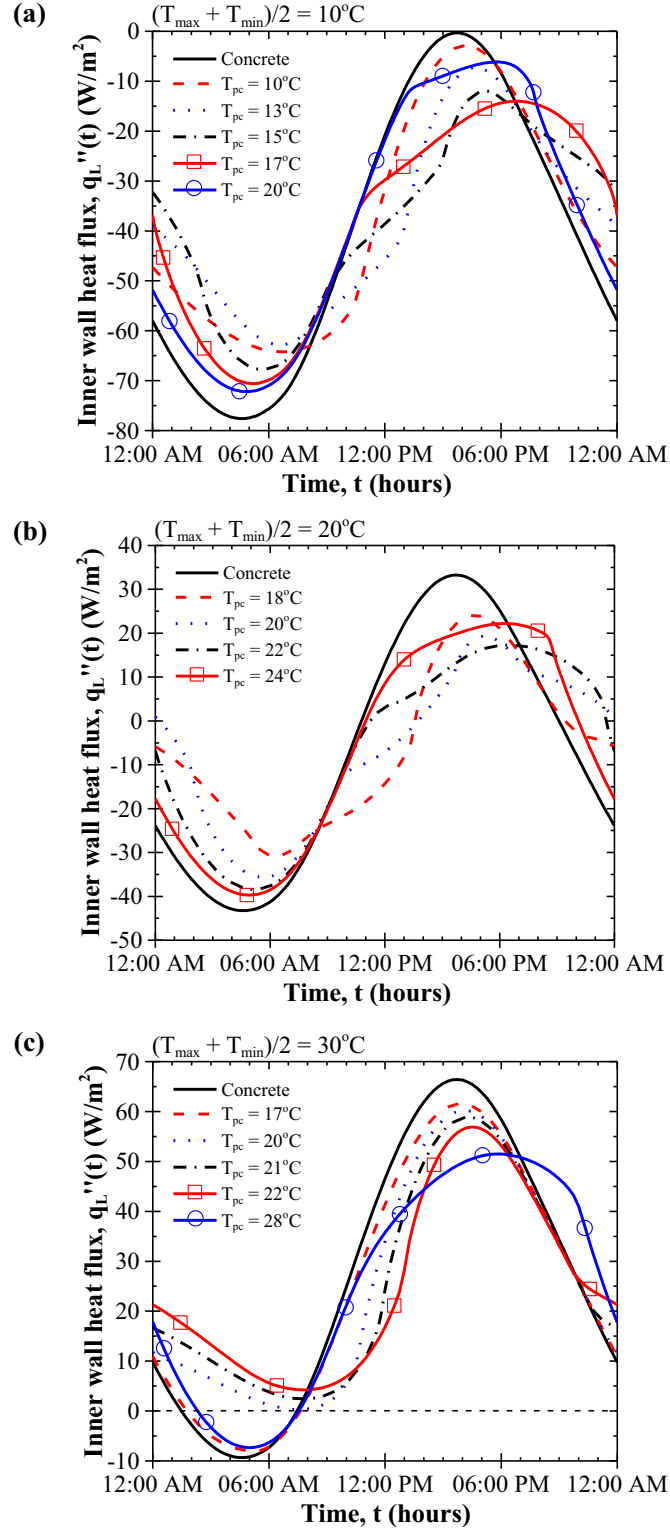


Figure 4.6: Inner heat flux $q_L''(t)$ as a function of time through a 10 cm microencapsulated PCM-concrete wall for T_{pc} ranging from 10 to 28°C with minimum and maximum outdoor temperatures $T_{\min}$ and $T_{\max}$ of (a) 0 and 20°C , (b) 10 and 30°C , and (c) 20 and 40°C , respectively. Here, $\phi_c = 0.1$, $h_{sf} = 180 \text{ kJ/kg}$, and $\Delta T_{pc} = 3^{\circ}\text{C}$.

perature T_{pc} for average outdoor temperature $(T_{max} + T_{min})/2$ of 10, 20, and 30°C and for $\phi_c = 0.1$, $h_{sf} = 180$ kJ/kg, and $\Delta T_{pc} = 3^\circ\text{C}$. First, it is interesting to note that, for an average daily outdoor temperature of 10°C, even though the shape of the heat flux curves varied dramatically (Figure 4.6a), the relative energy reduction was independent of T_{pc} . In fact, the value of E_r was equal to that achieved in the absence of phase change, i.e., energy saving was solely due to the increase in sensible heat storage and thermal resistance. Here, the heat flux was unidirectional from the inside to the outside (i.e., $q_L'' < 0$) throughout the day (Figure 4.6a). For an average outdoor temperature of 20°C, a distinct maximum relative energy reduction $E_{r,max}$ of 39% was achieved for a phase change temperature T_{pc} equal to the indoor temperature T_{in} of 20°C. This result was consistent with conclusions reported in the literature for multilayer composite walls containing a PCM layer [109, 110]. Lastly, for an average outdoor temperature of 30°C, the relative energy reduction E_r was also independent of the phase change temperature T_{pc} when the latter was either below 17°C, or above 31°C. In fact, it was identical to that obtained for $(T_{max} + T_{min})/2 = 10^\circ\text{C}$. For T_{pc} below 17°C, no phase change occurred since the PCM was liquid for the entire day. When T_{pc} was between 31 and 40°C, phase change occurred but the heat flux was only reduced and delayed in the afternoon when heat “flowed” into the building. In other words, the heat flux was unidirectional for the duration of the phase change cycle. The relative energy reduction E_r also featured a plateau when T_{pc} was between 20 and 23°C. Here, the PCM experienced phase transition, but the heat flux was unidirectional throughout the day and E_r was independent of T_{pc} . For other values of T_{pc} , the heat flux through the wall changed direction during the day and the relative energy reduction depended on the phase change temperature. Overall, these results showed that there were no optimization opportunities in terms of energy reduction for a homogeneous PCM composite wall subjected to sinusoidal outdoor temperature oscillations and solar irradiation when the heat flux at the inner wall surface was unidirectional during the entire diurnal cycle. Such situations can be encountered in extremely hot or cold climates.

Figure 4.7b plots the time delay τ_d as a function of phase change temperature T_{pc} corresponding to the heat flux shown in Figure 4.6 for $\phi_c = 0.1$, $h_{sf} = 180$ kJ/kg, and $\Delta T_{pc} = 3^\circ\text{C}$.

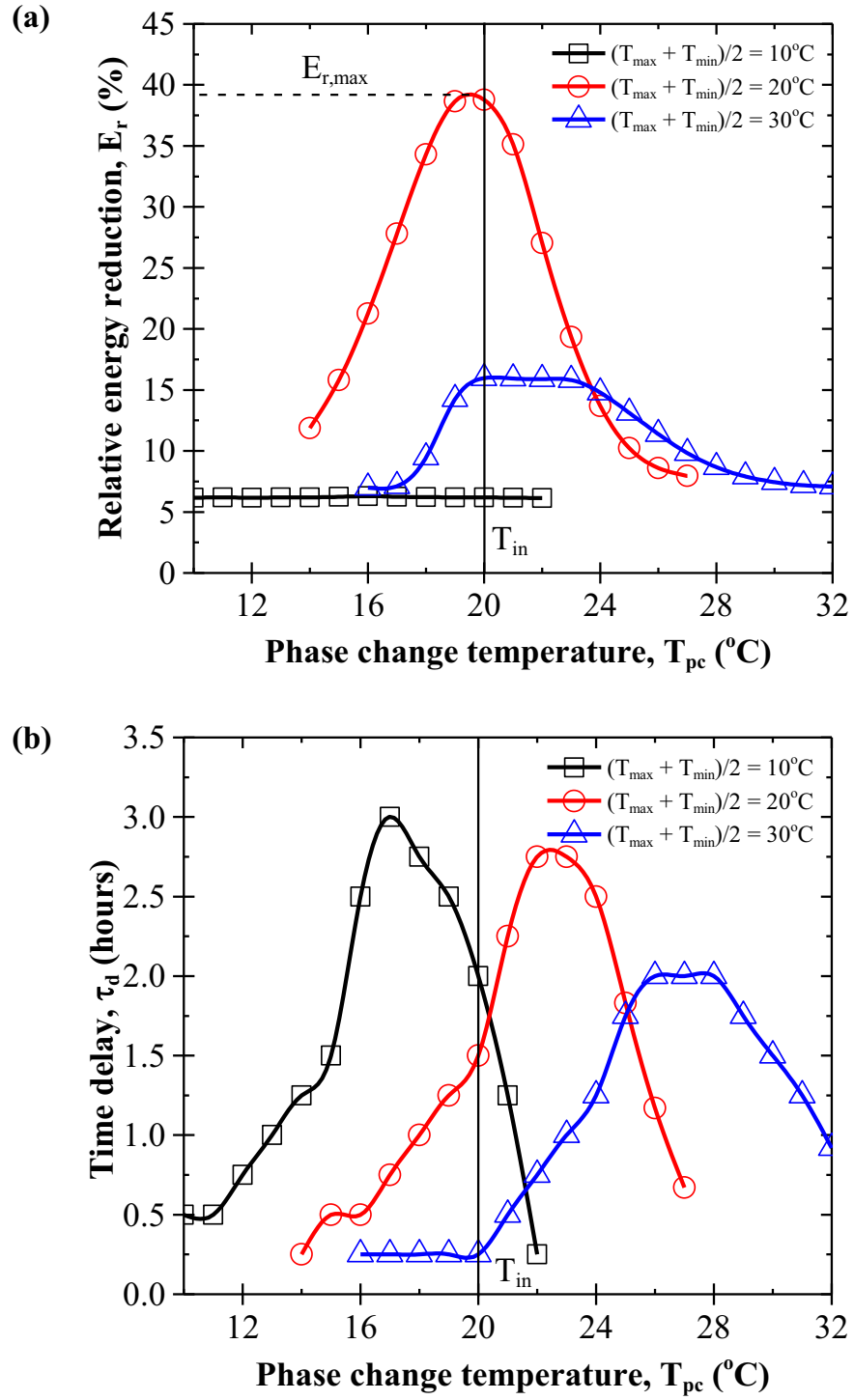


Figure 4.7: (a) Relative energy reduction E_r and (b) time delay τ_d as a function of phase change temperature T_{pc} for average outdoor temperature $(T_{max} + T_{min})/2$ of 10, 20, and 30°C and outdoor temperature amplitude $(T_{max} - T_{min})/2$ of 10°C . Here, $\phi_c = 0.1$, $h_{sf} = 180 \text{ kJ/kg}$, and $\Delta T_{pc} = 3^{\circ}\text{C}$.

In all cases, τ_d reached a maximum ranging from 2 to 3 hours as the average outdoor temperature decreased from 30 to 10°C. The value of T_{pc} corresponding to the maximum value of τ_d increased with increasing average outdoor temperature. Although there was no optimization opportunity in terms of the relative energy reduction for an average outdoor temperature of 10°C (Figure 4.7a), the time delay could be increased to up to 3 hours by adjusting T_{pc} . It can be further increased by increasing the PCM volume fraction ϕ_c and/or the latent heat of fusion h_{sf} . Therefore, adding PCM to a building wall in an extremely hot or cold climate may still provide financial savings to the ratepayer if TOU pricing is available, by shifting the heating or cooling load to an off-peak time of day.

4.3.2.5 Effect of outdoor temperature

Figure 4.8a plots the maximum relative energy reduction $E_{r,max}$ as a function of the average outdoor temperature $(T_{max} + T_{min})/2$ ranging from 5 to 35°C for outdoor temperature amplitude $(T_{max} - T_{min})/2$ of 10 or 15°C. The PCM volume fraction ϕ_c , latent heat of fusion h_{sf} , and phase change temperature window ΔT_{pc} were taken as 0.1, 180 kJ/kg, and 3°C, respectively. Figure 4.8a reveals that the maximum energy reduction could reach up to 40% and was achieved when the average outdoor temperature was about 22°C for both outdoor temperature amplitudes of 10 and 15°C. This was slightly higher than the imposed indoor temperature T_{in} of 20°C. Furthermore, the maximum relative energy reduction $E_{r,max}$ decreased as the amplitude of the outdoor temperature oscillations increased. As the average outdoor temperature $(T_{max} + T_{min})/2$ approached extremely hot or cold conditions, the maximum relative energy reduction $E_{r,max}$ reached a constant value of about 6%, equal to the relative energy reduction achieved for PCM volume fraction ϕ_c of 0.1 in absence of phase change. This confirms that phase change had no effect on the daily energy savings in extreme hot or cold climates. Figure 4.8b plots the optimum phase change temperature corresponding to the maximum relative energy reduction T_{pc,opt,E_r} as a function of average daily outdoor temperature ranging from 5°C to 35°C and for outdoor temperature amplitude of 10°C and 15°C. It shows that $E_{r,max}$ was achieved for an optimum phase change temperature T_{pc,opt,E_r} near the indoor temperature $T_{in} \pm 1^\circ\text{C}$, regardless of the average daily

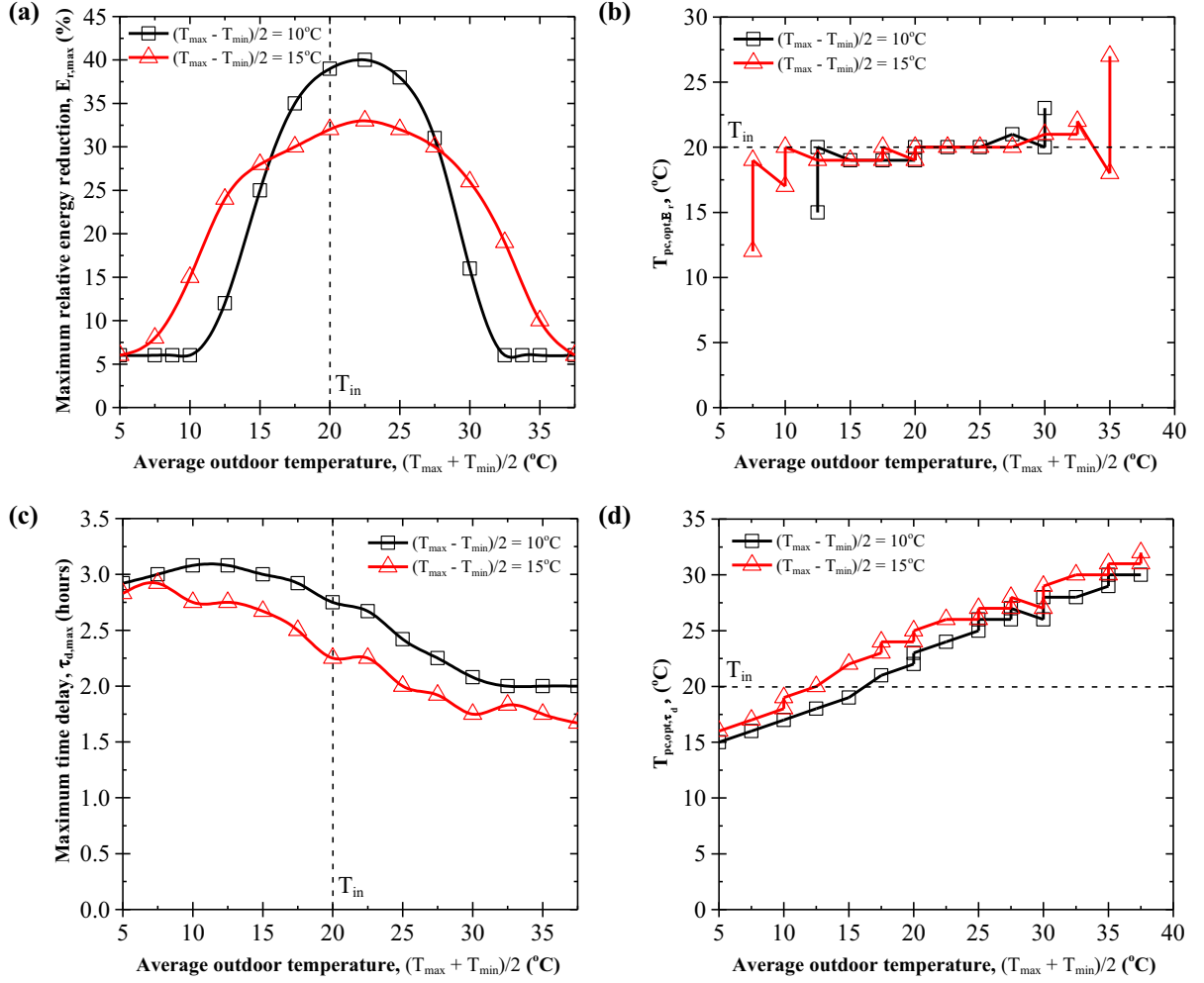


Figure 4.8: (a) Maximum relative energy reduction $E_{r,max}$, (b) phase change temperature corresponding to the maximum relative energy reduction T_{pc,opt,E_r} , (c) maximum time delay $\tau_{d,max}$, and (d) phase change temperature corresponding to the maximum time delay T_{pc,opt,τ_d} for average outdoor temperatures ranging from 5 to 37.5°C with an amplitude of either 10 or 15°C. Here, $\phi_c = 0.1$, $h_{sf} = 180$ kJ/kg, and $\Delta T_{pc} = 3$ °C.

outdoor temperature.

Figure 4.8c plots the maximum time delay $\tau_{d,max}$ as a function of the average outdoor temperature $(T_{max} + T_{min})/2$ ranging from 5 to 35°C for outdoor temperature amplitude $(T_{max} - T_{min})/2$ of 10 or 15°C. For the selected value of $\phi_c = 0.1$, the maximum time delay could reach up to about 3 hours and was achieved when $(T_{max} + T_{min})/2$ and $(T_{max} - T_{min})/2$ were 10°C. Additionally, $\tau_{d,max}$ decreased only slightly from 3 to 2 hours as the average daily outdoor temperature increased from 5-10 to 35°C. Figure 4.8d plots the optimum phase change temperature corresponding to the maximum time delay T_{pc,opt,τ_d} as a function of average daily outdoor temperature and for outdoor temperature amplitude $(T_{max} - T_{min})/2$ of 10 or 15°C. It shows that T_{pc,opt,τ_d} increased nearly linearly from 16 to 31°C as $(T_{max} + T_{min})/2$ increased from 5 to 35°C.

4.3.3 Equivalent wall thickness

The previous sections established that adding microencapsulated PCM reduced the diurnal energy flux through concrete walls. Alternatively, the following section investigates the idea that adding microencapsulated PCM could maintain a constant diurnal energy flux while reducing the thickness of a concrete wall. This section aims to predict the equivalent wall thickness L_{eq} such that the diurnal energy flux Q''_L through a microencapsulated PCM-composite wall is equivalent to the energy flux $Q''_{L,m}$ through a plain concrete wall of thickness L_m .

Figure 4.9a plots the energy flux ratio $Q''_L/Q''_{L,m}$ as a function of wall thickness ratio L_{eq}/L_m for $L_m = 10$ cm. The walls were subjected to sinusoidal diurnal boundary conditions as described by Equations (4.15) to (4.16). The outdoor temperature $T_\infty(t)$ described by Equation (4.15) oscillated sinusoidally around T_{pc} between $T_{min} = 10^\circ\text{C}$ and $T_{max} = 30^\circ\text{C}$. The composite walls had a thickness L_{eq} of 0.25, 0.5, or 0.75 cm and a microencapsulated PCM volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3. Figure 4.9a shows that the energy flux ratio $Q''_L/Q''_{L,m}$ decreased linearly with the wall thickness ratio L_{eq}/L_m for a given microencapsulated PCM volume fraction ϕ_{c+s} . Furthermore, it illustrates that increasing ϕ_{c+s} decreased

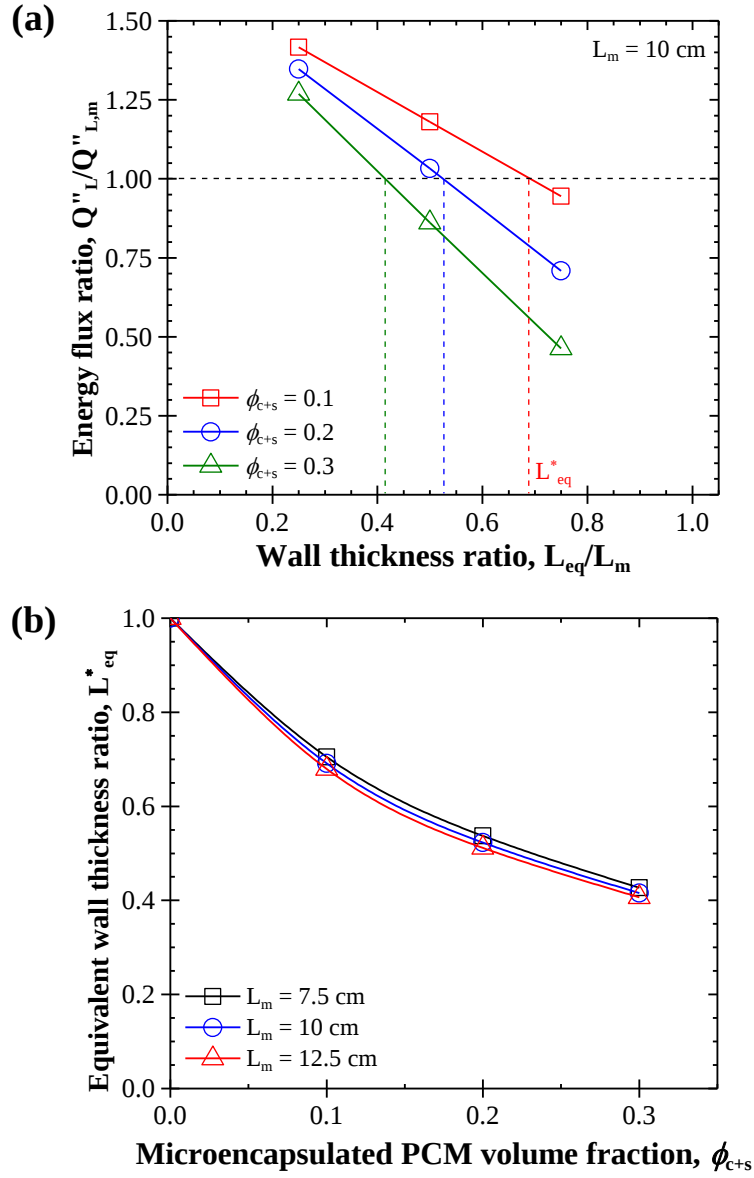


Figure 4.9: (a) Diurnal energy flux Q'' as a function of wall thickness ratio L_{eq}/L_m for a microencapsulated PCM volume fraction ϕ_{c+s} of 0.1, 0.2, and 0.3 and a concrete wall thickness $L_m = 10$ cm and (b) equivalent wall thickness ratio L_{eq}^* as a function of microencapsulated PCM volume fraction ϕ_{c+s} for concrete walls of thickness $L_m = 7.5, 10, \text{ and } 12.5$ cm.

the equivalent wall thickness L_{eq} required to maintain the same diurnal energy flux $Q''_{L,m}$ as a 10 cm thick plain concrete wall.

Figure 4.9b plots the equivalent wall thickness ratio L_{eq}^* as a function of microencapsulated PCM volume fraction ϕ_{c+s} for concrete walls of thickness $L_m = 7.5, 10, \text{ and } 12.5$ cm. It shows that adding microencapsulated PCM to concrete can enable the wall thickness to be substantially reduced while maintaining the same diurnal energy flux. Additionally, adding a given volume fraction of microencapsulated PCM offered nearly the same relative reduction in wall thickness in all cases considered. As a rule of thumb, these results suggest that adding 20 vol.% microencapsulated PCM to a concrete wall could enable its thickness to be reduced by half while maintaining the same diurnal energy flux $Q''_{L,m}$.

4.4 Conclusion

This study demonstrated that a composite wall containing microencapsulated PCMs can be accurately represented as a homogeneous wall with some effective thermal properties given by Equations (4.10) to (4.12). This time-dependent homogeneous thermal model was used to establish important design rules that can inform the selection of microencapsulated PCMs for concrete walls in various climates. First, adding microencapsulated PCM to concrete walls and increasing the latent heat of fusion both substantially reduced and delayed the thermal load on the building. Second, the phase change temperature leading to the maximum energy savings was equal to the desired indoor temperature regardless of the climate conditions. Third, to achieve the maximum time delay, the optimum phase change temperature increased with increasing average outdoor temperature. Fourth, in extremely hot or cold climates, the use of PCM delayed the thermal load to take advantage of TOU pricing even though the energy savings were not significant. Lastly, the phase change temperature window had little effect on the energy savings and the time delay. This analysis can inform future simulations of composite walls containing microencapsulated PCMs in any climate.

CHAPTER 5

Annual energy analysis of concrete containing phase change materials for building envelopes

This chapter aims to evaluate the potential annual energy and cost savings potential of adding microencapsulated PCM to the concrete walls of an average-sized single family home in California climate zones 3 (San Francisco, CA) and 9 (Los Angeles, CA). The effects of wall orientation, realistic outdoor temperature, and solar irradiation from weather data on the annual energy and cost savings was elucidated.

5.1 Background

Few studies have numerically investigated the transient thermal behavior of composite walls containing PCMs subjected to realistic boundary conditions based on weather data over an entire year [32, 33, 109, 110]. They have been limited to plane-parallel multilayer walls containing either a pure PCM layer [110], a PCM-wallboard layer [33, 109], or a shape stabilized PCM (SSPCM) layer [32].

Mathieu-Potvin and Gosselin [110] used genetic algorithm to minimize the annual thermal energy flux through a south-facing wall consisting of 20-layers with at least one made of PCM. Each layer was 0.5 cm thick and was made of concrete, polystyrene insulation, or pure PCM with one of six possible phase change temperatures and identical latent heat of fusion. The inner wall surface was subjected to convective heat transfer with a constant indoor temperature. The outer wall surface was subjected to combined convective and radiative heat transfer with outdoor temperature and solar irradiation taken from weather data for Quebec City, Canada. The optimum design contained a single PCM layer located

near the center of the wall with a phase change temperature equal to the desired indoor temperature and without a concrete layer. This design reduced the annual thermal load by about 7% compared with a slab of pure polystyrene insulation of identical thickness (10 cm). Furthermore, the optimized wall was found to reduce the cooling load in the summer substantially more than the heating load in the winter. Finally, the authors state that there was no opportunity to optimize the energy reduction using a PCM layer if the indoor temperature was not within the range of outdoor temperature oscillations, i.e., if the wall heat flux was unidirectional. In fact, the wall heat flux was unidirectional in Quebec City during the heating season (winter), and thus the PCM had little effect during this time.

Zwanzig et al. [33] simulated a room with 15.3 cm thick walls and a 12.4 cm thick ceiling of conventional multilayer construction. The outer walls and ceiling contained a 1.3 cm thick layer of gypsum wallboard impregnated with 25 vol.% PCM featuring a phase change temperature window between 25 and 27.5°C. The PCM-wallboard layers were assumed to be homogeneous with some effective thermal properties. Their effective density and specific heat were both determined by a weighted average using the mass fractions of PCM and gypsum. The effective thermal conductivity was determined using the Maxwell Garnett effective medium approximation (EMA) for inclusions in a continuous matrix. The indoor temperature was taken to be constant and equal to 20 or 24°C during the heating or cooling seasons, respectively. The exterior surfaces were subjected to annual outdoor temperature and solar irradiation representative of three U.S. cities, namely, Minneapolis, Louisville, or Miami from weather data. The relative energy reduction differed by up to 60% between wall orientations but was the largest for South-facing walls in most cases considered. Adding PCM to the walls and ceiling reduced the thermal load on the room more during the cooling season (summer) than during the heating season (winter). Unfortunately, the authors did not report the value of the total annual relative heating or cooling load reduction for the entire room.

Diaconu and Cruceru [109] simulated a room with multilayer building envelope consisting of a polystyrene insulation layer sandwiched between two PCM-wallboards. Each PCM-wallboard layer was assumed to be homogeneous with some arbitrarily chosen effec-

tive thermal properties and the enthalpy method was used to simulate phase change. The authors noted that the implementation of the walls was not addressed because the results were intended as a first order approximation to inform future investigation. The inner wall surface was exposed to convective heat transfer. The indoor temperature was computed based on an energy balance of the indoor space. The outer wall surface was subjected to combined convective and radiative heat transfer with outdoor temperature and solar irradiation taken from weather data for Bechar, Algeria. The authors found that the annual heating and cooling load could be reduced by up to 13 and 1%, respectively, when the phase change temperature in the inner and outer layer was about 20 and 24°C, respectively. Moreover, the conclusions contradict those of Mathieu-Potvin and Gosselin [110] and of Zwanzig et al. [33] who reported that the annual cooling energy savings was larger than the annual heating energy savings for a multilayer PCM composite wall. We speculate that this discrepancy was due to the fact that climate conditions in Algeria resulted in a unidirectional wall heat flux during a large portion of the summer but not during the winter. Indeed, Mathieu-Potvin and Gosselin [110] and Thiele et al. [35] found that the thermal load reduction through a PCM-composite wall was independent of phase change if the wall heat flux was unidirectional throughout the day. Unfortunately, the imposed outdoor temperature and the computed wall heat flux were not reported by the authors [109].

Chan [32] used EnergyPlus to simulate a three-bedroom residential flat located in Hong Kong with 10.3 cm thick multilayer exterior walls. A 0.5 cm thick SSPCM layer containing 60 vol.% PCM with a phase change temperature of 22°C was included in one of the exterior walls of both the living room and the master bedroom. The thermal properties of the SSPCM layer were obtained from DuPont de Nemours and the enthalpy method was used to simulate phase change. The building was subjected to outdoor temperature and solar irradiation from weather data in Hong Kong. The author only simulated the cooling season between May and October, since space heating demand was small and intermittent during the winter months. The cooling load was reduced by 2.9% by incorporating a SSPCM layer into the West-facing wall of the living room, and by a lesser extent in the East, South, and North orientations. The author attributed this to the subtropical location of Hong Kong, which results in larger

solar irradiation on the West and East walls during the summer months. Chan [32] also found that the cooling load actually increased by 0.3% when incorporating a SSPCM layer into the West-facing wall of the master bedroom. By considering the material and installation cost, the author determined that the payback period of installing a West-facing living room wall containing a SSPCM layer was excessively long at 91 years, assuming a flat electricity rate.

Kośny et al. [120] simulated one-dimensional heat transfer through a multilayer wall and ceiling with a 14 and 30 cm thick layer of insulation, respectively, including 30 wt.% microencapsulated PCM. The inner and outer surfaces of the wall and ceiling were respectively subjected to a constant indoor temperature and to one of three diurnal outdoor temperature profiles. The latter were assumed to be representative of summer thermal oscillations on exterior walls and attic floors including the effect of solar irradiation. They found that adding PCM to the wall and ceiling insulation layers respectively reduced the thermal load by about 22% and 72% compared with using insulation of identical thickness. Then, the authors used EnergyPlus to determine the annual cooling loads through the ceiling and exterior walls of a single story house in five different Southern U.S. climates in the absence of PCM. The reductions from the wall and ceiling simulations were applied to the cooling loads determined using EnergyPlus and local electricity rates were considered to estimate the associated cost savings in each of the five cities. Across most of the applications and locations considered, the cost of microencapsulated PCM must be less than \$2.00/lb in order to achieve a payback period of less than 10 years. However, the outdoor temperature profiles used in PCM-wall and ceiling simulations did not account for daily or location-based weather variations or for different wall orientations. Further, it is unclear what method the authors used to simulate phase change and whether they simulated a multilayer wall or a homogeneous wall with some effective thermal properties. As a result of the simplified outdoor boundary conditions used in this analysis, the effects of season, climate, and wall orientation on the cost savings associated with PCM composite walls and ceilings were not addressed.

In a recent study [35] we simulated heat transfer through a 10 cm thick microencapsulated PCM-concrete wall subjected to diurnal sinusoidal outdoor temperature and solar irradiation oscillations. We established that increasing the PCM volume fraction within the

wall increased both the daily energy savings and the time delay. In addition, the daily energy savings were maximized when the PCM phase change temperature and also the average outdoor temperature were close to the desired indoor temperature. Furthermore, when the average outdoor temperature was extremely hot or cold, the wall heat flux was unidirectional for the entire day and phase change had no effect on the daily energy reduction.

Overall, the literature reported contradictory conclusions when comparing the energy saving potential of PCM composite walls during the winter and summer seasons. Moreover, the studies concerning PCM composite walls subjected to realistic weather conditions either used EMAs that have not been validated against experimental data or detailed numerical simulations or they failed to report the values of the effective thermal properties used. Thus, these studies did not account for the effects of the PCM-layer morphology on the thermal behavior of the composite wall. Lastly, most of the literature neglects to report the annual outdoor temperature or PCM-composite wall heat flux data which is important to understand the energy savings. To the best of our knowledge, no study has performed an annual thermo-economic analysis of microencapsulated PCMs uniformly distributed in concrete while rigorously accounting for the thermal effects of the PCM, shell, and matrix materials, realistic weather conditions, and TOU electricity rate structures.

5.2 Analysis

5.2.1 Schematic and assumptions

Figure 5.1 illustrates a PCM-concrete composite wall of thickness $L = 10$ cm with effective thermal conductivity k_{eff} and effective volumetric heat capacity $(\rho c_p)_{eff}$. The wall was subjected to convective heat transfer at the inside surface and to combined convective and radiative heat transfer at the outside surface. The latter consisted of (i) diffuse and collimated solar irradiation, (ii) radiation exchange with the sky, and (iii) irradiation diffusely reflected by grass around the building. The variation of the solar irradiation on the North, South, East, or West wall was considered.

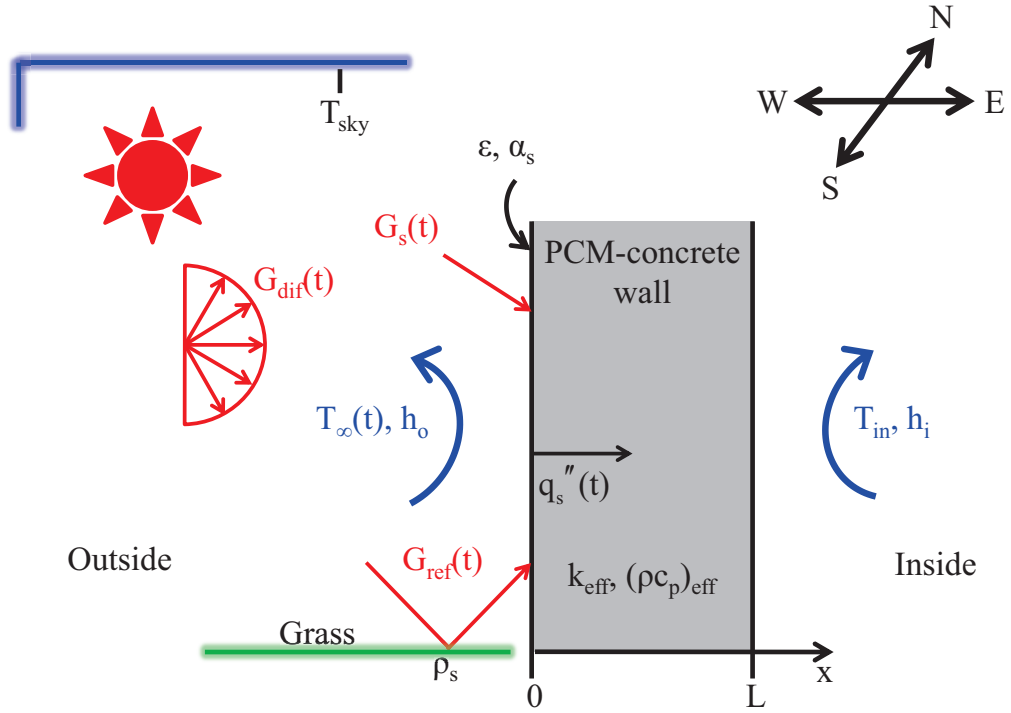


Figure 5.1: Schematic of a homogeneous wall of thickness L with effective thermal conductivity k_{eff} and effective volumetric heat capacity $(\rho c_p)_{eff}$, representative of a microencapsulated PCM-concrete composite. The wall was subjected to convection at the inside surface ($x = L$) and to combined convection and solar irradiation at the outside surface ($x = 0$).

The home energy efficient design (HEED) software [73] implements a standard methodology for simulating whole buildings. It complies with the California Energy Commission residential alternative calculation method [75]. Here, HEED was used to generate a reference simulation home that met California building code based on the average floor area of a single-family home built in 2013 in the Western U.S. of about 240 m² (2600 ft²) [121]. HEED determined the North and South wall areas to be 39.4 and 37.5 m², respectively, and both the East and West wall areas to be 27.9 m². These dimensions were used in the present study.

To make the problem mathematically tractable, the following assumptions were made: (1) the PCM-concrete composite wall had isotropic and constant thermal properties except for the temperature-dependent effective specific heat [Equation (4.10)]. (2) The specific heat of the PCM was the same for the solid and liquid phases, i.e., $(\rho c_p)_{c,s} = (\rho c_p)_{c,l}$ so that $(\rho c_p)_{eff,s} = (\rho c_p)_{eff,l}$. (3) There was no heat generation in the wall. (4) The outer wall surfaces were treated as gray and diffuse, and (5) Weekends and holidays had the same TOU electricity rate schedules as weekdays.

5.2.2 Governing equations

Under the above assumptions, the local wall temperature $T(x, t)$ at time t and location x was governed by the one-dimensional (1D) transient heat conduction equation [113],

$$\frac{\partial T}{\partial t} = \alpha_{eff}(T) \frac{\partial^2 T}{\partial x^2} \quad (5.1)$$

where $\alpha_{eff}(T) = k_{eff}/(\rho c_p)_{eff}(T)$ is the effective thermal diffusivity and k_{eff} and $(\rho c_p)_{eff}(T)$ are the effective thermal conductivity and the effective volumetric heat capacity, given by Equations (4.12) and (4.10), respectively.

5.2.3 Initial and boundary conditions

The initial temperature was assumed to be uniform throughout the material and equal to T_i , i.e.,

$$T(x, y, z, 0) = T_i. \quad (5.2)$$

Convective heat transfer was imposed at the interior wall surface $x = L$ with a constant indoor temperature T_{in} maintained by the heating, ventilation, and air-conditioning (HVAC) system so that [110],

$$-k_{eff} \frac{\partial T}{\partial x}(x = L, t) = h_i(T(L, t) - T_{in}) \quad (5.3)$$

where h_i is the mixed convective heat transfer coefficient accounting for both forced and natural convections. Combined convective and radiative heat transfer was imposed at the exterior wall surface such that [109, 110],

$$-k_{eff} \frac{\partial T}{\partial x}(x = 0, t) = h_o[T_\infty(t) - T(0, t)] + \alpha_s q_s''(t) - \epsilon \sigma [T(0, t)^4 - T_{sky}^4] \quad (5.4)$$

where h_o is the outdoor convective heat transfer coefficient, $T_\infty(t)$ and T_{sky} respectively represent the outdoor and average sky temperatures, $q_s''(t)$ is the solar irradiation at time t , and σ is the Stefan-Boltzmann constant (i.e., $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$). In addition, α_s and ϵ are the total hemispherical solar absorptivity and emissivity of the outdoor wall surface, respectively. They typically differ, as solar irradiation originating from the sun is concentrated in the visible and near infrared while the outer wall surface emits radiation in the mid-infrared [113].

5.2.4 Constitutive relationships

The density, thermal conductivity, and specific heat of the PCM, shell, and matrix corresponded to those of a commercial organic PCM PureTemp 20 by Entropy Solution Inc. (Plymouth, MN) [111], high density polyethylene (HDPE) [112], and concrete [113], respectively. Table 7.1 summarizes the thermophysical properties of these materials used to predict the effective thermal properties of the wall k_{eff} and $(\rho c_p)_{eff}$ according to Equations (4.12)

Table 5.1: Density ρ , specific heat capacity c_p , and thermal conductivity k of PCM, high density polyethylene (HDPE), and concrete.

		ρ	c_p	k	
Material	Subscript	(kg/m ³)	(J/kg·K)	(W/m·K)	Ref.
PCM	c	860	2590	0.21	[111]
HDPE	s	930	2250	0.49	[112]
Concrete	m	2300	880	1.4	[113]

and (4.10). The shell volume fraction ϕ_s was kept constant and equal to 0.08. The phase change temperature window ΔT_{pc} and the latent heat of fusion h_{sf} of the PCM were taken to be 3°C and 180 kJ/kg, respectively. The resulting effective thermal conductivity k_{eff} decreased and the effective volumetric heat capacity $\rho c_p(T)_{eff}$ increased nearly linearly with PCM volume fraction ϕ_c increasing from 0.0 to 0.5. Thus, both the thermal resistance and the sensible heat storage capacity of the composite wall increased with the addition of PCM. The phase change temperature T_{pc} of the PCM was treated as a parameter varying between 10 and 25°C.

The indoor heat transfer coefficient h_i was taken to be 8 W/m²·K. This value was consistent with experimental measurements for mixed forced and natural convections on a vertical wall reported by Awbi and Hatton [115]. The outdoor heat transfer coefficient h_o was taken as 20 W/m²·K, based on previous numerical simulations of walls exposed to outdoor weather conditions [116, 117]. The total hemispherical solar absorptivity α_s and emissivity ϵ of the outer wall surface were taken as 0.26 and 0.9, respectively corresponding to typical values for white paint [113]. Finally, the average sky temperature T_{sky} was taken as 2°C throughout the year [113].

The outdoor temperature $T_\infty(t)$ and solar irradiation $q_s''(t)$ used in Equation (5.4) were obtained from Climate Consultant software [17] for a typical year in California climate zones 3 (San Francisco) and 9 (Los Angeles) with a 1 hour increment. Figures 5.2a and 5.2b plot the outdoor temperature $T_\infty(t)$ as a function of time over the entire year in San Francisco and in Los Angeles, respectively. The average outdoor temperature is notably lower in San

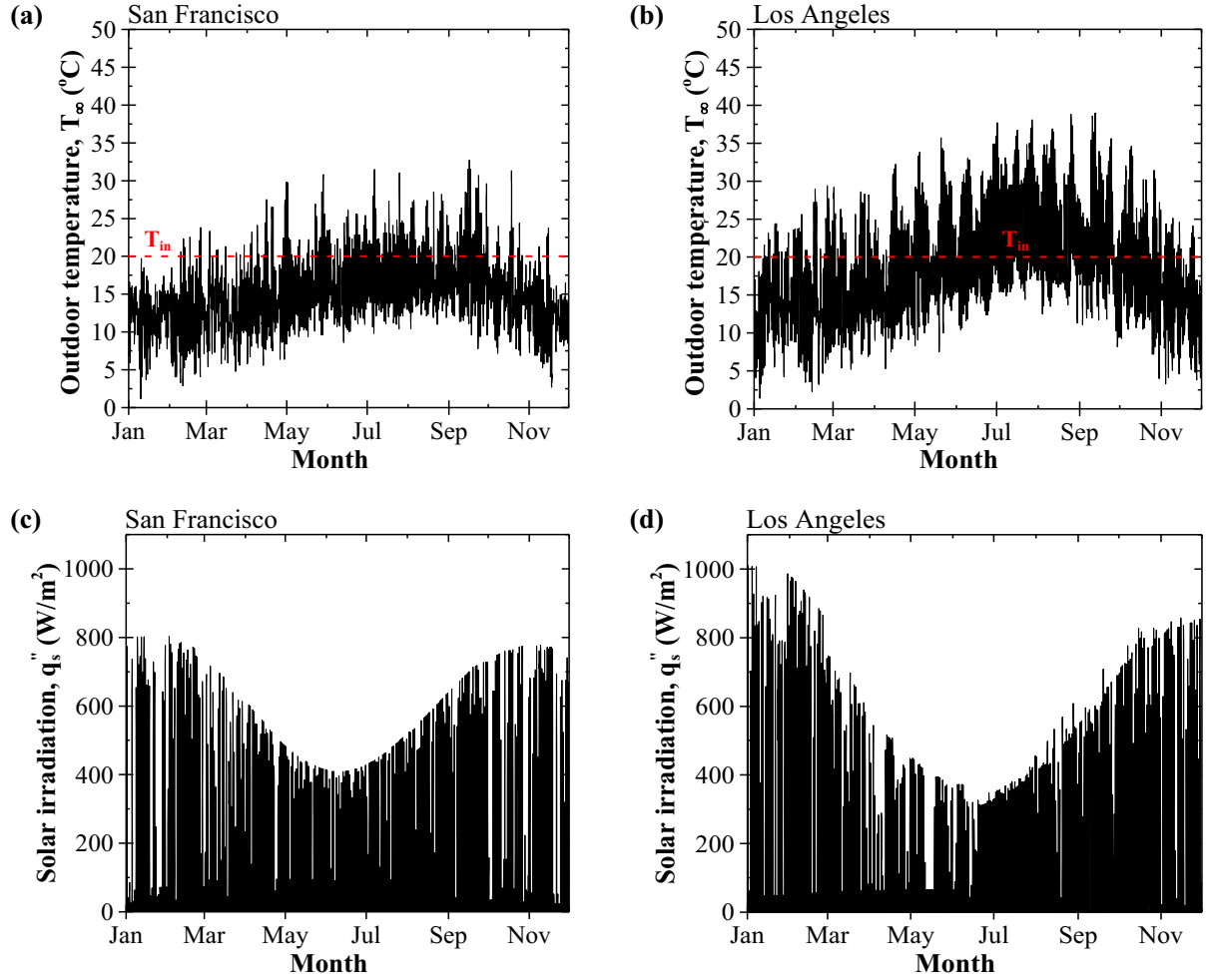


Figure 5.2: (a) and (b) Outdoor temperature T_{∞} and (c) and (d) solar irradiation q_s'' incident upon a South-facing vertical wall as functions of time throughout the year in San Francisco and in Los Angeles, respectively. These data were used as boundary conditions in the present study.

Francisco, particularly during the summer months. Similarly, Figures 5.2c and 5.2d plot the solar irradiation $q_s''(t)$ upon a South-facing vertical wall as a function of time over the entire year in San Francisco and in Los Angeles, respectively.

5.2.5 Data processing

5.2.5.1 Building envelope

An HVAC system was assumed to operate throughout the year in order to maintain the indoor temperature T_{in} constant and equal to 20°C. The seasonal energy efficiency ratio (SEER) is defined as the ratio of the total thermal energy removed from a space (in BTU) by an AC system to the electrical energy consumed over the same time period (in Wh) [122]. On the other hand, the annual fuel utilization efficiency (AFUE) is defined as the ratio of annual heat output by a furnace or boiler to the corresponding fossil fuel energy consumed [122]. In the present study, the current minimum value of SEER of 13 BTU/Wh set by the U.S. Department of Energy was used [122]. The average value of AFUE of 81 for modern furnaces and boilers was also used [122]. These values of SEER and AFUE were necessary in order to relate the cooling and heating loads to the corresponding electricity and gas consumption and to determine the associated costs.

5.2.5.2 Energy and cost savings

The relative energy reduction and the cost savings were used to evaluate the performance of microencapsulated PCM-concrete walls compared with that of plain concrete walls. First, the relative energy reduction $E_{r,j}$ for a single wall of orientation j was defined as the relative difference between the total thermal energy $Q_{m,j}$ (in J) transferred through a plain concrete wall (both inward and outward) and that through a PCM-concrete composite wall Q_j , for the same conditions and duration, expressed as,

$$E_{r,j} = \frac{Q_{m,j} - Q_j}{Q_{m,j}}. \quad (5.5)$$

Similarly, the relative energy reduction E_r for an entire home was defined as the relative difference between the total thermal energy Q_m transferred through the walls of a house made of plain concrete and through those made of PCM-concrete composite Q and was expressed as,

$$E_r = \frac{Q_m - Q}{Q_m}. \quad (5.6)$$

The sum of the thermal energy Q_m through all four plain concrete walls and through all four concrete-PCM walls Q was given by,

$$Q_m = \sum_{j=N,S,E,W} Q_{m,j} \quad \text{and} \quad Q = \sum_{j=N,S,E,W} Q_j. \quad (5.7)$$

Here, $Q_{m,j}$ and Q_j were defined as,

$$Q_{m,j} = \int_{t_i}^{t_f} A_j |q''_{L,m,j}(t)| dt \quad \text{and} \quad Q_j = \int_{t_i}^{t_f} A_j |q''_{L,j}(t)| dt \quad (5.8)$$

where t_i and t_f are the initial and final times of interest (e.g., 1 month or 1 year), and A_j is the surface area (in m^2) of the wall of orientation j . The conductive heat fluxes (in W/m^2) at the inner surface located at $x = L$ for a plain concrete wall $q''_{L,m,j}$ and for a PCM-concrete composite wall $q''_{L,j}$ of orientation j were given by Fourier's law as,

$$q''_{L,m,j}(t) = -k_m \frac{\partial T_m}{\partial x}(L, t) \quad \text{and} \quad q''_{L,j}(t) = -k_{eff} \frac{\partial T}{\partial x}(L, t). \quad (5.9)$$

The absolute values of $q''_{L,m,j}$ and $q''_{L,j}$ in Equation (5.8) were considered to account for the fact that there is an energy cost associated with maintaining the indoor temperature at T_{in} , regardless of the direction of the heat flux across the wall.

Finally, the relative heating and cooling energy reductions, denoted by $E_{r,H}$ and $E_{r,C}$, for an entire home were expressed as,

$$E_{r,H} = \frac{Q_{H,m} - Q_H}{Q_{H,m}} \quad \text{and} \quad E_{r,C} = \frac{Q_{C,m} - Q_C}{Q_{C,m}}. \quad (5.10)$$

The total heating load $Q_{H,m}$ (in J) through a house with plain concrete walls or with PCM-concrete composite walls Q_H were defined as,

$$Q_{H,m} = \sum_{j=N,S,E,W} Q_{H,m,j} \quad \text{and} \quad Q_H = \sum_{j=N,S,E,W} Q_{H,j} \quad (5.11)$$

Here $Q_{H,m,j}$ and $Q_{H,j}$ are the heating loads through plain concrete and through PCM-concrete walls with orientation j and were expressed as,

$$\begin{aligned} Q_{H,m,j} &= \int_{t_i}^{t_f} A_j H_H(q''_{L,m,j}) |q''_{L,m,j}(t)| dt \\ \text{and } Q_{H,j} &= \int_{t_i}^{t_f} A_j H_H(q''_{L,j}) |q''_{L,j}(t)| dt \end{aligned} \quad (5.12)$$

where $H_H(q''_L)$ is a Heaviside step function for heating ($q''_L < 0$) given by,

$$H_H(q''_L) = \begin{cases} 1 & \text{if } q''_L \leq 0 \\ 0 & \text{if } q''_L > 0 \end{cases}. \quad (5.13)$$

Lastly, the total cooling load $Q_{C,m}$ (in J) through plain concrete walls and through PCM-concrete composite walls Q_C of the entire home was defined as,

$$Q_{C,m} = \sum_{j=N,S,E,W} Q_{C,m,j} \quad \text{and} \quad Q_C = \sum_{j=N,S,E,W} Q_{C,j} \quad (5.14)$$

where $Q_{C,m,j}$ and $Q_{C,j}$ are the cooling loads through plain concrete and through PCM-concrete walls with orientation j and were expressed as,

$$\begin{aligned} Q_{C,m,j} &= \int_{t_i}^{t_f} A_j H_C(q''_{L,m,j}) |q''_{L,m,j}(t)| dt \\ \text{and } Q_{C,j} &= \int_{t_i}^{t_f} A_j H_C(q''_{L,j}) |q''_{L,j}(t)| dt \end{aligned} \quad (5.15)$$

where $H_C(q''_L)$ is a Heaviside step function for cooling ($q''_L > 0$) given by,

$$H_C(q''_L) = \begin{cases} 0 & \text{if } q''_L \leq 0 \\ 1 & \text{if } q''_L > 0 \end{cases}. \quad (5.16)$$

Finally, in order to determine the heating cost savings, the heating loads $Q_{H,m}$ and Q_H were divided into off-peak and peak loads in the winter denoted by subscripts op and p . Similarly, the cooling loads $Q_{C,m}$ and Q_C were divided into off-peak, partial-peak, and peak loads denoted by subscripts op , pp , and p , in the summer, respectively. These TOU loads were isolated by adjusting t_i and t_f in Equation (5.15) according to the summer or winter electricity rate schedules.

The cost savings over a given time period, denoted by S_H , S_C , and S_T , were defined as the differences between the heating, cooling, and total costs (in \$) $C_{H,m}$, $C_{C,m}$, and $C_{T,m}$ when walls are made of plain concrete and C_H , C_C , and C_T when they are made of PCM-concrete composite. They were expressed as,

$$S_T = S_H + S_C, \quad \text{where} \quad S_H = C_{H,m} - C_H \quad \text{and} \quad S_C = C_{C,m} - C_C. \quad (5.17)$$

Here, the heating and cooling costs C_H and C_C were given by,

$$\begin{aligned} C_H &= \frac{1}{AFUE} Q_H R_G \\ \text{and} \quad C_C &= \frac{1}{D \cdot SEER} \left[(Q_C R_E)_{op} + (Q_C R_E)_{pp} + (Q_C R_E)_p \right] \end{aligned} \quad (5.18)$$

where $D = 1.055 \times 10^6$ J·Wh/BTU·kWh is a unit-conversion constant, R_G is the gas cost used for heating (in \$/J), and R_E is the electricity rate used for cooling (in \$/kWh). Additionally, the cost savings through an individual wall with orientation j per unit wall area was given by $s_{T,j} = S_{T,j}/A_j$. Equations (5.17) through (5.18) were applied both on a monthly and on an annual basis as well as both for individual walls and for the entire home.

5.2.6 Method of solution

The governing Equation (5.1) along with the initial and boundary conditions given by Equations (5.2) to (5.4) were solved using finite element methods on unstructured grids. To account for the uncertainty in the initial conditions throughout the wall, the simulation time period was extended two days before January 1st. Extending the simulation period by an additional day resulted in less than 1% relative difference in temperature and heat flux predictions on January 1st. Numerical convergence was considered to be reached when the maximum relative difference in the predicted inner wall surface heat flux $q_L''(x, t)$ was less than 1% when reducing the mesh size or time step by a factor of 2. In practice, converged solutions were obtained by imposing a time step of 400 s and minimum mesh size and maximum growth rate to be 500 μm and 1.35, respectively. The number of finite elements needed to obtain a converged solution was 3233.

5.3 Results and discussion

5.3.1 Inner surface heat flux

Figure 5.3 plots the inner surface heat flux $q_L''(t)$ as a function of time over one year for a South-facing wall located either in San Francisco (left) or in Los Angeles (right) with thermal properties corresponding to a plain concrete wall or to a concrete wall containing microencapsulated PCM with a volume fraction ϕ_c ranging from 0.1 to 0.5. The phase change temperature T_{pc} was taken to be equal to the desired indoor temperature $T_{in} = 20^\circ\text{C}$. Figure 5.3 shows that adding microencapsulated PCM to the concrete wall decreased the amplitude of the inner surface heat flux $q_L''(t)$ throughout the year. The amplitude of the positive heat flux q_L'' into the building requiring cooling was reduced substantially more than that of the heat flux out of the building (i.e. $q_L'' < 0$), requiring heating. Furthermore, the total thermal load was reduced much more during summer months when the temperature oscillations were centered closer to the desired indoor temperature T_{in} . This can be attributed to the fact that q_L'' was nearly unidirectional during the heating season (winter) in both cities but not during the cooling season (summer), as previously discussed. These results support recent findings that the energy reduction potential decreased as the difference between the time-averaged outdoor temperature and the desired indoor temperature T_{in} increased, such as in extremely hot or cold climates [35, 110].

Figures 5.4a through 5.4d plot the inner surface heat flux $q_L''(t)$ and the corresponding electricity rate $R_E(t)$ as functions of time over the course of one day for South-facing concrete walls located either in San Francisco or in Los Angeles on January 31st and on July 12th. The shaded areas below and above the line $q_L'' = 0 \text{ W/m}^2$ respectively represent the daily heating Q_H and cooling loads Q_C required to maintain a constant indoor temperature T_{in} . The figures illustrate a general trend that buildings in Los Angeles require more cooling than those in San Francisco, due to the warmer climate (Figure 5.2). They also show that the electricity providers in both cities divide the day into two and three pricing periods during the winter and summer, respectively. Summer pricing is applied from May to October in San Francisco and from June to September in Los Angeles. Moreover, the ratio of peak to

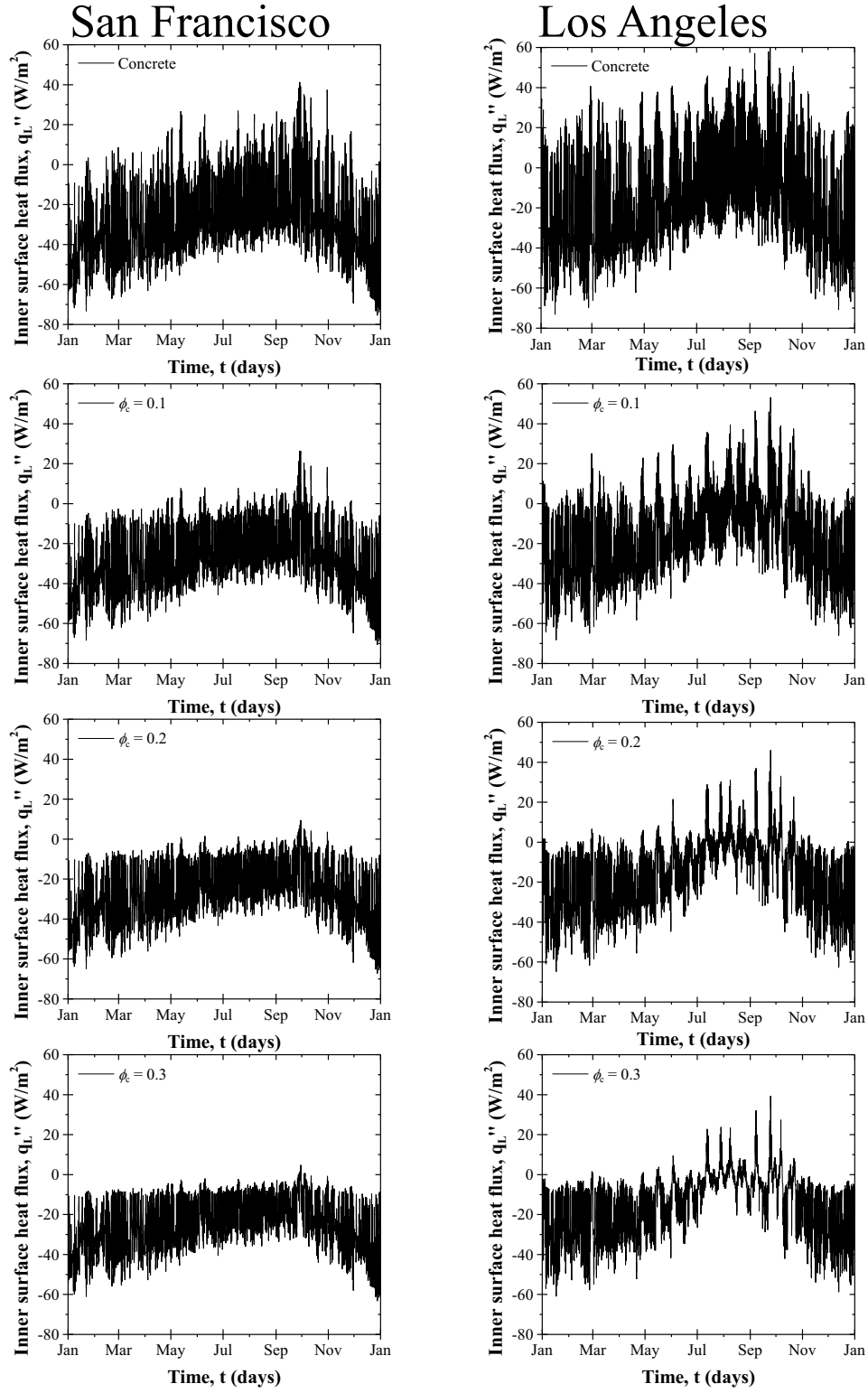


Figure 5.3: Inner surface heat flux $q_L''(t)$ as a function of time for a South-facing wall over one year in San Francisco or in Los Angeles for a plain concrete wall or for a microencapsulated PCM-concrete wall with ϕ_c ranging from 0.1 to 0.5.

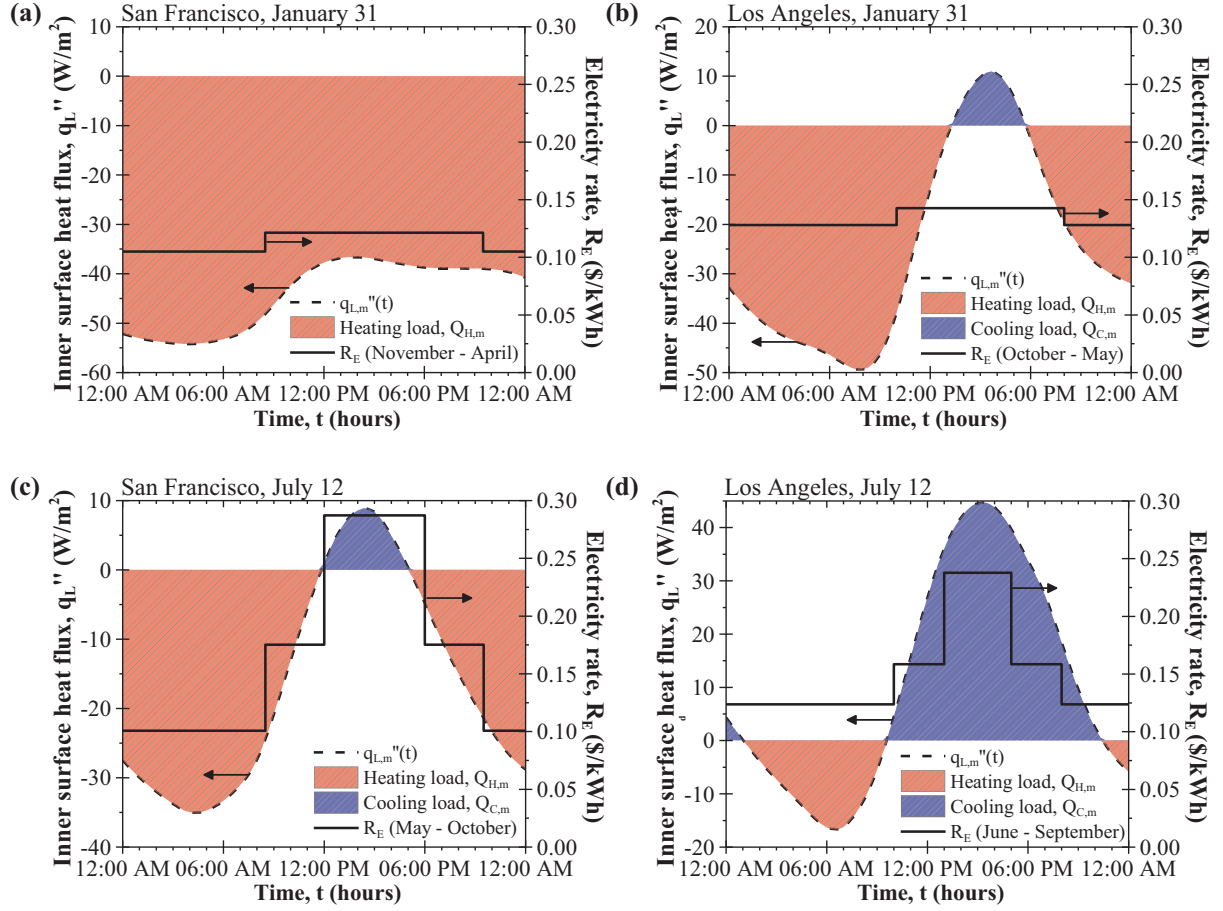


Figure 5.4: Inner surface heat flux $q_L''(t)$ as a function of time for a South-facing wall and the associated TOU electricity rate schedule on January 31 (winter) in (a) San Francisco and in (b) Los Angeles and on July 12 (summer) in (c) San Francisco and in (d) Los Angeles. The heating and cooling loads Q_H and Q_C are illustrated by the shaded area enclosed by the heat flux curve below and above $q_L'' = 0$ W/m², respectively.

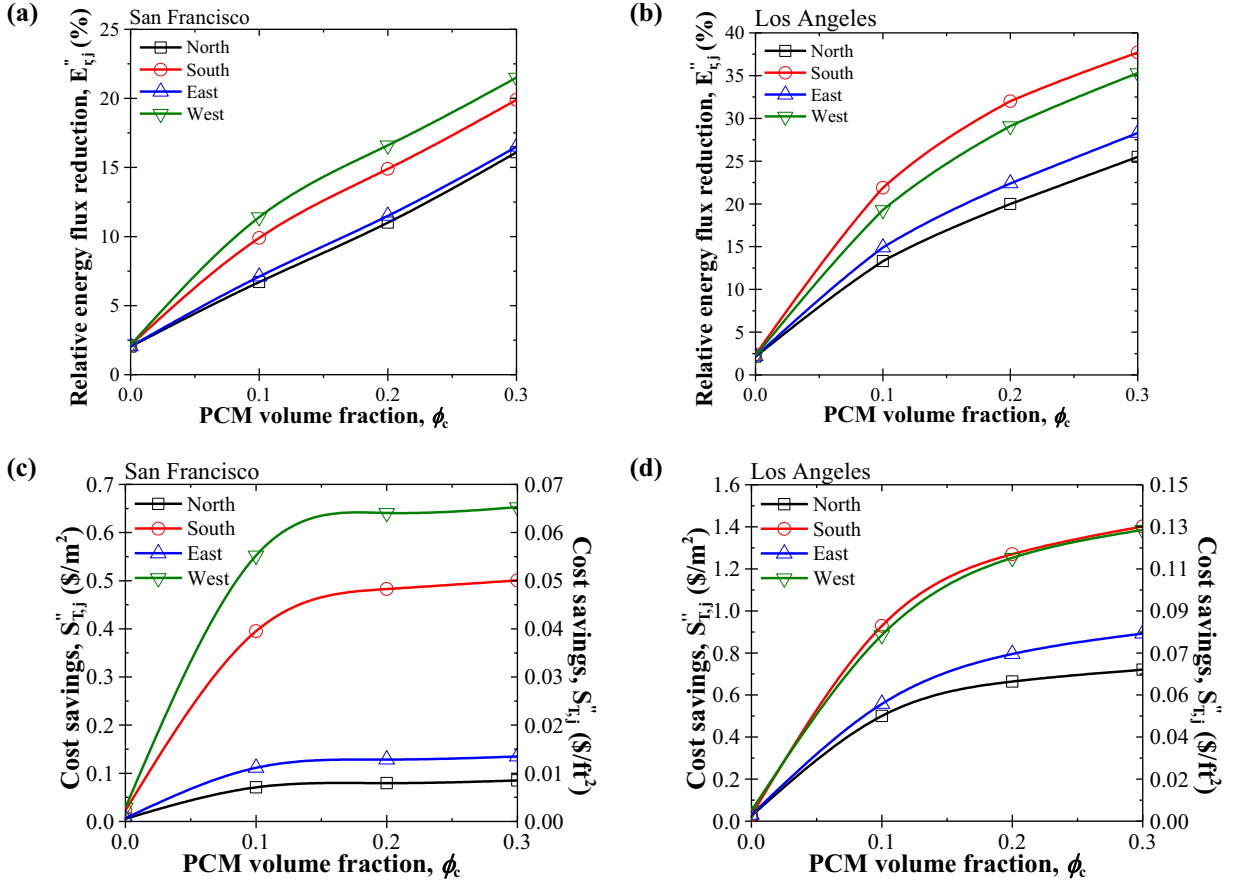


Figure 5.5: Relative energy reduction E_r for North-, South-, East-, and West-facing walls (a) in San Francisco and (b) in Los Angeles, and corresponding cost savings per unit wall surface area $s_{T,j}$ (c) in San Francisco and (d) in Los Angeles, as functions of PCM volume fraction ϕ_c ranging from 0 to 0.3.

off-peak electricity rates and the length of the peak period are larger in San Francisco than in Los Angeles. Figure 5.4a shows the situation of unidirectional heat flux (heat loss) in San Francisco on January 31st. In this case, the energy savings was independent of phase change, as previously discussed.

5.3.2 Effect of wall orientation

Figures 5.5a and 5.5b plot the annual relative energy reduction $E_{r,j}$ achieved for the North-, South-, East-, and West-facing PCM-concrete composite walls as a function of PCM volume fraction ϕ_c ranging from 0 to 0.3 in San Francisco and in Los Angeles, respectively. Here also, the phase change temperature T_{pc} was taken to be equal to the desired indoor temperature

T_{in} of 20°C. First, it is evident that for every wall orientation, the annual energy reduction $E_{r,j}$ increased with increasing PCM volume fraction ϕ_c . It was the largest for the West- and South-facing walls in both San Francisco and Los Angeles, reaching up to about 22 and 38%, respectively. In fact, the energy reduction was significantly smaller for the East- and North-facing walls than for the West- and South-facing walls. This can be attributed to the fact that the solar irradiation $q_s''(t)$ on the South- and West-facing walls resulted in oscillations in the inner wall surface temperature $T_L(t)$ centered closer to T_{in} than those at the East- and South-facing walls.

Figures 5.5c and 5.5d plot the annual cost savings per unit surface area $s_{T,j}$ of PCM-concrete composite wall (in \$/m² and in \$/ft²) with different orientations corresponding to the energy savings presented in Figures 5.5a and 5.5b and accounting for TOU pricing practiced by PG&E (San Francisco) and by LADWP (Los Angeles). The annual cost savings per unit wall surface area $s_{T,j}$ increased with increasing PCM volume fraction ϕ_c . It approached a plateau as ϕ_c increased above 15% in San Francisco for all four orientations considered. Additionally, it ranged from about \$0.07 to \$0.65/m² in San Francisco and from about \$0.5 to \$1.4/m² in Los Angeles. Here also, the West- and South-facing walls featured the largest cost savings $s_{T,j}$ in both climates. However, $s_{T,j}$ was nearly equivalent for the West- and South-facing walls in Los Angeles, while it was larger by 30% for the West-facing wall than for the South-facing wall in San Francisco. Furthermore, in both cities, $s_{T,j}$ for the North- and East-facing walls was significantly smaller than for the West- and South-facing walls.

Overall, Figures 5.5a through 5.5d establish that the wall orientation had a substantial impact on the energy and cost savings associated with microencapsulated PCM-concrete walls in both San Francisco and Los Angeles. They also suggest that it may be more energy- and cost-effective to add microencapsulated PCM only to the West- and South-facing walls of a building envelope. Finally, adding PCM beyond ϕ_c of 0.1-0.2 in San Francisco did not make sense from a cost saving point of view although it was beneficial from an energy saving standpoint. Indeed, adding 0.1-0.2 vol.% microencapsulated PCM to the concrete walls time-shifted the maximum inner wall surface heat flux $q_L''(t)$ to a partial- or off-peak time of day with a cheaper electricity rate. Beyond this point, further increasing the time-

shift by adding microencapsulated PCM resulted in less additional cost savings because the maximum energy consumption already occurred during the cheapest electricity rate period. This effect was much more pronounced in San Francisco since the ratio of peak to off-peak electricity rates was much larger than in Los Angeles (Figure 5.4).

5.3.3 Effect of phase change temperature

Figures 5.6a and 5.6b respectively plot the relative energy reduction E_r and the cost savings S_T for each month of the year in San Francisco achieved by adding 10 vol.% of PCM ($\phi_c = 0.1$) to all four exterior walls of the typical single family home considered. Five different values of phase change temperature T_{pc} were considered, namely, 10, 19, 20, 21, and 25°C. Here also, the phase change temperature window and latent heat of fusion were taken as 3°C and 180 kJ/kg, respectively. The results indicate both E_r and S_T were maximized for $T_{pc} = 19^\circ\text{C}$. The monthly energy reduction ranged from about 6 to 17% throughout the year. However, the cost savings was very small, ranging from \$0.1/month in the winter to \$9/month in September. In fact, E_r and S_T were the smallest and were nearly independent of T_{pc} between November and March. This can be attributed to the fact that the inner wall surface heat flux was unidirectional ($q_L''(t) < 0$) for most of this period, as previously discussed (Figure 5.3). Throughout the year, E_r and S_T were almost equivalent and equal to 6% for $T_{pc} = 10$ and 25°C. This can be explained by the fact that the PCM remained liquid or solid on most days since the outdoor temperature typically remained above 10°C and below 25°C (Figure 5.2a), respectively. The 6% energy reduction corresponding to T_{pc} of 10 and 25°C can be attributed to the thermal insulating effects of adding the microencapsulated PCM, i.e., $k_{eff} < k_m$.

Similarly, Figures 5.6c and 5.6d respectively plot E_r and S_T for the same typical home in Los Angeles, for each month of the year, for $\phi_c = 0.1$ and for T_{pc} ranging from 10 to 25°C. They show that E_r and S_T reached a maximum in the summer months when the phase change temperature T_{pc} was equal to the desired indoor temperature T_{in} of 20°C. However, both E_r and S_T were slightly larger for $T_{pc} = 19^\circ\text{C}$ during the rest of the year. For

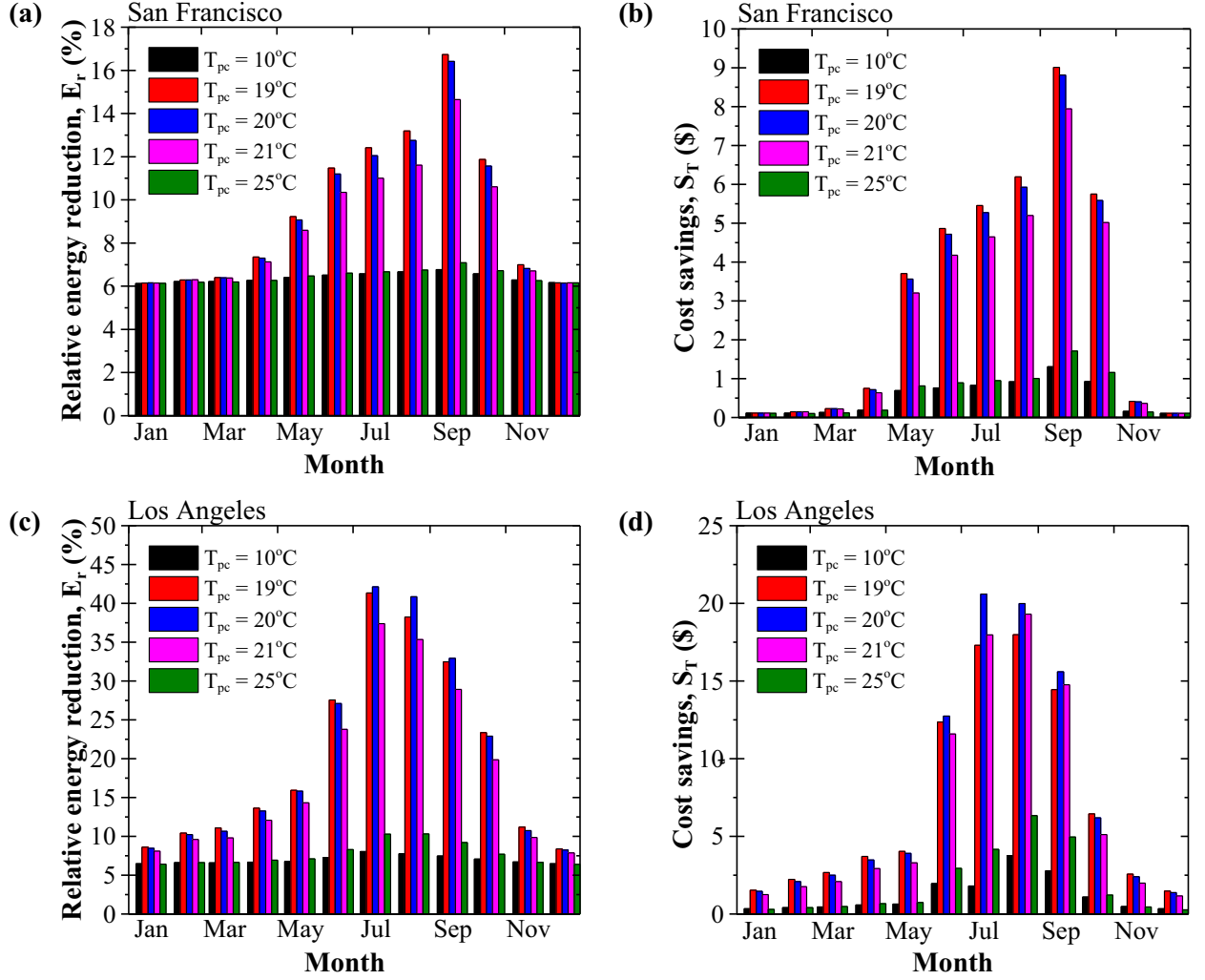


Figure 5.6: (a) Relative energy reduction E_r and (b) cost savings S_T in San Francisco and (c) E_r and (d) S_T in Los Angeles for each month of the year for an average single family home. The PCM volume fraction in all four exterior walls ϕ_c was taken to be 0.1 and the phase change temperature T_{pc} ranged from 10 to 25°C.

$T_{pc} = 20^\circ\text{C}$, the relative energy reduction E_r ranged from 6 to 42% while the cost savings S_T varied from \$0.3 to \$21/month throughout the year.

Here also, E_r and S_T had similar values and were much smaller between October and May for $T_{pc} = 10$ and 25°C . Then, the PCM did not completely change phase on most days and only the smaller thermal insulating effects of the PCM microcapsules had an effect on the thermal load. Finally, the monthly cost savings was generally much larger in Los Angeles than in San Francisco, it remained relatively small, even in September when the energy savings reached 42%. Overall, the cost saving potential was limited by the cost of heating and cooling the home under consideration.

5.3.4 Effect of season

Figures 5.6a and 5.6c show that E_r was the largest during the summer months (June through September). This was due to the fact that the monthly time-averaged outdoor temperature $\bar{T}_\infty(t)$ in the summer months was 17°C in San Francisco and 22°C in Los Angeles. It was the closest to the desired indoor temperature $T_{in} = 20^\circ\text{C}$ during these months.

Figures 5.6b and 5.6d indicate that the cost savings S_T reached a maximum during the summer months and was small in the winter months. In fact, the monthly cost savings in San Francisco was much smaller than in Los Angeles throughout the year and was negligible between November and April. This was due to the fact that cooling was achieved by consuming electricity for which the cost was based on summer TOU schedules featuring a large ratio of peak to off-peak electricity rates. By contrast, during the winter months, the heating load reduction was very small. Additionally, gas was inexpensive and sold based on a flat rate thus resulting in small cost savings.

Figures 5.7a and 5.7b respectively compare E_r and S_T between San Francisco and Los Angeles for each month of the year for a PCM volume fraction $\phi_c = 0.3$. Here, T_{pc} was equal to 19 and 20°C in San Francisco and in Los Angeles, respectively. E_r reached up to 28% and 70% and S_T reached up to \$11.00 and \$32.00/month in San Francisco and in Los Angeles, respectively. The increase in E_r and in S_T with increasing ϕ_c was much less pronounced in

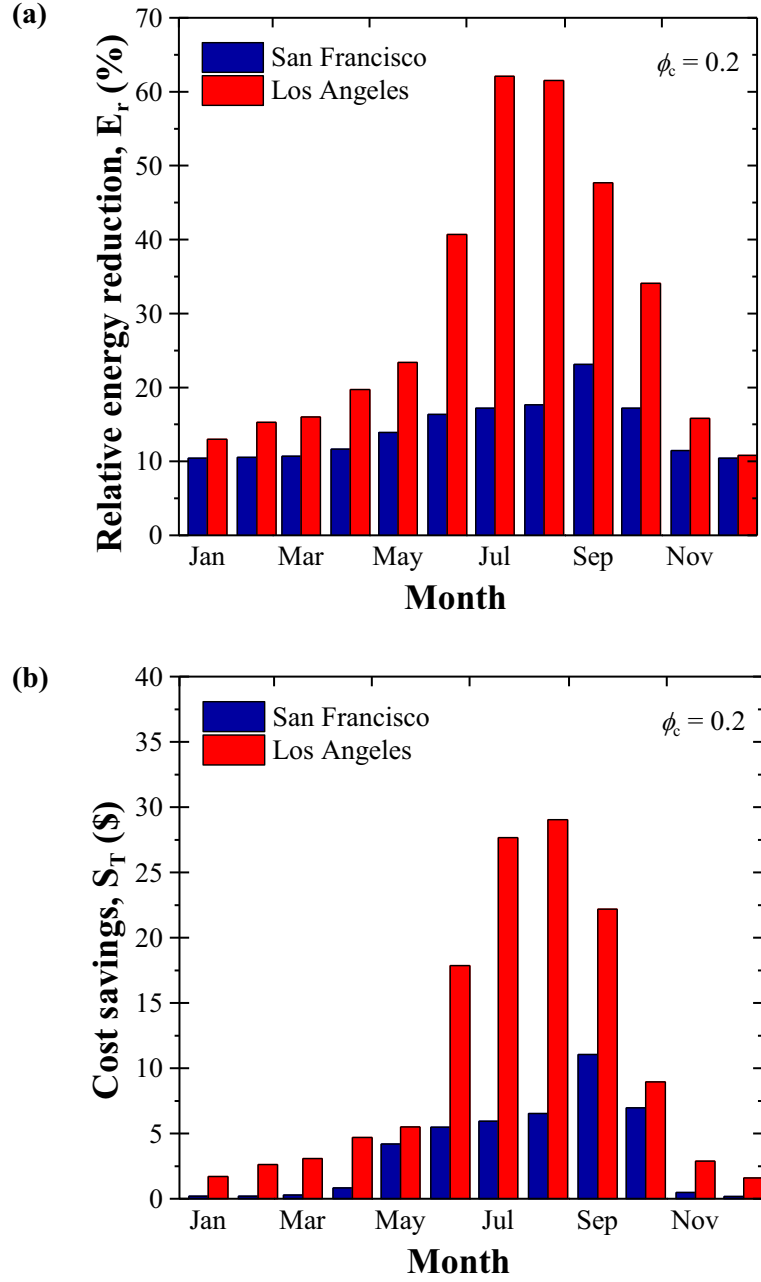


Figure 5.7: Comparison of (a) the relative energy reduction E_r and (b) the cost savings S_T between San Francisco and Los Angeles for each month of the year for an average single family home. Here, the PCM volume fraction ϕ_c was 0.2, the phase change temperature T_{pc} was taken to be 19°C in San Francisco and 20°C in Los Angeles.

San Francisco than in Los Angeles. The monthly cost savings remained very small during the winter months in both cities.

5.3.5 Annual energy and cost savings

Table 5.2 shows the annual relative energy reduction for heating $E_{r,H}$, cooling $E_{r,C}$, and total E_r thermal loads on a typical single family home in San Francisco, Los Angeles, and Phoenix. A PCM volume fraction ϕ_c equal to 0.1, 0.2, and 0.3 was included either within all four walls of the home or strictly within the South- and West-facing walls as designated by “(PCM: S,W).” The annual cooling load was reduced by 98% in San Francisco for ϕ_c exceeding 0.2 and the reduction in the annual heating load was comparatively small. The total annual relative energy reduction ranged from 9 to 18% in San Francisco and from 17 to 32% in Los Angeles as ϕ_c increased from 0.1 to 0.3. It is interesting to note that the annual energy reduction $E_r = 11.6\%$ in Phoenix, an extremely hot climate, fell in between those in San Francisco and Los Angeles for $\phi_c = 0.1$. Furthermore, the heating, cooling, and total thermal load reductions in Phoenix were small and nearly identical for a given PCM volume fraction. These results suggest that the comparative potential of a PCM-composite wall to reduce the heating or cooling loads individually depends on the climate. Overall, the best climate for energetic performance of PCM-composite walls is one in which the daily average outdoor temperature remains relatively close to the desired indoor temperature throughout the year, as in Los Angeles. Then, the heat flux from the outside to the inside is bi-directional and thus the PCM will melt during the day and solidify at night. The total relative energy reduction E_r achieved by adding PCM strictly to the South- and West-facing walls of the home was significant but was much smaller than that achieved by including PCM within all four walls.

Table 5.2 also shows the annual cost savings S_T associated with the reduction in the heating, cooling, and total thermal loads in San Francisco and in Los Angeles for ϕ_c ranging from 0.1 to 0.3. In both cities, the annual cost savings consisted almost entirely of cooling cost savings in the form of electricity savings. Overall the total annual cost savings S_T ranged

Table 5.2: Annual heating, cooling, and total relative energy reduction E_r and total cost savings S_T for an average single family home in San Francisco and in Los Angeles for different PCM volume fractions. Here, $\Delta T_{pc} = 3^\circ\text{C}$, $h_{sf} = 180 \text{ kJ/kg}$, and $T_{pc} = 19$ and 20°C for San Francisco and Los Angeles, respectively.

	$\phi_c = 0.1$	$\phi_c = 0.2$	$\phi_c = 0.3$
Annual relative energy reduction (%)			
San Francisco			
$E_{r,H}$	7.5	12	17
$E_{r,C}$	85.1	98.3	99.6
E_r	8.8	13.4	18.3
E_r (PCM: S,W)	5.1	7.5	9.8
Los Angeles			
$E_{r,H}$	12.5	19.4	24.8
$E_{r,C}$	52.5	73.1	81.5
E_r	17.3	25.8	31.6
E_r (PCM: S,W)	10.3	15.2	18.1
Phoenix			
$E_{r,H}$	11.1	-	-
$E_{r,C}$	12.2	-	-
E_r	11.6	-	-
Annual cost savings (\$)			
San Francisco (annual electricity cost \$840)			
S_H	\$1	\$2	\$2
S_C	\$36	\$41	\$42
S_T	\$37	\$43	\$44
S_T (PCM: S,W)	\$31	\$36	\$37
Los Angeles (annual electricity cost \$600)			
S_H	\$1	\$1	\$1
S_C	\$94	\$130	\$143
S_T	\$95	\$131	\$145
S_T (PCM: S,W)	\$60	\$83	\$91

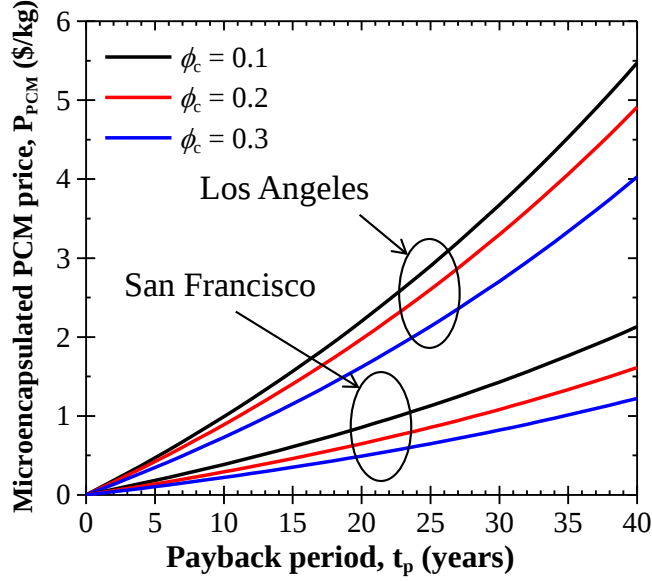


Figure 5.8: Price of microencapsulated PCM (in \$/kg) as a function of payback period (in years) for a concrete wall with a PCM volume fraction ϕ_c of 0.1, 0.2, 0.3 and located in Los Angeles or San Francisco.

from \$37-\$44 in San Francisco and from \$95 to \$145 in Los Angeles as ϕ_c increased from 0.1 to 0.3. Between 1990 and 2005, the average annual electricity cost over all residential customers in San Francisco and in Los Angeles was about \$840 and \$600, respectively [123]. Thus, the annual cost savings incurred by adding 20 vol.% microencapsulated PCM to concrete walls represented about 5 and 22% of the annual electricity expenditures in San Francisco and Los Angeles, respectively. Interestingly, the total annual cost savings S_T achieved by including PCM only within the South- and West-facing PCM-composite walls was only slightly smaller than that for four PCM-composite walls in San Francisco. This can be attributed to the very small annual cost savings for the North- and East-facing walls (Figure 5.5). On the other hand, S_T was substantially smaller in Los Angeles when PCM was only included within the South- and West-facing walls than when it was included within all four walls.

5.3.6 Payback period

Figure 5.8 plots the price of microencapsulated PCM (in \$/kg) as a function of payback period t_p (in years) for a concrete wall with a PCM volume fraction ϕ_c of 0.1, 0.2, 0.3 and located in Los Angeles or San Francisco. These results were based on the annual cost savings

associated with adding microencapsulated PCM to all four walls of a typical single-family home located in either Los Angeles or San Francisco, CA as described in Table 5.2. It was assumed that the annual cost savings increased by 2% each year to approximate the effect of inflation on the payback period t_p . Figure 5.8 shows that, for a given price P_{PCM} of microencapsulated PCM, the payback period (i) increased with microencapsulated PCM volume fraction ϕ_{c+s} and (ii) was substantially longer in San Francisco than in Los Angeles. In practice, the payback period will depend on additional factors including: (1) financial incentives such as governmental subsidies, (2) the level and structure of electricity pricing, and (3) the climate within the region of interest. However, Figure 5.8 provides a guideline to estimate the price P_{PCM} of microencapsulated PCM required to achieve a desired payback period.

5.4 Conclusion

This study demonstrated that adding microencapsulated PCM to the exterior concrete walls of an average-sized single family residence can lead to significant annual energy savings both in San Francisco and in Los Angeles. Several important design guidelines for the PCM-composite wall system were obtained.

1. The annual energy reduction and cost savings were dependent on wall orientation, and were the largest for the South- and West-facing walls in the climates considered.
2. The annual energy and cost savings were maximized when the phase change temperature was near the desired indoor temperature.
3. Microencapsulated PCM-concrete walls have the best energetic performance in climates where the outdoor temperature oscillates around the desired indoor temperature.
4. Adding PCMs to the building envelop can reduce significantly the need for cooling in the hotter months in the climates considered.
5. Their effects on heating energy needs and the associated cost were small.

Overall, the annual combined heating and cooling load reduction ranged from 9-18% and from 17-32% in San Francisco and in Los Angeles, respectively, for PCM volume fraction ranging from 0.1 to 0.3. The corresponding electricity cost savings ranged from \$37-\$44 in San Francisco and from \$95-\$145 in Los Angeles. The present study establishes that the location of PCM within the building envelope is an important design choice, particularly from a financial standpoint. Future studies could assess creative design strategies such as incorporating microencapsulated PCM into ceiling or roof assemblies.

CHAPTER 6

Figure of Merit for the Thermal Performance of Cementitious Composites Containing Phase Change Materials

This chapter describes an experimental method, supported by physical modeling, to quantitatively characterize the thermal behavior of PCM-mortar composites. It introduces a novel figure of merit termed the energy indicator capturing the combined effects of microencapsulated PCM on the effective thermal conductivity and on the sensible and latent thermal energy storage of PCM composites. Advantages of this method include (i) specimen geometry commonly used to measure experimentally the mechanical properties of cementitious materials, (ii) straightforward experimental implementation, and (iii) sensitivity to relevant design parameters such as PCM volume fraction and thermal properties.

6.1 Background

6.1.1 Performance metrics of PCM-composite materials

Evola et al. [124] proposed two metrics to quantify the effectiveness of gypsum wallboards containing PCM for improving the thermal comfort of building occupants during summer months. They offered two other metrics to quantify how often and to what extent the PCM latent heat storage was utilized. First, the intensity of thermal discomfort for overheating ITD_{over} (in $^{\circ}\text{C}\cdot\text{h}$) was defined as the time integral, over the room occupancy period, of the difference between the operative room temperature and the upper limit of thermal comfort temperature range. Second, the frequency of thermal comfort FTC was defined as the

percentage of time, within the room occupancy period, during which the operative room temperature fell within the thermal comfort temperature range. Third, the frequency of activation FA was defined as the percentage of time, over an entire day or a given occupancy period, during which the PCM was experiencing phase change. Finally, the PCM energy storage efficiency η_{PCM} was defined as the ratio of the thermal energy stored by the PCM, over one day, to the PCM latent heat of fusion. In order to maximize the thermal comfort within the room, ITD should be minimized and FTC should be maximized. Additionally, FA and η_{PCM} should both be maximized in order to take full advantage of the PCM.

Castell and Farid [125] tested the methodology proposed by Evola et al. [124] using experimental measurements of the air temperature within enclosures made of concrete, brick, or timber walls containing PCM and located in Spain or New Zealand. They proposed two modifications to the metrics proposed by Evola et al. [124]: (i) ITD could include periods when the indoor temperature fell below the thermal comfort temperature range ITD_{under} , such as at night time so that $ITD = ITD_{over} + ITD_{under}$ and (ii) FTC could be evaluated over the entire day rather than only during the occupancy period. With these modifications, Castell and Farid [125] evaluated the thermal comfort of the enclosures over three occupancy profiles: (i) between 9:00 am and 5:00 pm, (ii) between 6:00 pm and 8:00 am, and (iii) over the entire day. For all types of enclosures considered, ITD decreased as PCM was added to the wall and also depended strongly on the occupancy profile. In general, the FTC increased as PCM was added to the wall. Lastly, the FA provided contradictory and misleading indication of PCM performance. Castell and Farid [125] concluded that the ITD was the most relevant indicator suggested by Evola et al. [124] and that it should be evaluated during periods both when the indoor temperature exceeded (ITD_{over}) and when it fell below (ITD_{under}) the thermal comfort temperature range.

Overall, these metrics were useful to assess the thermal comfort within large-scale PCM-building envelopes subjected to realistic operating conditions. However, characterization using these metrics is costly both in terms of time and materials. In fact, they cannot be readily applied to a simple experimental setup to assess the thermal performance of novel PCM-composite materials. As such, there is a need for metrics to compare the attractiveness

of different PCM-composite materials using straightforward experimental tests on relatively small samples. Such performance metrics should be sensitive to relevant design parameters such as the volume fractions and thermal properties of constituent materials, the phase change properties of the PCM, and the sample dimensions.

6.1.2 Numerical modeling of phase change in three-component composites

In Chapter 4, we showed that transient heat transfer through three-component composite materials consisting of ordered monodisperse PCM microcapsules and of either monodisperse or polydisperse PCM microcapsules randomly distributed in a continuous matrix can be accurately described by simulating a homogeneous material with some effective thermal conductivity and heat capacity [34, 35]. The effective thermal conductivity k_{eff} of the three-component composites was predicted by the Felske model [89]. On the other hand, their effective volumetric heat capacity $(\rho c_p)_{eff}(T)$ was estimated based on simple thermodynamic arguments [35]. The effective thermal conductivity and effective volumetric heat capacity depended only on the constituent phase properties and on their volume fractions and were independent of the microcapsule spatial arrangement and polydispersity, as established numerically [34, 35].

Two of the most common methods of simulating phase change are the enthalpy method and heat capacity method [59]. These methods involve solution of the transient heat conduction equation expressed in terms of temperature and either enthalpy or specific heat, respectively [59]. Lamberg et al. [62] concluded that both of these methods provided a “good estimation” of melting and freezing processes and that the heat capacity method agreed more closely with experimental data. According to the heat capacity method for simulating phase change, the specific heat capacity of the PCM $c_{p,c}(T)$ can be defined as a step function in terms of temperature with a rectangular peak of (i) width ΔT_{pc} centered around the phase change temperature denoted by T_{pc} and (ii) enclosed area equal to the PCM latent heat of fusion h_{sf} [35]. Thus, the effective volumetric heat capacity was also

temperature-dependent and expressed as [35],

$$(\rho c_p)_{eff}(T) = \begin{cases} (\rho c_p)_{eff,s} & \text{for } T < T_{pc} - \Delta T_{pc}/2 \\ (\rho c_p)_{eff,s} + \phi_c \frac{\rho_{c,s} h_{sf}}{\Delta T_{pc}} & \text{for } T_{pc} - \Delta T_{pc}/2 \leq T \leq T_{pc} + \Delta T_{pc}/2 \\ (\rho c_p)_{eff,l} & \text{for } T > T_{pc} + \Delta T_{pc}/2 \end{cases} \quad (6.1)$$

Here, T_{pc} , ΔT_{pc} , and h_{sf} represent the phase change temperature, temperature window, and latent heat of fusion, respectively. The effective volumetric heat capacities $(\rho c_p)_{eff,s}$ and $(\rho c_p)_{eff,l}$ of the microencapsulated PCM-concrete wall correspond to situations when the PCM is solid and liquid, respectively. If the PCM is unmelted, then $(\rho c_p)_{eff,s} = \phi_c (\rho c_p)_{c,s} + \phi_s (\rho c_p)_s + (1 - \phi_c - \phi_s) (\rho c_p)_m$ where $(\rho c_p)_{c,s}$ is the volumetric heat capacity of solid PCM. The volumetric heat capacities of the solid and fully melted PCM were assumed to be equal so that $(\rho c_p)_{c,s} = (\rho c_p)_{c,l}$ and $(\rho c_p)_{eff,s} = (\rho c_p)_{eff,l}$. Indeed, the volumetric heat capacity of commercial organic PCM does not differ significantly between the solid and the liquid phases.

Alternatively, the PCM specific heat $c_{p,c}(T)$ can be expressed as a Gaussian function of temperature as,

$$c_{p,c}(T) = c_{p,c,s} + \frac{4h_{sf}}{\sqrt{2\pi}\Delta T_{pc}} e^{-0.5 \left(\frac{4(T - T_{pc})}{\Delta T_{pc}} \right)^2}. \quad (6.2)$$

Note that this representation resembles more closely the typical temperature response of PCMs. Here, the PCM specific heat $c_{p,c}(T)$ reaches its maximum value at the phase change temperature T_{pc} . The area enclosed by Equation (6.2) and the line $c_{p,c} = c_{p,c,s}$ represents the latent heat of fusion h_{sf} . Furthermore, expressing $c_{p,c}(T)$ using Equation (6.2) indicates that 68% and 95% of the latent heat is stored and released within the temperature ranges $T_{pc} \pm \Delta T_{pc}/4$ and $T_{pc} \pm \Delta T_{pc}/2$, respectively. Note that the heat capacity method and the Gaussian approximation are idealized representations of the PCM specific heat. In reality, PCMs exhibit superheating and subcooling during melting and freezing, respectively, delaying phase change and causing hysteresis in $c_{p,c}(T)$. Additionally, commercially available PCMs may contain constituents with different molecular weights, resulting in multiple specific heat peaks in a single heating-cooling cycle [38].

6.2 Materials and Methods

6.2.1 Material synthesis

In the present study, two types of microencapsulated PCM (MPCM24D and MPCM32D, Microtek Laboratories Inc.) were used, featuring melting temperatures around 24°C and 32°C, respectively. Each consisted of a polymeric melamine-formaldehyde (MF) shell surrounding a paraffinous core.

Cementitious composites containing these microencapsulated PCMs were fabricated using a commercially available Type I/II ordinary portland cement (OPC) and deionized (DI) water. Composite specimens were formulated as mortars, wherein the microencapsulated PCM occupied a volume fraction $\phi_{c+s} = \phi_c + \phi_s$ ranging from 0.0 to 0.3 in 0.1 increments. The desired microencapsulated PCM volume fraction ϕ_{c+s} was achieved by measuring and adding the required mass based on the microencapsulated PCM density ρ_{c+s} . The mortars were prepared as described by ASTM C305 [126] at a water to cement ratio $w/c = 0.45$ on a mass basis. To enhance the fluidity of fresh mortars, a commercially available water-reducing admixture (Glenium 7500, BASF Corporation) was added at a dosage ranging from 0-2% of the cement mass. The mortar formulations were allowed to cure in sealed conditions for 7 days prior to thermal cycling to limit the influence of exothermic cement hydration reactions on the measured temperatures. Then, the sealed specimens were exposed to thermal cycles. The thermal properties of cementitious specimens may change as a function of their internal moisture content and temperature. However, since the specimens were cured in sealed conditions, the pores were assumed to be near liquid saturation and remain in that state over the course of the experiment. It should be noted that Kim et al. [127] showed that the thermal conductivity of wet and dry cement paste with a given w/c varied within up to 34%.

6.2.2 Specimens

The PCM-mortar composites previously described were cast into a cylindrical PVC mold with wall thickness of about 2 mm. Figure 6.1 shows a schematic of the cylindrical specimen

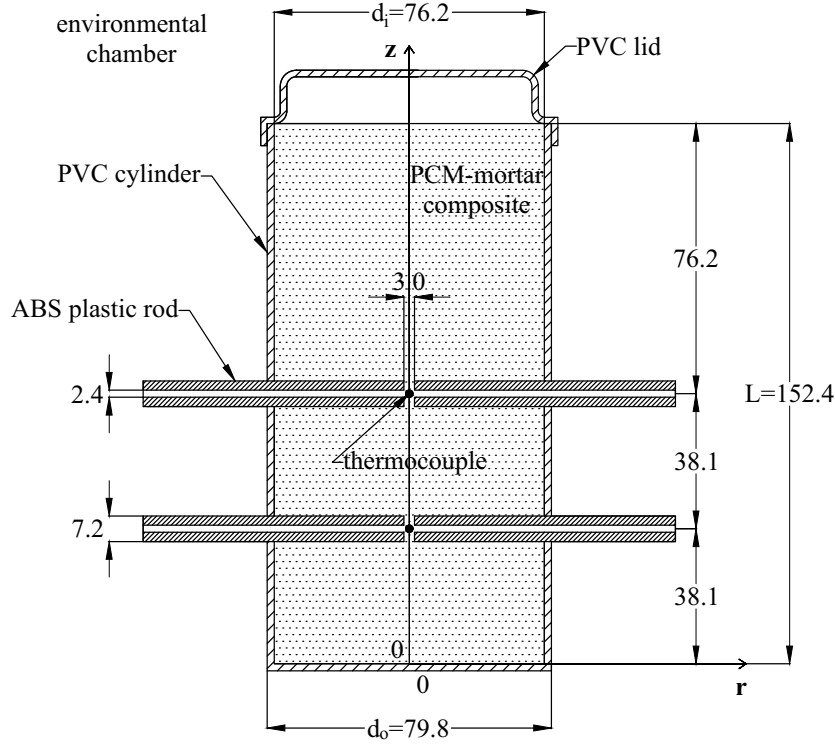


Figure 6.1: Schematic illustration of the dimensions of a PVC cylinder containing a 76.2 x 152.4 mm microencapsulated PCM-mortar composite specimen and detailing the locations of thermocouples and with the coordinate system. All units are in mm.

with height $L = 152.4$ mm and cylindrical mold featuring inner d_i and outer d_o diameters of 76.2 and 79.8 mm, respectively. This geometry was chosen for the ease in (i) casting various cementitious formulations and (ii) imposing one-dimensional (1D) heat transfer along the specimen's radial direction. Thermocouples were embedded along the cylinders' axes at 3.81 and 7.62 cm from the bottom of the cast specimen. These locations were selected to ensure that the temperature measurements would not be influenced by the air gap between the top of the specimen and the lid sealing the container. They were also selected to verify experimentally that 1D radial heat transfer prevailed. The thermocouples were placed by threading them through a hollow acrylonitrile butadiene styrene (ABS) plastic rod oriented perpendicular to the axis of the cylinder prior to pouring the mortar into the mold. To ensure proper thermal contact between the thermocouple element and the cementitious formulation, a 3 mm diameter hole was drilled perpendicular to the axis of the hollow ABS plastic rod, enabling the mortar to intrude into the cavity and surround the thermocouple. The center of

each plastic rod, coinciding with the drilled hole and the thermocouple junction, was located at the axis of the cylindrical mold.

6.2.3 Material characterization

The particle size distribution (PSD) of the microencapsulated PCM was measured using a static light scattering particle analyzer (LS13-320, Beckman Coulter) operating at a wavelength of 750 nm. As PCM microcapsules tend to agglomerate, they were first dispersed into individual particles before characterization. To do so, PCM microcapsules were placed in isopropanol and subjected to vibrations in an ultrasonic bath prior to PSD measurement. As a significant quantity of PCM microcapsules were expected to have small diameters ($D_o < 7.5 \mu\text{m}$), the Lorenz-Mie theory for light scattering by spherical particles was used for analysis. The refractive indices of isopropanol and PCMs at 750 nm were respectively taken as $1.37 + 0.00i$ [128] and $1.53 + 0.00i$ [129].

The density of cement paste samples of the same formulation described in Section 6.2.1 was determined based on volume and mass measurements, compliant with ASTM C138 [130]. The density ρ_{c+s} of each microencapsulated PCM was reported by the manufacturer as 900 kg/m^3 . The phase change properties of the microencapsulated PCMs including phase transition temperatures, heat capacity, and enthalpy of phase change were determined by differential scanning calorimetry (DSC 8500, Perkin Elmer) using the dynamic method. Test samples of approximately 5 mg of microencapsulated PCM contained in aluminum pans were subjected to a temperature cycle ranging from -45 to 45°C for MCPM24D and -40 to 60°C for MPCM32D at temperature ramp rates between 1 and 10°C/min . The DSC was calibrated in terms of its temperature and heat flow measurements using zinc and indium as calibration standards. The heat capacity of the PCM was measured using a three-curve method compliant with ASTM E1269 [131] wherein sapphire was used as the heat capacity reference [132].

The measured core-shell specific heat capacity $c_{p,c+s}(T)$ was used to define the core-shell

volumetric heat capacity as

$$(\rho c_p)_{c+s}(T) = \phi_{c/s}(\rho c_p)_c(T) + (1 - \phi_{c/s})(\rho c_p)_s \quad (6.3)$$

where the volume fraction of core with respect to shell material is defined as $\phi_{c/s} = \phi_c/(\phi_c + \phi_s)$. It was taken as 0.15, based on manufacturer specification.

6.2.4 Experimental apparatus

The PCM-mortar composite specimens synthesized according to the protocol previously described were placed in a freeze-thaw chamber (TH024, Darwin Chambers Company). Temperature evolution within specimens subjected to an ambient temperature $T_\infty(t)$ was measured using solid 24 gauge Type T (copper-constantan) thermocouple wires in FEP insulation. These thermocouples were connected to 16-channel input modules (NI 9213, National Instruments) in a CompactDAQ chassis (cDAQ-9178, National Instruments). Each input module provided built-in cold-junction compensation. Data acquisition was facilitated by a PC running LabVIEW 2014. Thermocouple calibration was performed using a refrigerating/heating circulating water bath (AD28R-30-A11B, PolyScience). Each thermocouple junction was allowed to equilibrate in the water bath for 30 minutes at 5°C intervals within the range 4-60°C and the voltage was measured in 60 s intervals. Temperature was plotted as a linear function of voltage for each thermocouple.

6.2.5 Experimental procedure

After the specimens were cured for seven days, they were placed within a freeze-thaw chamber and subjected to a temperature profile consisting of three cycles over a temperature range of 5 - 45°C. This range was selected based on the DSC results (Figure 6.4) such that the PCM experienced nearly complete melting/solidification during each cycle. The applied temperature ramp rate was successively 20, 5, and 2°C/h over three consecutive cycles. Isothermal holds were imposed for 6 hours at the minimum and maximum temperatures during each cycle and for 24 hours at $T_\infty = 25^\circ\text{C}$ between cycles to ensure that the specimen reached thermal equilibrium with the chamber before starting a new cycle.

6.2.6 Experimental uncertainty

The uncertainty in median particle diameter was less than 3.5% based on three replicate measurements. The uncertainty in the microencapsulated PCM volume fraction ϕ_{c+s} was estimated to be less than 0.13% based on the precision of the balance used in the mass measurements. The temperature of the environmental chamber was controlled within $\pm 0.2^\circ\text{C}$, based on manufacturer specification. Throughout the chamber, temperature was expected to vary by no more than 1°C . On completion of the thermocouple calibration procedure, the maximum uncertainty in the measured temperatures was on the order of $\pm 1^\circ\text{C}$. The uncertainty in the axial and radial locations of the thermocouples were on the order of ± 1.5 mm.

6.3 Analysis

6.3.1 Schematic and assumptions

Figure 6.2 illustrates the two-dimensional (2D) domain numerically simulated. By virtue of symmetry, it corresponds to a quarter of the cylindrical PVC mold used experimentally to synthesize microencapsulated PCM-mortar composite and shown in Figure 6.1.

To make the problem mathematically tractable, the following assumptions were made: (1) The PCM-mortar composite behaved as a homogeneous and isotropic medium with some effective thermal conductivity k_{eff} and effective volumetric heat capacity $(\rho c_p)_{eff}$. (2) All thermal properties were constant except for the temperature-dependent specific heat to account for phase change. (3) 2D axysymmetric transient heat conduction prevailed. (4) There was no heat generation in the PCM-mortar composite. (5) Thermal contact resistances between the PVC container and the PCM-mortar composite and between the mortar and the microencapsulated PCM were negligible. (6) The side and bottom of the PVC container were subjected to convective heat transfer with uniform and constant heat transfer coefficient h and time-dependent imposed chamber temperature $T_\infty(t)$.

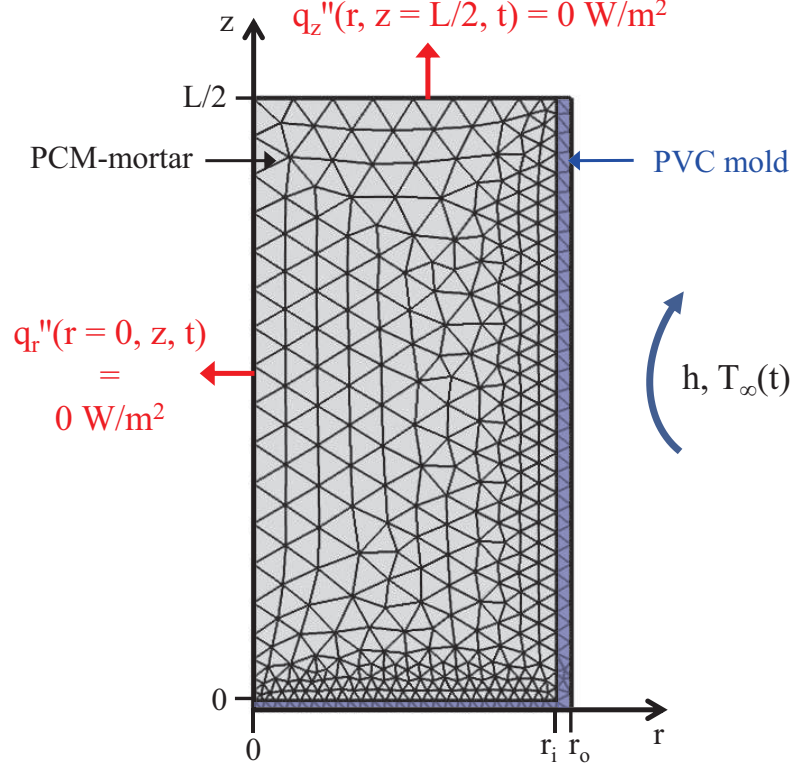


Figure 6.2: Schematic of the numerically simulated two-dimensional heat transfer in a quarter of the cylindrical PVC container of microencapsulated PCM-mortar composite along with the coordinate system and the associated boundary conditions used in numerical simulation.

6.3.2 Governing equations

Under the above assumptions, the local temperatures in the PCM-mortar composite and PVC mold at time t and location $\mathbf{r} = \langle r, z \rangle$, denoted by $T(\mathbf{r}, t)$ and $T_{PVC}(\mathbf{r}, t)$, were governed by the 2D transient heat conduction equation expressed in cylindrical coordinates as [113],

$$\frac{1}{\alpha_{eff}(T)} \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \quad \text{and} \quad (6.4)$$

$$\frac{1}{\alpha_{PVC}} \frac{\partial T_{PVC}}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_{PVC}}{\partial r} \right) + \frac{\partial^2 T_{PVC}}{\partial z^2} \quad (6.5)$$

where $\alpha_{eff}(T) = k_{eff} / (\rho c_p)_{eff}(T)$ and $\alpha_{PVC} = k_{PVC} / (\rho c_p)_{PVC}$ are the effective thermal diffusivity of the PCM-mortar composite and of the PVC mold, respectively. Here, the effective thermal conductivity k_{eff} was determined using the Felske model [89] and the effective volumetric heat capacity $(\rho c_p)_{eff}(T)$ was estimated using basic thermodynamic arguments, as discussed in Section 6.1.2. The effective volumetric heat capacity $(\rho c_p)_{eff}(T)$ was expressed

in terms of microencapsulated PCM volume fraction $\phi_{c+s} = \phi_c + \phi_s$ and core-shell volumetric heat capacity $(\rho c_p)_{c+s}(T)$ given by Equation (6.3). In order to compare numerical predictions with experimental measurements, the measured specific heat $c_{p,c+s}(T)$ of the microencapsulated PCM was used in numerical simulations, including the hysteresis observed during the melting and freezing cycle. For subsequent parametric study, the volumetric heat capacity of the PCM $(\rho c_p)_c(T)$ was defined as a step or as a Gaussian function of temperature given by Equations (6.1) and (6.2), respectively [35].

6.3.3 Initial and boundary conditions

The initial temperature was assumed to be uniform throughout the microencapsulated PCM-mortar composite and the PVC mold and equal to T_i , i.e.,

$$T(r, z, 0) = T_i \quad \text{and} \quad T_{PVC}(r, z, 0) = T_i. \quad (6.6)$$

Convective heat transfer was imposed at the outer ($r = r_o$) and bottom ($z = z_b$) surfaces of the PVC mold with a time-dependent ambient temperature $T_\infty(t)$ such that,

$$\begin{aligned} -k_{PVC} \frac{\partial T_{PVC}}{\partial r}(r_o, z, t) &= h[T_{PVC}(r_o, z, t) - T_\infty(t)] \quad \text{and} \\ -k_{PVC} \frac{\partial T_{PVC}}{\partial z}(r, z_b, t) &= h[T_{PVC}(r, z_b, t) - T_\infty(t)] \end{aligned} \quad (6.7)$$

where h is the convective heat transfer coefficient between the PVC mold and the freeze-thaw chamber.

The heat flux was continuous at the radial ($r = r_i$) and bottom ($z = 0$) PVC/PCM-mortar composite interfaces, i.e.,

$$\begin{aligned} -k_{PVC} \frac{\partial T_{PVC}}{\partial r}(r_i, z, t) &= -k_{eff} \frac{\partial T}{\partial r}(r_i, z, t) \quad \text{and} \\ -k_{PVC} \frac{\partial T_{PVC}}{\partial r}(r, 0, t) &= -k_{eff} \frac{\partial T}{\partial r}(r, 0, t). \end{aligned} \quad (6.8)$$

Finally, by virtue of symmetry, the radial heat flux through the centerline $r = 0$ m and the axial heat flux through the $z = L/2$ plane were zero, i.e.,

$$\frac{\partial T}{\partial r}(0, z, t) = \frac{\partial T_{PVC}}{\partial r}(0, z, t) = \frac{\partial T}{\partial z}(r, L/2, t) = \frac{\partial T_{PVC}}{\partial z}(r, L/2, t) = 0. \quad (6.9)$$

6.3.4 Constitutive relationships

Table 7.1 summarizes the density, thermal conductivity, and specific heat of the mold, PCM, shell, and matrix corresponding to those of PVC, commercial paraffin-based PCM [133], melamine-formaldehyde (MF) [134], and cement paste [135], respectively. The density of

Table 6.1: Density ρ , specific heat capacity c_p , and thermal conductivity k of PCM, melamine-formaldehyde (MF), cement paste, and PVC.

Material	Subscript	ρ (kg/m ³)	c_p (J/kg·K)	k (W/m·K)	Ref.
PCM	c	900	1900	0.21	[38, 133]
MF	s	1500	1670	0.42	[134]
Cement paste	m	1965	1530	1	[135]
PVC	PVC	1420	1000	0.16	[136]

cement paste samples ρ_m with w/c of 0.45 was measured as described in Section 6.2.3 to be 1965 kg/m³. According to the Microtek MPCM24D datasheet [133], the microcapsules contained about 85 mass % of PCM. Then, the densities of the paraffin PCM and of the MF shell (Table 7.1) were used to determine the core and shell volume fractions corresponding to a given core-shell volume fraction ϕ_{c+s} . The effective thermal conductivity k_{eff} and effective volumetric heat capacity $(\rho c_p)_{eff}(T)$ of the PCM-mortar composites both decreased nearly linearly with microencapsulated PCM volume fraction ϕ_{c+s} increasing from 0.0 to 0.3. Thus, the thermal resistance increased and the sensible heat storage capacity decreased slightly with the addition of PCM.

Finally, the experimentally measured temperature was compared to the numerically predicted temperature at the centerpoint of a plain cement paste specimen subjected to heating and cooling cycles with a convective heat transfer coefficient h ranging from 10-30 W/m²·K in 5 W/m²·K increments. The average relative error between the numerically predicted and experimentally measured centerpoint temperature was less than 2.5% for $h = 20$ W/m²·K during both heating and cooling (see Supplementary material). Therefore, h was taken as 20 W/m²·K in simulations of PCM-mortar composites for comparison with experimental

measurements.

6.3.5 Method of solution

The governing Equation (6.4) along with the initial and boundary conditions given by Equations (6.6) to (6.9) were solved using the commercial finite element solver COMSOL Multiphysics 4.3. Numerical convergence was considered to be reached when the maximum relative difference in the centerpoint temperature $T_c(r = 0, z)$ was less than 1% when reducing the mesh size or time step by a factor of 2. In practice, converged solutions were obtained by imposing a time step of 240 s. Figure 6.2 shows the mesh consisting of triangular elements on an unstructured grid. The minimum mesh element edge size and maximum growth rate for converged solutions were $23.1 \mu\text{m}$ and 1.3, respectively. The number of finite elements needed to obtain a converged solution was 876.

6.3.6 Data processing

The temporal evolution of the temperature at the centerpoint $(0, L/2)$ of the PCM-mortar composite $T_{c,comp}(t) = T(0, L/2, t)$ and within the plain cement paste $T_{c,m}(t) = T(0, L/2, t)$ were compared during a given melting and freezing cycle. They were nearly identical when the PCM was entirely solid or liquid. However, they expectedly diverged when the PCM was undergoing phase transition. The energy indicator EI (in $^{\circ}\text{C}\cdot\text{h}$) was defined as a metric to quantify the thermal performance of microencapsulated PCM-mortar compared with plain cement paste and was expressed as,

$$EI = \int_{t_i}^{t_f} |T_{c,comp}(t) - T_{c,m}(t)| dt. \quad (6.10)$$

where the times t_i and t_f were defined as the earliest points where $T_{c,comp}(t)$ and $T_{c,m}(t)$ differed by more (for t_i) or less (for t_f) than a small arbitrary value, taken as 0.15°C , at the beginning or end of a phase change process, respectively. The energy indicator EI is graphically represented by the area enclosed by the temperature curves $T_{c,comp}(t)$ of PCM-mortar and $T_{c,m}(t)$ of plain cement paste specimens during phase change.

The criteria for t_i and t_f were selected for two reasons: (i) to integrate only over the times corresponding to phase change, since there is no effect of latent heat storage outside of this time period and (ii) to have a reference time from where integration could be applied. Criteria for integration bounds were varied between 0.1 and 0.5°C to determine the smallest suitable bounds within which $T_{c,comp}(t)$ and $T_{c,m}(t)$ converged. When the criteria was too small, many $T_{c,comp}(t)$ and $T_{c,m}(t)$ curves did not converge due to noise in the thermocouple signal and systematic experimental uncertainty and EI could not be determined. On the other hand, large criteria led to significant underestimation of EI , particularly at slower temperature ramp rates. Therefore, a balance must be struck when selecting criteria used to define t_i and t_f for determining EI .

6.3.7 Validation

In order to verify that the centerpoint temperature was independent of the thermal effects of the ends of the specimen, the experimentally measured temperature at 3.81 and 7.62 cm from the bottom of the cement paste specimens without and with microencapsulated PCM was compared. The measured temperature at the two locations agreed within experimental uncertainty for most of the test period. It differed by more than 2°C only in some cases and during periods when the PCM was undergoing phase change and never for more than a 1 h duration. The temperature difference during phase change was greater in specimens containing larger microencapsulated PCM volume fractions ϕ_{c+s} and when they were subjected to faster heating and cooling ramp rates. The numerically predicted temperature at 3.81 and 7.62 cm from the bottom of cement paste specimens without and with microencapsulated PCM was nearly identical at all times.

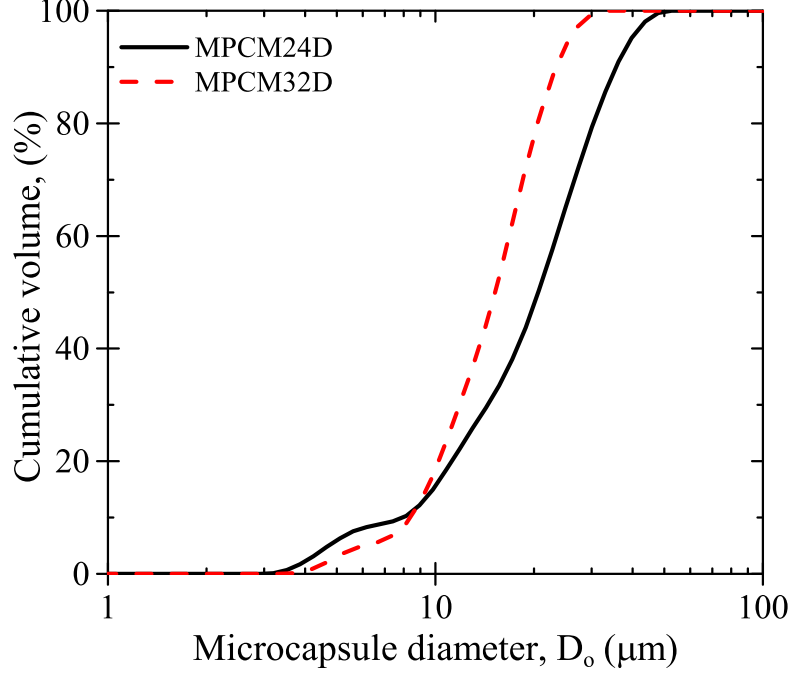


Figure 6.3: Measured particle size distribution of solid constituents of microencapsulated PCM-cement paste composites.

6.4 Results and discussion

6.4.1 Material characterization

Figure 6.3 shows the measured PSD of microencapsulated PCMs MPCM24D and MPCM32D. The median microcapsule diameters for MPCM24D and MPCM32D were respectively $D_{50} = 20.0 \mu\text{m}$ and $D_{50} = 15.2 \mu\text{m}$, both within the ranges reported by the manufacturer. As noted by the manufacturer, each PCM microcapsule was comprised of 85 - 90 mass % PCM core and 10 - 15 mass % shell. The median shell thickness ranged from 0.7 - 1.1 μm for MPCM24D and from 0.5 - 0.8 μm for MPCM32D.

Figure 6.4a plots the measured specific heat $c_{p,c+s}$ of MPCM24D as a function of temperature with temperature ramp rate of $1^\circ\text{C}/\text{min}$. The peak melting temperature was 24°C , while the peak solidification temperature was 19°C . In addition, multiple peaks can be observed in the measured specific heat. This can be attributed to the presence of constituents (potentially impurities) with different molecular weights. Indeed, the desired phase change

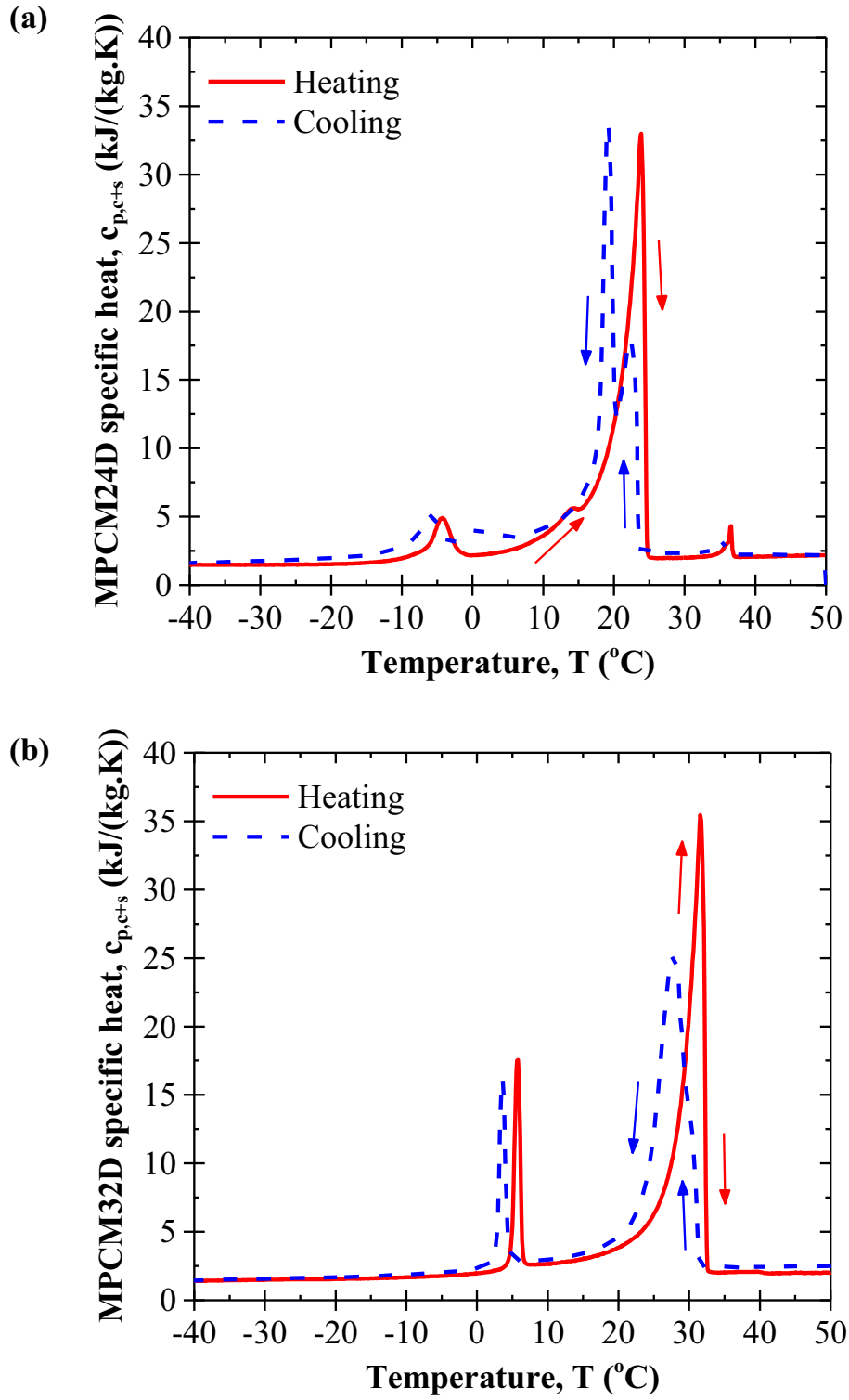


Figure 6.4: Specific heat of microencapsulated PCM (a) MPCM24D and (b) MPCM32D (Microtek Laboratories Inc.) as a function of temperature measured by DSC with a temperature ramp rate of $1^{\circ}\text{C}/\text{min}$.

temperature of commercial paraffin PCMs is achieved by blending constituents with different alkane chain lengths [38]. The latent heat of fusion h_{sf} , averaged between melting and solidification cycles over three measurements between -45 and 45°C , was determined to be 160.6 ± 0.6 kJ/kg. This was larger than the manufacturer-reported value of 124.4 kJ/kg. Note, however, that the enthalpy corresponding to the main specific heat peak between 10 and 25°C was measured to be about 124 kJ/kg.

Similarly, Figure 6.4b plots the measured specific heat $c_{p,c+s}$ of MPCM32D as a function of temperature with a temperature ramp rate of $1^\circ\text{C}/\text{min}$. The peak melting temperature was about 32°C , while the peak solidification temperature was about 28°C . MPCM32D exhibited only two distinct peaks in $c_{p,c+s}(T)$, suggesting that there were fewer constituents than in MPCM24D. Here also, phase transition occurred over a very wide temperature range during melting and solidification. Slight hysteresis was observed in the specific heat of both MPCM32D and MPCM24D. This was attributed to the lack of heterogeneous nucleation sites for PCM solidification within the small microcapsules [137]. The latent heat of fusion h_{sf} of MPCM32D, averaged between melting and solidification cycles over three measurements between -40 and 60°C , was determined to be 164.4 ± 0.6 kJ/kg.

The microencapsulated PCM specific heat was also measured using DSC temperature ramp rates of 2, 5, and $10^\circ\text{C}/\text{min}$. The difference between the peak melting and solidification temperatures increased and the main specific heat peaks grew wider as the temperature ramp rate increased. However, the measured latent heat of fusion did not strongly depend on the DSC ramp rate. This was consistent with the findings of Albright et al. [138].

6.4.2 Experimental/numerical comparison

6.4.2.1 Centerpoint temperature

Figure 6.5 plots the experimentally measured centerpoint temperature $T_c(t)$ as a function of time for specimens made of cement paste without and with MPCM32D with a volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3. It also plots the imposed chamber temperature $T_\infty(t)$ as a function of time featuring three successive heating/cooling cycles with temperature ramp

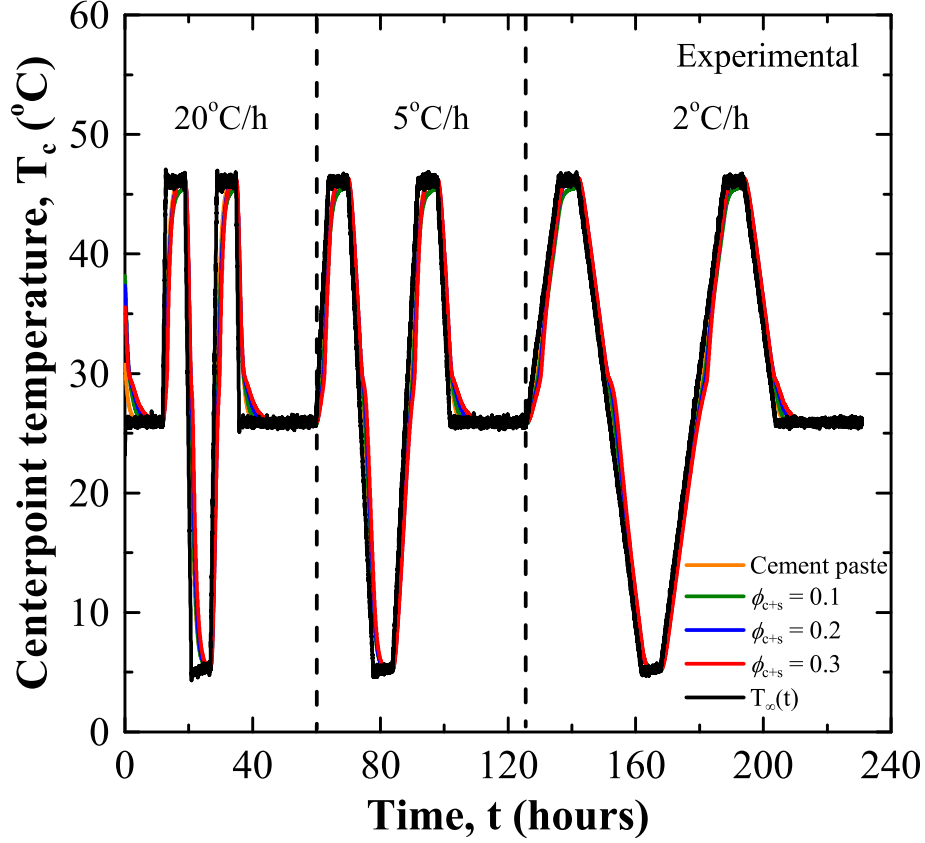


Figure 6.5: Centerpoint temperature $T_c(t)$ as a function of time within cement paste specimens without and with MPCM32D with a volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3 subjected to an imposed chamber temperature $T_\infty(t)$ varying at a ramp rate of 20, 5, and 2°C/h.

rate of 20, 5, and 2°C/h.

Figure 6.6 plots the centerpoint temperature $T_c(t)$ (a) experimentally measured and (b) numerically predicted as a function of time t during *cooling* at a temperature ramp rate of 20°C/h for cement paste specimens without and with MPCM32D with a volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3. The temperatures within the PCM-mortar composite and the pure cement paste specimens were nearly identical until they diverged sharply at about 30°C. This corresponded to the sharp onset of phase change during cooling illustrated in Figure 6.4b. Figure 6.6a features well-defined divergence and convergence points between the temperatures within cement paste and PCM-mortar composite specimens. This was observed in cooling curves for all ramp rates considered and for cylinders containing either MPCM24D or MPCM32D (see Supplementary material). As the microencapsulated PCM volume fraction

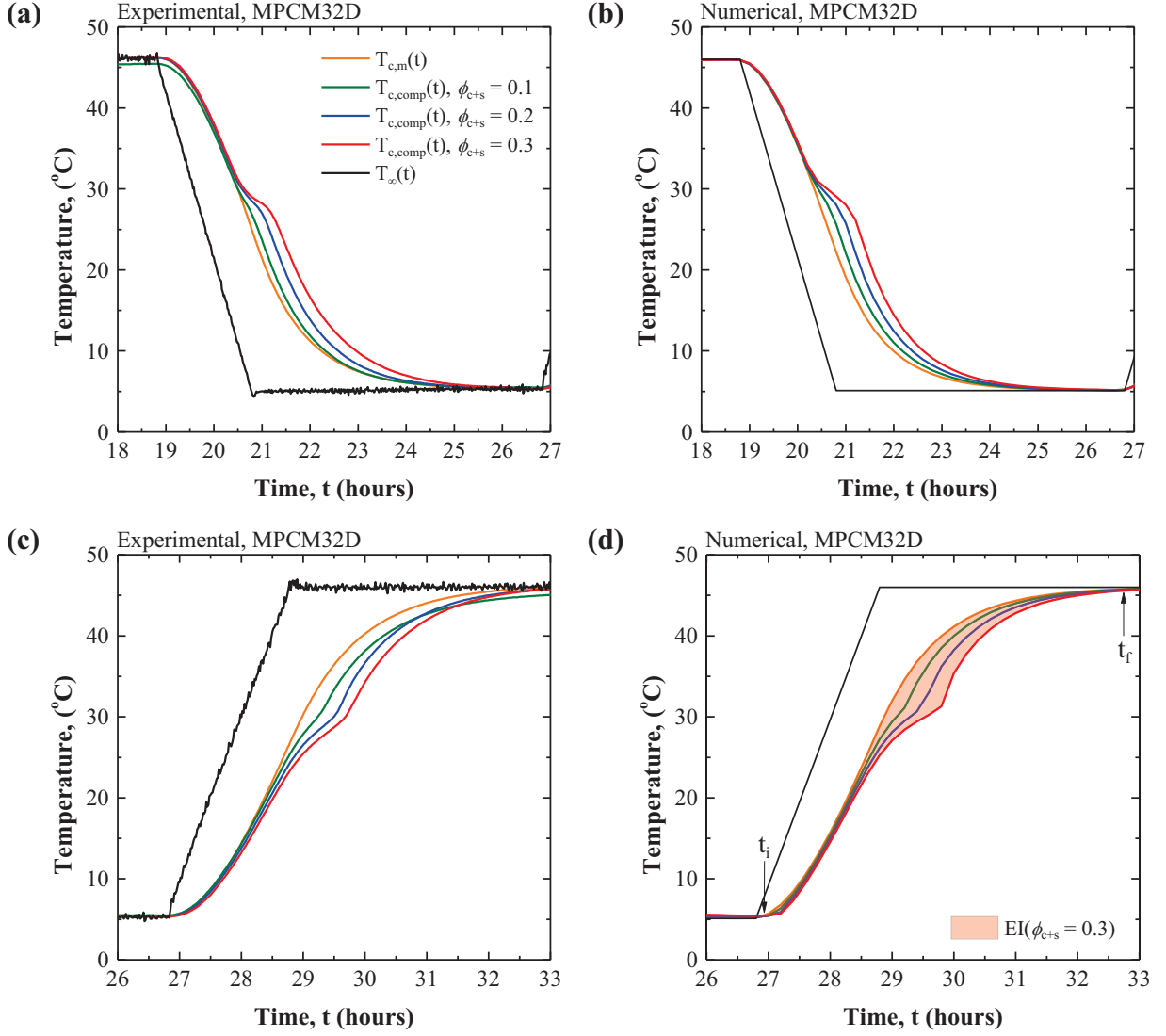


Figure 6.6: Centerpoint temperature $T_c(t)$ as a function of time within cement paste specimens without and with MPCM32D with volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3 subjected to an imposed chamber temperature $T_\infty(t)$ during cooling at temperature ramp rate of 20°C/h (a) measured experimentally and (b) predicted numerically and also during heating at temperature ramp rate of 20°C/h (c) measured experimentally and (d) predicted numerically.

ϕ_{c+s} increased, the temperature within the PCM-mortar specimens diverged more dramatically from that within the cement paste specimens during phase change. The PCM-mortar composite also took longer to cool down to the imposed chamber temperature. This can be attributed to the fact that the thermal energy stored within the specimen in the form of PCM latent heat during heating and released during cooling increased as ϕ_{c+s} increased. Figure 6.6b indicates that the numerically predicted centerpoint temperature $T_c(t)$ during cooling at 20°C/h agreed very well with experimental measurements and captured the above mentioned features. The numerical simulations used the measured specific heat $c_{p,c+s}(T)$ of the microencapsulated PCM shown in Figure 6.4b. The centerpoint temperature of the PCM-mortar composite specimens $T_{c,comp}(t)$ converged with that of the pure cement paste $T_{c,m}(t)$ during the isothermal hold at $T_\infty(t) = 5^\circ\text{C}$ around the same time experimentally and numerically.

Figure 6.6 also plots the centerpoint temperature $T_c(t)$ (c) experimentally measured and (d) numerically predicted as a function of time t during *heating* at a temperature ramp rate of 20°C/h for cement paste specimens without and with MPCM32D with a volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3. The centerpoint temperature within PCM mortar specimens $T_{c,comp}(t)$ diverged gradually from that within cement paste $T_{c,m}(t)$ between 10 and 20°C. This was consistent with the gradual onset of phase change during heating observed in Figure 6.4b. Figure 6.6d indicates that the numerically predicted centerpoint temperature $T_c(t)$ during heating at 20°C/h also agreed very well with experimental measurements.

Finally, similar agreement was observed between experimental measurements and numerical predictions of $T_c(t)$ during cooling and heating at a temperature ramp rate of 5 and 2°C/h and for cement paste containing MPCM24D (see Supplementary material). These results established experimentally the validity of the numerical simulation tool and of the expressions of the effective thermal properties numerically validated in previous studies [34, 35, 89].

6.4.2.2 Energy indicator

The shaded area in Figure 6.6d illustrates the energy indicator EI associated with heating a PCM-mortar composite specimen containing microencapsulated PCM with volume fraction ϕ_{c+s} of 0.3. The small area enclosed between 27 and 28 hours corresponds to the minor phase change peak in $c_{p,c+s}(T)$ shown in Figure 6.4b around 5°C. It was important to define t_i and t_f to include this area to avoid underestimating EI . It is evident that the surface area enclosed between $T_{c,comp}(t)$ and $T_c(t)$, i.e., the energy indicator, increased with increasing microencapsulated PCM volume fraction ϕ_{c+s} . The energy indicator accounts for the cumulative effects of adding microencapsulated PCM to a cementitious mortar on its latent and sensible thermal energy storage and on its thermal resistance. Therefore, it should be larger when the temporal evolution within a PCM-mortar specimen is significantly delayed by larger latent or sensible heat storage and/or by smaller effective thermal conductivity compared with a PCM-free (i.e., plain cement-based) composite specimen.

Figure 6.7a shows the experimentally measured energy indicator EI as a function of microencapsulated PCM volume fraction ϕ_{c+s} during heating and cooling at a temperature ramp rate of 20, 5, and 2°C/h for PCM-mortar composite specimens containing MPCM24D. The experimental uncertainties were estimated based on three repeated experiments on specimens containing MPCM24D. The error bars shown correspond to a 95% confidence interval. Figure 6.7a indicates that the energy indicator EI increased nearly linearly with ϕ_{c+s} during heating and cooling at any temperature ramp rate. In addition, EI did not depend strongly on the temperature ramp rate. In fact, the linear fit was $EI = 38\phi_{c+s}$ with a coefficient of determination R^2 larger than 0.99 for all conditions considered. Figure 6.7b shows the numerical predictions of EI as a function of ϕ_{c+s} corresponding to the experimental conditions of Figure 6.7a. The numerically predicted values of EI , averaged between heating and cooling for each ramp rate and fitted as $EI = 47\phi_{c+s}$, were 15-25% larger than the experimental measurements shown in Figure 6.7a.

Similarly, Figure 6.7c shows the experimentally measured energy indicator EI as a function of ϕ_{c+s} during cooling and heating at a ramp rate of 20, 5, and 2°C/h for PCM-mortar

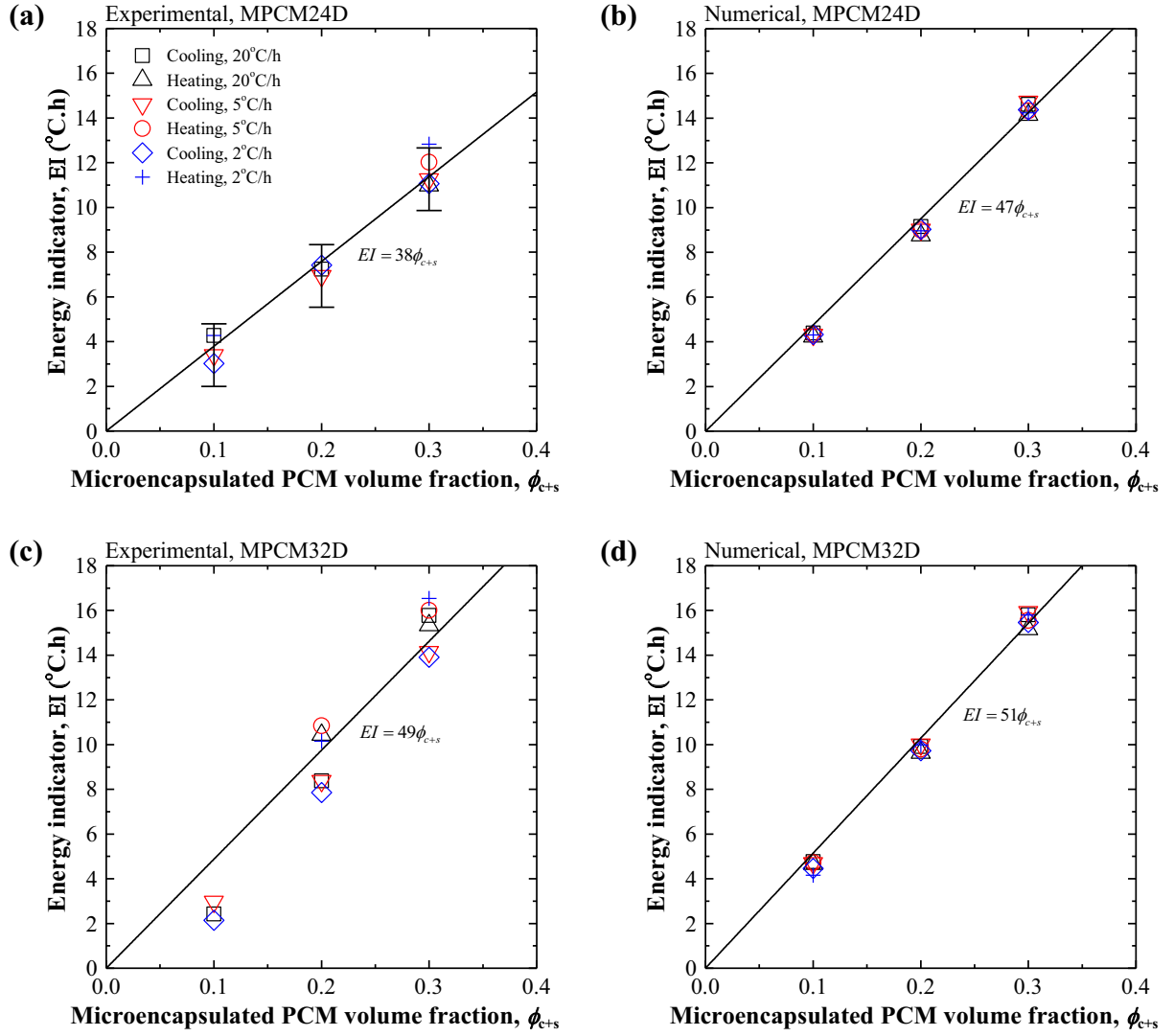


Figure 6.7: Energy indicator EI as a function of microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0.1 to 0.3 for microencapsulated PCM-mortar specimens subjected to heating and cooling at a temperature ramp rate of 20, 5, and 2 $^{\circ}\text{C}/\text{h}$ for (a) experimental measurements and (b) numerical predictions for MPCM24D and (c) experimental measurements and (d) numerical predictions for MPCM32D. The linear fits feature R^2 larger than 0.98.

composite specimens containing MPCM32D. For this different PCM, the energy indicator EI also increased nearly linearly with ϕ_{c+s} during heating and cooling at any ramp rate. The slope of the linear fit was steeper than that observed for MPCM24D. This can be attributed to the larger latent heat of fusion h_{sf} of MPCM32D. Here also, EI did not depend strongly on the imposed chamber temperature ramp rate. The linear fit was such that $EI = 49\phi_{c+s}$ with R^2 larger than 0.98 for all conditions considered. This suggests that EI may be evaluated at any ramp rate. Figure 6.7d shows the numerical predictions of EI as a function of ϕ_{c+s} corresponding to the conditions of Figure 6.7c. The numerically predicted values of EI , averaged between heating and cooling for each ramp rate and fitted as $EI = 51\phi_{c+s}$, were 2-6% larger than those measured experimentally and shown in Figure 6.7c.

The numerically predicted values of EI fell very close to experimental measurements. However, they systematically exceeded experimental data by up to 25 and 6% for PCM-mortar composite specimens containing MPCM24D or MPCM32D, respectively. Indeed, the numerical predictions shown in Figures 6.7b and 6.7d represent the ideal case in which the full latent heat storage capacity of the microencapsulated PCM may be utilized during melting or solidification. Experimentally, however, some microcapsules may have burst during the synthesis process. In addition, we speculate that the enthalpy of phase change may decrease in caustic aqueous environments such as those encountered in cementitious pore solutions due to chemical interactions between the PCM and sulfate ions. These phenomena may explain the mismatch between the experimentally measured and numerically predicted values of EI .

The energy indicator EI was also predicted numerically using the microencapsulated PCM specific heat $c_{p,c+s}(T)$ measured experimentally at a temperature ramp rate of 10°C/min (see Supplementary material). This led to a greater difference between EI predicted during heating and cooling. However, EI was on the same order of magnitude as that using $c_{p,c+s}(T)$ obtained at 1°C/min (Figure 6.7). This can be attributed to the facts that (i) the measured PCM latent heat of fusion h_{sf} did not strongly depend on the temperature ramp rate and (ii) EI captured the effect of latent heat over a complete melting or freezing period. Numerical predictions using $c_{p,c+s}(T)$ obtained at 10°C/min also captured the linear dependence of EI

on ϕ_{c+s} and independence of EI on heating and cooling ramp rate. In practice, this is useful since DSC measurements at 1°C/min can be very time consuming while they are faster and routinely practiced at 10°C/min. Indeed, ASTM E1269-11 specifies a heating and cooling ramp rate of 20°C/min when measuring specific heat capacity by DSC [131].

6.4.3 Parametric study

The following section presents a parametric study using the simulation tool previously validated to assess the effects of (i) latent heat of fusion h_{sf} , (ii) specimen radius r_i , and (iii) PCM thermal conductivity k_c on the energy indicator EI . Such a study would be very time consuming and costly if it were performed experimentally. In order to better parametrize the problem, the PCM specific heat was taken to be a step or a Gaussian function of temperature given by Equations (6.1) and (6.2), respectively. The simulated PCM-mortar composite specimen was exposed to the same temperature cycle $T_\infty(t)$ shown in Figure 6.5. The plots of centerpoint temperature $T_c(t)$ during successive heating and cooling cycles showed the same qualitative behavior as the plots shown in Figures 6.6a through 6.6d.

The idealized PCM specific heat profiles simulated did not include hysteresis and thus the energy indicator was the same during heating and cooling and for any temperature ramp rate. Additionally, the energy indicator was found to be independent of the phase change temperature T_{pc} and of the temperature window ΔT_{pc} as long as the imposed temperature cycle contained the entire phase change temperature window. Thus, in the following sections, T_{pc} and ΔT_{pc} were arbitrarily taken to be 20 and 10°C, respectively.

6.4.3.1 Effect of latent heat of fusion

Figure 6.8a plots the energy indicator EI predicted as a function of latent heat of fusion h_{sf} ranging from 100 to 250 kJ/kg for ϕ_{c+s} equal to 0.1, 0.2, and 0.3 for the baseline case with $r_i = 38.1$ mm and $k_c = 0.21$ W/m·K. Figure 6.8a indicates that the energy indicator EI increased linearly with h_{sf} for any given value of ϕ_{c+s} considered. Additionally, EI increased more steeply with h_{sf} for larger values of ϕ_{c+s} .

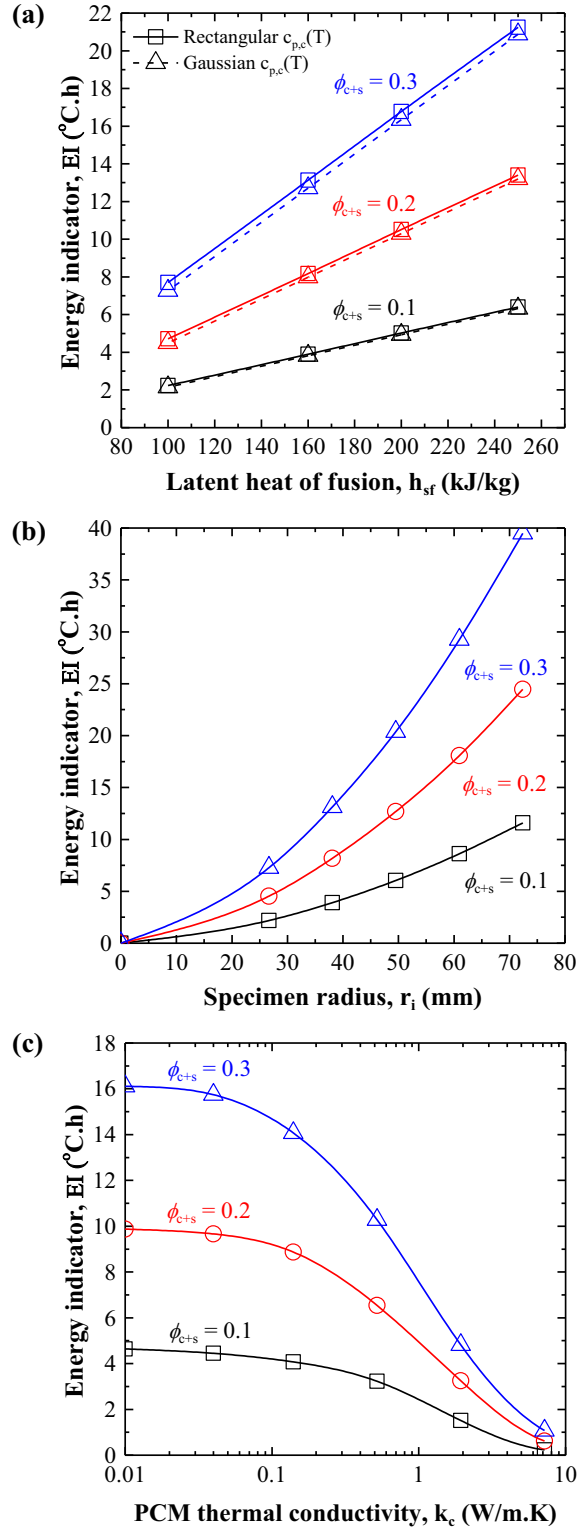


Figure 6.8: Energy indicator EI as a function of (a) latent heat of fusion h_{sf} ranging from 100 to 250 kJ/kg, (b) specimen radius r_i up to 72 mm, and (c) PCM thermal conductivity k_c ranging from 0.01 to 10 W/m.K. Microencapsulated PCM volume fraction ϕ_{c+s} was taken as either 0.1, 0.2, or 0.3.

Finally, the temporal evolution of the centerpoint temperature within specimens during phase change, and thus the value of EI , were nearly identical when imposing the PCM specific heat $c_{p,c}(T)$ as a step or as a Gaussian function of temperature (see Supplementary material). Thus, any PCM specific heat function may be used to predict EI numerically, as long as (i) the area enclosed by the curve $c_{p,c}(T)$ and the line $c_{p,c} = c_{p,c,s}$ corresponds to h_{sf} and (ii) the complete phase change temperature window is included in the range of temperature variation within the specimen. Henceforth, the PCM specific heat was imposed as a step function of temperature given by Equation (6.1).

6.4.3.2 Effect of specimen radius

Figure 6.8b plots the energy indicator EI predicted numerically as a function of the specimen radius r_i up to 72 mm for microencapsulated PCM volume fraction ϕ_{c+s} equal to 0.1, 0.2, and 0.3. The latent heat of fusion h_{sf} and thermal conductivity k_c of the PCM were the same as in the baseline case (Table 7.1) and equal to 160 kJ/kg and 0.21 W/m·K, respectively. The length L of the cylinder was also varied such that the aspect ratio d_i/L was constant and equal to 0.5. This ensured that 1D radial heat conduction prevailed at the center plane $z = L/2$. The duration of the isothermal holds at the maximum and minimum temperatures was increased from 4 up to 14 hours with increasing specimen radius r_i to ensure that the PCM-mortar composite specimen reached thermal equilibrium during each isothermal hold. Figure 6.8b indicates that the energy indicator increased quadratically with increasing specimen radius, i.e., $EI = ar_i + br_i^2$ where the coefficients a and b depend on ϕ_{c+s} , h_{sf} , and on the thermal properties (ρ , c_p , and k) of the core, shell, matrix, and mold materials. As the specimen radius and thus the mass of microencapsulated PCM increased, more thermal energy was stored or released in the form of latent heat during heating or cooling, respectively.

6.4.3.3 Effect of PCM thermal conductivity

Figure 6.8c plots the energy indicator EI as a function of PCM thermal conductivity k_c ranging from 0.01 to 10 W/(m·K) for ϕ_{c+s} of 0.1, 0.2, and 0.3, $h_{sf} = 160$ kJ/kg, and

$r_i = 38.1$ mm. It shows that EI decreased sharply with increasing k_c between about 0.1 and 10 W/(m·K). Note that this range of k_c encompasses most commercially available PCMs [46]. In fact, most commercially available organic PCMs have thermal conductivities between 0.1 and 0.3 W/(m·K), while inorganic and eutectic PCMs can have thermal conductivities reaching as high as 1 W/(m·K) [46]. Within this range, EI was increasingly sensitive to k_c as ϕ_{c+s} increased. In all cases, it reached a plateau for low PCM thermal conductivity and tended toward zero for k_c exceeding 10 W/(m·K). Interestingly, the upper limit for small values of k_c increased substantially with increasing ϕ_{c+s} , while the lower limit for large k_c did not depend strongly on ϕ_{c+s} . For energy efficient building envelopes, augmentation of the thermal resistance provided by the PCM-mortar composite is desired and thus PCMs with small thermal conductivity k_c are preferred.

6.4.4 Correlation to performance metrics

6.4.4.1 Energy flux reduction

This section utilizes a numerical model presented in a recent study [35] to simulate 1D transient heat transfer through a 10 cm thick microencapsulated PCM-concrete composite wall. The inner wall surface was subjected to a constant indoor temperature $T_{in} = 20^\circ\text{C}$ while the outer wall surface was subjected to sinusoidal outdoor temperature oscillations between T_{min} and T_{max} and to solar radiation flux. The convective heat transfer coefficients at the inner and outer wall surfaces were taken to be 8 and 20 W/m²·K, respectively [35]. The PCM specific heat was taken to be a step function of temperature given by Equation (6.1) where T_{pc} was equal to the indoor temperature T_{in} and $\Delta T_{pc} = 3^\circ\text{C}$. We defined the diurnal energy flux reduction E_r as the relative difference between the daily energy fluxes (in J/m²) through a plain concrete wall and through a microencapsulated PCM-concrete composite wall [35]. The diurnal energy flux reduction E_r (i) increased linearly with both the PCM volume fraction and the latent heat of fusion and their product (not shown) and (ii) was independent of the phase change temperature window as long as it did not extend beyond the range of wall temperature variation [35].

Table 6.2 summarizes six cases considered featuring microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0 to 0.3, latent heat of fusion h_{sf} ranging from 100 to 200 kJ/kg, and PCM thermal conductivity k_c ranging from 0.21 to 2 W/m·K. In Cases 1-5, T_{min} and T_{max} were chosen as 0 and 40°C, respectively, such that the diurnal variation of the inner wall surface temperature included the entire phase change temperature window. On the other hand, Case 6 features more realistic conditions with outdoor temperature varying between 10 and 30°C. Figure 6.9 plots the diurnal energy flux reduction E_r through the composite wall estimated for the six different cases of Table 6.2 as a function of energy indicator EI for a cylinder of radius $r_i = 38.1$ mm and of the same composition as the wall. The energy flux reduction E_r for Cases 1-5 collapsed on the same curve and was linearly proportional to the energy indicator EI , i.e., $E_r = 3.73EI$. For Case 6, E_r was larger than previous cases since the amplitude of outdoor temperature oscillation was smaller [35]. It also increased with increasing ϕ_{c+s} before saturating. This can be attributed to the fact that the PCM within the wall did not experience complete melting and freezing during the diurnal temperature cycle for large volume fractions ϕ_{c+s} . Figure 6.9 establishes the direct correlation between the energy savings achieved by a wall and the energy indicator for a small cylindrical specimen of the same material. Thus, EI can be used to compare the potential of microencapsulated PCM-mortar composite specimens of differing compositions

	ϕ_{c+s}	h_{sf} (kJ/kg)	k_c (W/m·K)	T_{min} (°C)	T_{max} (°C)
1	0.1	100 - 200	0.21	0	40
2	0.2	100 - 200	0.21	0	40
3	0.3	100 - 200	0.21	0	40
4	0.15	180	0.21 - 2	0	40
5	0.25	180	0.21 - 2	0	40
6	0.05 - 0.3	180	0.21	10	30

T_{max} were chosen as 0 and 40°C, respectively, such that the diurnal variation of the inner wall surface temperature included the entire phase change temperature window. On the other hand, Case 6 features more realistic conditions with outdoor temperature varying between 10 and 30°C. Figure 6.9 plots the diurnal energy flux reduction E_r through the composite wall estimated for the six different cases of Table 6.2 as a function of energy indicator EI for a cylinder of radius $r_i = 38.1$ mm and of the same composition as the wall. The energy flux reduction E_r for Cases 1-5 collapsed on the same curve and was linearly proportional to the energy indicator EI , i.e., $E_r = 3.73EI$. For Case 6, E_r was larger than previous cases since the amplitude of outdoor temperature oscillation was smaller [35]. It also increased with increasing ϕ_{c+s} before saturating. This can be attributed to the fact that the PCM within the wall did not experience complete melting and freezing during the diurnal temperature cycle for large volume fractions ϕ_{c+s} . Figure 6.9 establishes the direct correlation between the energy savings achieved by a wall and the energy indicator for a small cylindrical specimen of the same material. Thus, EI can be used to compare the potential of microencapsulated PCM-mortar composite specimens of differing compositions

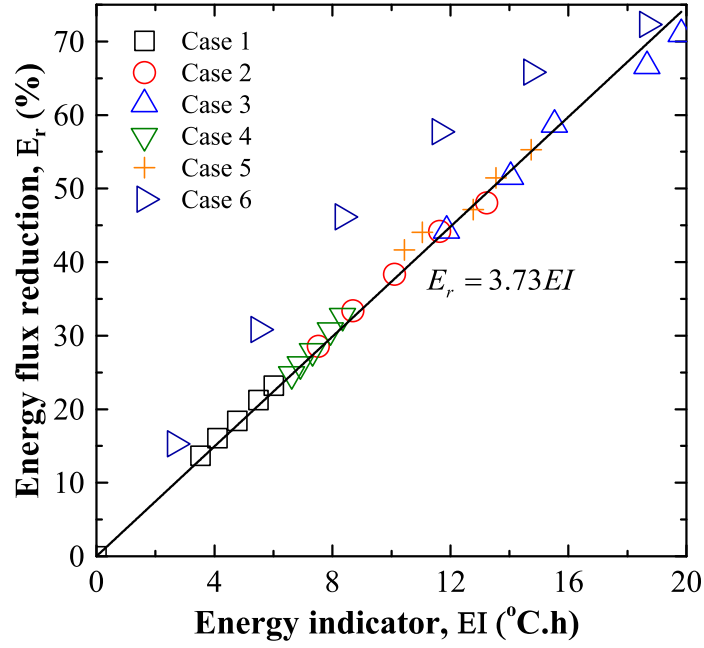


Figure 6.9: Correlation between the diurnal energy flux reduction E_r achieved by a 10 cm thick PCM-mortar composite wall and the energy indicator EI of a small specimen of the same material predicted numerically. The parameters corresponding to Cases 1-6 are summarized in Table 6.2. The microencapsulated PCM volume fraction ϕ_{c+s} ranged from 0.05 to 0.3, the latent heat of fusion h_{sf} from 100 to 200 kJ/kg, and the PCM thermal conductivity k_c from 0.21 to 2 W/m.K. The linear fit features R^2 larger than 0.99.

to reduce the energy flux through building walls. This is particularly useful in cases where the experimentalist lacks precise knowledge of the constituent material properties and volume fractions or experience with numerical modelling techniques. Moreover, in contrast to the energy flux reduction, the energy indicator does not require heat flux measurements but instead relies on simple temperature measurements.

6.4.4.2 Peak temperature reached during early hydration

Cylindrical PCM-mortar composite specimens were prepared using the method presented in Section 6.2.1 with different volume fractions ϕ_{c+s} . They were cast in PVC molds of inner radius 38.1 mm and immediately placed in the freeze-thaw chamber and subjected to a constant air temperature $T_\infty(t)$ of 26°C.

Figure 6.10a plots the temporal evolution of the centerpoint temperature $T_c(t)$ within

cement paste specimens without and with MPCM24D with volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3 during the cement hydration period. It shows that, for all specimens, the centerpoint temperature $T_c(t)$ increased to a peak temperature T_p during hydration before decreasing to the imposed chamber temperature of 26°C. This temperature rise was due to thermal energy generated by the exothermic hydration reaction occurring upon mixing cement and water. Figure 6.10a shows that the peak hydration temperature T_p decreased and was delayed with increasing microencapsulated PCM volume fraction ϕ_{c+s} .

Figure 6.10b plots the peak hydration temperature T_p in PCM-mortar composite specimens with ϕ_{c+s} ranging from 0 to 0.3 as a function of energy indicator EI previously measured for identical specimen compositions. The energy indicator was obtained by averaging measurements for cooling rates of 20, 5, and 2°C/h. The peak hydration temperature was obtained by averaging measurements of three specimens. The error bars shown for EI and T_p correspond to 95% and 63% confidence intervals, respectively. Figure 6.10b indicates that the peak hydration temperature T_p decreased nearly linearly with increasing energy indicator EI such that $T_p = 40.1 - 0.45EI$ with $R^2 \approx 0.96$. Note that the peak hydration temperature T_p observed here was smaller than that which would be expected in realistic concrete sections. This is attributable, in part, to the very slight insulating effect offered by the 2 mm mold wall. If the quantity of insulation were increased, e.g., to better capture semi-adiabatic temperature as occurs in realistic concrete sections, we would expect to observe higher peak hydration temperature T_p . This is significant, as reducing the peak hydration temperature T_p has been suggested as a method of reducing the risk of early-age cracking in cementitious elements [139, 140]. These results establish that EI is a relevant figure of merit to compare the potential of microencapsulated PCM-mortar composites of different compositions to mitigate this risk.

6.5 Conclusion

An energy indicator was introduced as a novel figure of merit to quantify the thermal performance of PCM composite materials. It can be evaluated based on a single heating, hold, and

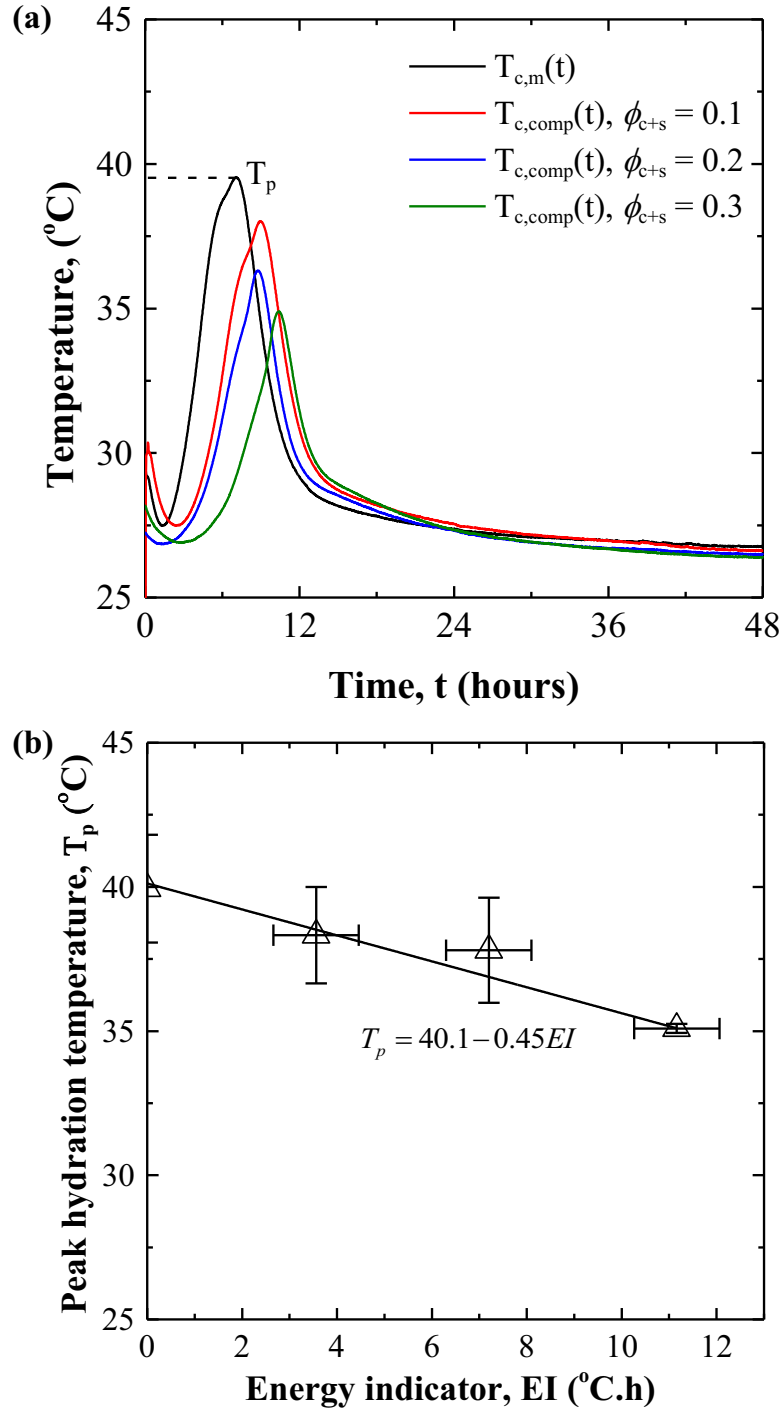


Figure 6.10: (a) Experimentally measured centerpoint temperature $T_c(t)$ as a function of time within cement paste specimens without and with MPCM24D at volume fraction ϕ_{c+s} of 0.1, 0.2, or 0.3 during the cement hydration period. (b) Peak centerpoint temperature T_p reached during cement hydration as a function of the corresponding energy indicator EI .

cooling test encompassing the PCM phase change temperature window at any ramp rate. Numerical predictions of the centerpoint temperature within cylindrical PCM-mortar composite specimens and the associated predictions of the energy indicator agreed very well with experimental measurements. The energy indicator was found to (i) increase linearly with increasing microencapsulated PCM volume fraction ϕ_{c+s} and latent heat of fusion h_{sf} , (ii) increase quadratically with the specimen radius r_i , and (iii) decrease with increasing PCM thermal conductivity k_c . The energy indicator measured for small cylindrical specimens was shown to correlate with the diurnal energy flux reduction achieved by adding microencapsulated PCM to a concrete wall. Similarly, the peak hydration temperature reached within cementitious materials decreased nearly linearly with increasing energy indicator. Thus, the energy indicator EI can be used as a figure of merit to rapidly evaluate and select PCM-mortar composites for energy efficient buildings and crack-resistant concrete.

CHAPTER 7

Simple Thermal Evaluation of Building Envelopes Containing Microencapsulated Phase Change Materials Using the Admittance Method

This chapter extends the widely-used admittance method to predict the diurnal energy flux reduction E_r associated with adding microencapsulated phase change materials (PCM) to single and multilayer building envelopes. The admittance method represents a simpler and less computationally intensive alternative to finite element models. It may enable straightforward evaluation of the energy benefits of PCM-composite walls using user-friendly design software for a wide range of users.

7.1 Background

7.1.1 Sol-air temperature

The thermal load through a building envelope depends on the outdoor climate conditions. The description of these conditions may include factors such as the outdoor dry-bulb temperature and humidity, incident solar radiation flux, and thermal radiation exchange between outdoor surfaces. Mackey and Wright [141, 142] proposed a method to account for the thermal effects of outdoor air temperature and incident solar radiation flux on the outer surface of a building wall. They defined an equivalent outdoor temperature sol-air temperature $T_{sa}(t)$ as [141, 142],

$$T_{sa}(t) = T_{\infty}(t) + \frac{\alpha_s q_s''(t)}{h_o} \quad (7.1)$$

where $T_\infty(t)$ is the outdoor air temperature, α_s is the total hemispherical solar absorptivity of the outer wall surface, $q_s''(t)$ is the incident solar radiation flux, and h_o is the convective heat transfer coefficient at the outer wall surface. Parmelee and Aubele [143] later noted the significance of emissive radiation exchange between the wall and sky and proposed that $T_{sa}(t)$ be defined as,

$$T_{sa}(t) = T_\infty(t) + \frac{\alpha_s q_s''(t)}{h_o} - \frac{\epsilon \sigma [T_o^4(t) - T_{sky}^4]}{h_o} \quad (7.2)$$

where ϵ is the emissivity of the outer wall surface, $\sigma = 5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$ is the Stefan-Boltzmann constant, $T_o(t)$ is the outer wall surface temperature, and T_{sky} is the sky temperature. Because the outer wall surface temperature $T_o(t)$ is not known explicitly, the American Society of Heating and Refrigeration Engineers (ASHRAE) recommends that the last term in Equation (7.2) be approximated as [144],

$$\frac{\epsilon \sigma [T_o^4(t) - T_{sky}^4]}{h_o} = 4 \cos \theta \quad (7.3)$$

where θ represents the angle that a wall surface makes with a horizontal plane, i.e., $\theta = \pi/2$ for vertical walls. Based on this recommendation, studies simulating vertical building walls have ignored the emissive radiation term altogether and defined $T_{sa}(t)$ based on Equation (7.1) [110, 116, 144].

7.1.2 Decrement factors and time lags

Analytical methods have been developed to relate the temperature $T_L(t)$ [141] and heat flux $q_L''(t)$ [76] at the inner surface of a building wall to a sinusoidal sol-air temperature $T_{sa}(t)$ at the exterior of the building. These methods have relied upon so-called decrement factors and their associated time lags. There is a family of decrement factors and time lags represented in the literature, each with their own physical interpretation. Unfortunately, the same terminology of “decrement factor” and “time lag” is often used without further clarification. As a result, it can be challenging to discern which definition is being used. A detailed discussion of the mathematical definition of each decrement factor is provided below.

Mackey and Wright [141] related the inner wall surface temperature $T_L(t)$ to a sinusoidal sol-air temperature $T_{sa}(t)$ as,

$$T_L(t) = f_{MW} (T_{sa}(t - \phi_{MW}) - \bar{T}_{sa}) + \frac{U}{h_i} \bar{T}_{sa} + \left(1 - \frac{U}{h_i}\right) T_{in} \quad (7.4)$$

where U is the overall heat transfer coefficient of the wall, $\bar{T}_{sa}$ is the daily-averaged sol-air temperature, f_{MW} is the fundamental equivalent thermal resistance ratio or so-called decrement factor and ϕ_{MW} is the time lag. The decrement factor f_{MW} represented the ratio of the amplitude of temperature oscillation at the inner wall surface ΔT_L to that of the sol-air temperature ΔT_{sa} , i.e.,

$$f_{MW} = \frac{\Delta T_L}{\Delta T_{sa}} = \frac{T_{L,max} - T_{L,min}}{T_{sa,max} - T_{sa,min}}. \quad (7.5)$$

The associated time lag ϕ_{MW} represented the difference between the time (in hours) when the inner wall surface and the sol-air temperatures reached their respective maximum. The decrement factor f_{AM} and time lag ϕ_{AM} can be expressed as [141, 142],

$$f_{MW} = \frac{1.414 h_o k \sigma_n}{\sqrt{A^2 + B^2}} \quad \text{and} \quad \phi_{MW} = \frac{12}{\pi} \tan^{-1} \left(\frac{A - B}{A + B} \right). \quad (7.6)$$

Here, $\sigma_n = (\pi/86400\alpha)^{0.5}$, where $\alpha = k/(\rho c_p)$ is the thermal diffusivity and the parameters A and B were given by [141],

$$\begin{aligned} A &= (h_o + h_i) k \sigma_n [\cos(\sigma_n L) \cosh(\sigma_n L) + \sin(\sigma_n L) \sinh(\sigma_n L)] \\ &\quad + h_o h_i \sin(\sigma_n L) \cosh(\sigma_n L) + 2k^2 \sigma_n^2 \cos(\sigma_n L) \sinh(\sigma_n L) \\ \text{and } B &= (h_o + h_i) k \sigma_n [\cos(\sigma_n L) \cosh(\sigma_n L) - \sin(\sigma_n L) \sinh(\sigma_n L)] \\ &\quad + h_o h_i \cos(\sigma_n L) \sinh(\sigma_n L) - 2k^2 \sigma_n^2 \sin(\sigma_n L) \cosh(\sigma_n L). \end{aligned} \quad (7.7)$$

Alternatively, Pipes [145] offered an analytical solution to the one-dimensional (1D) transient heat conduction equation for a wall subjected to convective heat transfer to a constant indoor temperature T_{in} and to a sinusoidal sol-air temperature $T_{sa}(t)$. Pipes [145] related the sol-air temperature $T_{sa}(t)$ and outer wall surface heat flux $q_o''(t)$ to the indoor temperature T_{in} and inner wall surface heat flux $q_L''(t)$ as,

$$\begin{bmatrix} T_{sa} \\ q_o'' \end{bmatrix} = \begin{bmatrix} 1 & 1/h_o \\ 0 & 1 \end{bmatrix} \begin{bmatrix} m_1 & m_2 \\ m_3 & m_1 \end{bmatrix} \begin{bmatrix} 1 & 1/h_i \\ 0 & 1 \end{bmatrix} \begin{bmatrix} T_{in} \\ q_L'' \end{bmatrix} = \begin{bmatrix} M_1 & M_2 \\ M_3 & M_4 \end{bmatrix} \begin{bmatrix} T_{in} \\ q_L'' \end{bmatrix} \quad (7.8)$$

where m_1 , m_2 , and m_3 are elements of the wall transmission matrix expressed as [145, 146],

$$m_1 = \cosh \zeta, \quad m_2 = \frac{L}{k\zeta} \sinh \zeta, \quad \text{and} \quad m_3 = \frac{k\zeta}{L} \sinh \zeta. \quad (7.9)$$

Here, $\zeta = P + iP$, where $P = (\pi L^2 / 3600 t_p \alpha)^{0.5}$ and t_p is the period of the sinusoidal sol-air temperature (in hours). Note that this formulation may also be used for a multilayer wall by determining $m_{1,i}$, $m_{2,i}$, and $m_{3,i}$ for each plain-parallel layer i of the wall as a function of its thickness L_i , thermal conductivity k_i , and thermal diffusivity α_i . In other words, for a wall with n layers, the transmission matrix in Equation (7.8) becomes,

$$\begin{bmatrix} T_{sa} \\ q_o'' \end{bmatrix} = \begin{bmatrix} 1 & 1/h_o \\ 0 & 1 \end{bmatrix} \begin{bmatrix} m_{1,1} & m_{2,1} \\ m_{3,1} & m_{1,1} \end{bmatrix} \cdots \begin{bmatrix} m_{1,n} & m_{2,n} \\ m_{3,n} & m_{1,n} \end{bmatrix} \begin{bmatrix} 1 & 1/h_i \\ 0 & 1 \end{bmatrix} \begin{bmatrix} T_{in} \\ q_L'' \end{bmatrix}. \quad (7.10)$$

Danter [76] used the solution described by Pipes [145] for the case of constant indoor temperature T_{in} to define the decrement factor f_{AM} and the corresponding time lag ϕ_{AM} as,

$$f_{AM} = \left| \frac{1}{UM_2} \right| \quad \text{and} \quad \phi_{AM} = \frac{t_p}{2\pi} \tan^{-1} \left(\frac{\text{Im}(1/M_2)}{\text{Re}(1/M_2)} \right). \quad (7.11)$$

The time lag can ϕ_{AM} can also be expressed as,

$$\phi_{AM} = t_{L,max} - t_{sa,max} \quad (7.12)$$

where $t_{L,max}$ and $t_{sa,max}$ correspond to the times when the inner wall surface heat flux $q_L''(t)$ and the sol-air temperature $T_{sa}(t)$ reach their maximum values, respectively. Considering the discontinuous nature of the inverse tangent function, it is useful to define the time lag ϕ_{AM} on a piecewise basis as,

$$\phi_{AM} = \begin{cases} \left| \frac{t_p}{2\pi} \tan^{-1} \left(\frac{\text{Im}(1/M_2)}{\text{Re}(1/M_2)} \right) \right| & \text{for } \text{Re}(1/M_2) > 0 \text{ and } \text{Im}(1/M_2) < 0 \\ \left| \frac{t_p}{2\pi} \left(\tan^{-1} \left(\frac{\text{Im}(1/M_2)}{\text{Re}(1/M_2)} \right) - \pi \right) \right| & \text{for } \text{Re}(1/M_2) < 0 \\ \left| \frac{t_p}{2\pi} \left(\tan^{-1} \left(\frac{\text{Im}(1/M_2)}{\text{Re}(1/M_2)} \right) - 2\pi \right) \right| & \text{for } \text{Re}(1/M_2) > 0 \text{ and } \text{Im}(1/M_2) > 0 \end{cases}. \quad (7.13)$$

Using this definition, the time lag ϕ_{AM} ranges from 0 to 24 hours.

The decrement factor f_{AM} , proposed by Danter [76], has been described as the ratio of the periodic or cyclic thermal transmittance $\Delta q_L''(t) / \Delta T_{sa}(t)$ to the steady-state thermal

transmittance U of a wall and can be expressed as [146, 147],

$$f_{AM} = \frac{\Delta q_L''}{U \Delta T_{sa}} = \frac{q_{L,max}'' - q_{L,min}''}{U (T_{sa,max} - T_{sa,min})} \quad (7.14)$$

where $\Delta q_L''$ and ΔT_{sa} are the amplitudes of oscillation in the inner wall surface heat flux $q_L''(t)$ and sol-air temperature $T_{sa}(t)$, respectively. Note that the amplitudes of oscillation in heat flux and temperature at the inner wall surface are related by $\Delta q_L'' = h_i \Delta T_L$. Thus, the decrement factor f_{MW} defined by Mackey and Wright [141] is related to the decrement factor f_{AM} defined in the admittance method [76] as,

$$f_{MW} = \frac{U}{h_i} f_{AM}. \quad (7.15)$$

Moreover, several studies have defined the decrement factor f_S as the ratio of the amplitudes of oscillation in temperature at the inner ΔT_L and outer ΔT_o surfaces of a wall. They also defined time lag ϕ_S as the difference between the times $t_{L,max}$ and $t_{o,max}$ at which the inner and outer wall surfaces reached their maximum temperatures, respectively. Mathematically, they are expressed as [77, 144, 148, 149],

$$f_s = \frac{\Delta T_L}{\Delta T_o} = \frac{T_{L,max} - T_{L,min}}{T_{o,max} - T_{o,min}} \quad \text{and} \quad \phi_s = t_{L,max} - t_{o,max}. \quad (7.16)$$

We will refer to these parameters as the surface decrement factor f_S and surface time lag ϕ_S . The solution described by Pipes [145] [Equations (7.8)-(7.13)] and used in the admittance method can be used to define the surface decrement factor f_S as,

$$f_S = \left| \frac{1}{h_i N_2} \right| \quad \text{where} \quad N_2 = M_2 - \frac{m_3}{h_i h_o} - \frac{m_1}{h_o}. \quad (7.17)$$

The corresponding surface time lag ϕ_S may then be determined by substituting N_2 for M_2 in Equations (7.11) and (7.13).

Finally, the decrement factor has also been described as the ratio of the amplitudes of oscillation in indoor and outdoor temperatures [150]. Unfortunately, it is not straightforward to reconcile this definition with those previously discussed, as f_{MW} , f_{AM} , and f_S were all defined for cases where the indoor temperature was assumed to be constant. In fact, Equations (7.8)-(7.13) cannot be used to define any decrement factor in the case of a time-dependent indoor temperature.

Ruivo et al. [151] identified that “the decrement factors f_{AM} and f_{MW} of a particular wall are imperatively different and the following relationship holds: $f_{AM} = f_{MW}h_i/U$.” The authors compared f_{AM} and f_{MW} for numerous composite wall designs and observed that predictions of f_{AM}/f_{MW} were not equivalent to h_i/U . This was likely due to the fact that the authors defined at least one of the decrement factors using some sort of graphical estimation. Indeed, if f_{MW} and f_{AM} are determined using Equations (7.6) and (7.7) and (7.8)-(7.11), respectively, the ratio f_{AM}/f_{MW} will always be equivalent to h_i/U . Ruivo et al. [151] also asserted that the time lags ϕ_{MW} and ϕ_{AM} were equivalent because “the sol-air temperature and the outer surface temperature of the wall reach the maximum values at the same instant.” Rather, the time lags ϕ_{MW} and ϕ_{AM} are equivalent because the temperature $T_L(t)$ and heat flux $q_L''(t)$ at a wall’s inner surface ($x = L$) always reach their maximum values at the same instant.

7.1.3 Estimating thermal loads through building envelopes

Methods that estimate the thermal load through a building envelope include (i) the response factor, (ii) the total equivalent temperature difference/time-averaging (TETD-TA), (iii) the transfer function (TF), (iv) the cooling load temperature difference (CLTD), (v) the heat balance (HB), (vi) the radiant time series (RTS), and (vii) the admittance methods [152, 153]. Rees et al. [152] provided an in-depth discussion of these methods and summarized the timeline of their development. Rees and coworkers also performed a thorough quantitative [154, 155] and qualitative [152] comparative analysis of the HB and RTS methods recommended by ASHRAE in the United States and the admittance method recommended by the CIBSE. Both the admittance and TETD-TA methods rely upon decrement factors and time lags to estimate the thermal load through a building envelope.

The admittance method was developed to describe the transient indoor air temperature of a room subjected to a sinusoidal outdoor sol-air temperature $T_{sa}(t)$ [146]. It can account for heat conduction through the building envelope, solar radiation heat flux incident on the inner wall surfaces through windows, radiative exchange between indoor surfaces, and

sensible heat storage by the indoor air. Marletta et al. [146] extended the admittance method to predict the transient indoor air temperature of a room subjected to non-sinusoidal weather conditions by decomposing the sol-air temperature into a series of harmonics using Fourier analysis. Then, the admittance method was applied to each harmonic.

The total equivalent temperature difference $TETD(t)$ is defined as the difference between the indoor temperature T_{in} and the outdoor sol-air temperature $T_{sa}(t)$ such that [153],

$$q_L''(t) = U \cdot TETD(t) = h_i[T_L(t) - T_{in}] \quad (7.18)$$

where h_i is the convective heat transfer coefficient at the inner wall surface. Mackey and Wright [141] related the inner wall surface temperature $T_L(t)$ to the sinusoidal sol-air temperature $T_{sa}(t)$ as,

$$T_L(t) = f_{MW} [T_{sa}(t - \phi_{MW}) - \bar{T}_{sa}] + \frac{U}{h_i} \bar{T}_{sa} + \left(1 - \frac{U}{h_i}\right) T_{in} \quad (7.19)$$

where $\bar{T}_{sa}$ is the daily-averaged sol-air temperature defined as,

$$\bar{T}_{sa} = \frac{1}{P} \int_0^P T_{sa}(t) dt \quad (7.20)$$

where $P = 86400$ s is the period of a day. Then, $TETD(t)$ can be expressed as a function of f_{MW} and ϕ_{MW} ,

$$TETD(t) = \frac{h_i f_{MW}}{U} [T_{sa}(t - \phi_{MW}) - \bar{T}_{sa}] + \bar{T}_{sa} - T_{in}. \quad (7.21)$$

Note that $TETD(t)$ can also be written in terms of f_{AM} [151]. Ruivo et al. [153] compared $TETD(t)$ predicted numerically and analytically for several multilayer wall constructions subjected to a constant indoor temperature and to a realistic (i.e., non-sinusoidal) sol-air temperature. The authors illustrated that $TETD(t)$ calculated using Equation (7.21) agreed fairly well with numerical predictions for wall constructions with small thermal mass but agreed poorly for walls with large thermal mass, such as PCM-composite walls. Finally, they decomposed the sol-air temperature $T_{sa}(t)$ into a Fourier series with four harmonics and superposed, i.e., added $TETD(t)$ determined for each harmonic. Using this approach, the numerical and analytical predictions of $TETD(t)$ agreed very well for all wall constructions considered.

Overall, the TETD and admittance methods were limited to standard wall constructions with constant thermal properties. The present study extends the admittance method to materials with temperature-dependent properties such as those embedded with microencapsulated PCM. The predictions of this extended admittance method were compared with those based on numerical predictions for single and multilayer walls subjected to either sinusoidal or realistic sol-air temperatures.

7.2 Analysis

7.2.1 Schematic and model assumptions

Two wall configurations were considered, namely (i) a single-layer concrete slab of thickness $L_c = 10$ cm and (ii) a standard three-layer wall consisting of plaster board of thickness $L_{pb} = 1.6$ cm as the inner-most layer, wood wool insulation of thickness $L_{ins} = 5$ cm, and concrete wall of thickness $L_c = 15$ cm as the outer-most layer [147]. Figure 7.1 illustrates the multilayer wall configuration subjected to convection to indoor air at constant temperature T_{in} at the inner wall surface and to a sol-air temperature $T_{sa}(t)$ at the outer wall surface. The convective heat transfer coefficients at the inner and outer wall surfaces were represented by h_i and h_o , respectively. The sol-air temperature $T_{sa}(t)$ accounts for the thermal effects of outdoor air temperature and incident solar radiation flux on the outer surface of the building wall and is defined as [143],

$$T_{sa}(t) = T_{\infty}(t) + \frac{\alpha_s q_s''(t)}{h_o} \quad (7.22)$$

where α_s is the outer wall surface total hemispherical solar absorptivity.

To make the problem mathematically tractable, the following assumptions were made: (1) one-dimensional (1D) transient heat transfer prevailed, (2) each wall material had isotropic and constant thermal properties except for the temperature-dependent effective specific heat, (3) the specific heat of the PCM was the same for the solid and liquid phases, and (4) contact resistances between wall layers were negligible.

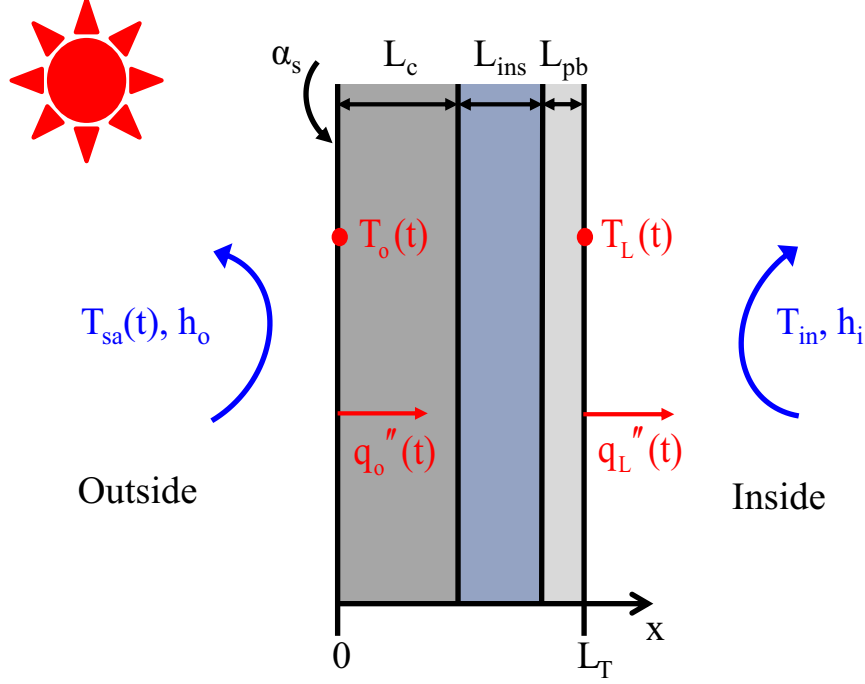


Figure 7.1: Schematic of a multilayer wall consisting of a concrete layer of thickness L_c and exterior surface total hemispherical solar absorptivity α_s , an insulation layer of thickness L_{ins} , and a plaster board layer of thickness L_{pb} . The wall was subjected to convection to a constant indoor temperature T_{in} at the inside surface ($x = L_T$) and to a sol-air temperature at the outside surface ($x = 0$ m). The temperature at the inner $T_L(t)$ and outer $T_o(t)$ surfaces and the heat flux at the inner $q_L''(t)$ and outer $q_o''(t)$ surfaces are also shown.

7.2.2 Governing equations for numerical model

Under the above assumptions, the local wall temperature T_j within layer j at any time t and location x was governed by the 1D transient heat conduction equation given by [113],

$$\frac{\partial T_j}{\partial t} = \alpha_j \frac{\partial^2 T_j}{\partial x^2} \quad (7.23)$$

where $\alpha_j = k_j/(\rho c_p)_j$ is the thermal diffusivity of layer j and k , ρ , and c_p are the thermal conductivity, density, and specific heat capacity of layer j , respectively. For cases when a layer j contained microencapsulated PCM, the effective thermal conductivity k_{eff} of the three-component composite was given by the Felske model expressed as [89],

$$k_{eff} = \frac{2k_m(1 - \phi_c - \phi_s) \left(3 + 2\frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_s} \right) + (1 + 2\phi_c + 2\phi_s) \left[\left(3 + \frac{\phi_s}{\phi_c} \right) k_c + 2\frac{\phi_s k_s}{\phi_c} \right]}{(2 + \phi_c + \phi_s) \left(3 + 2\frac{\phi_s}{\phi_c} + \frac{\phi_s k_c}{\phi_c k_s} \right) + (1 - \phi_c - \phi_s) \left[\left(3 + \frac{\phi_s}{\phi_c} \right) \frac{k_c}{k_m} + 2\frac{\phi_s k_s}{\phi_c k_m} \right]} \quad (7.24)$$

where k_c , k_s , and k_m are respectively the thermal conductivities of the core, shell, and matrix, while ϕ_c and ϕ_s are the core and shell volume fractions. The effective volumetric heat capacity $(\rho c_p)_{eff}(T)$ was given by [35],

$$(\rho c_p)_{eff}(T) = \phi_c (\rho c_p)_c(T) + \phi_s (\rho c_p)_s + (1 - \phi_c - \phi_s) (\rho c_p)_m \quad (7.25)$$

where $(\rho c_p)_c(T)$, $(\rho c_p)_s$, and $(\rho c_p)_m$ are the volumetric heat capacities of the core, shell, and matrix materials, respectively. According to the heat capacity method for simulating phase change, the specific heat capacity of the PCM $c_{p,c}(T)$ can be defined as a step function in terms of temperature with a rectangular peak of (i) width ΔT_{pc} centered around the phase change temperature denoted by T_{pc} and (ii) enclosed area equal to the PCM latent heat of fusion h_{sf} such that [35],

$$c_{p,c}(T) = \begin{cases} c_{p,c,s} & \text{for } T < T_{pc} - \Delta T_{pc}/2, \\ c_{p,c,s} + \frac{h_{sf}}{\Delta T_{pc}} & \text{for } T_{pc} - \Delta T_{pc}/2 \leq T \leq T_{pc} + \Delta T_{pc}/2, \\ c_{p,c,l} & \text{for } T > T_{pc} + \Delta T_{pc}/2. \end{cases} \quad (7.26)$$

Here $c_{p,s}$ and $c_{p,l}$ are the heat capacity of the solid and liquid PCM, respectively. Here, T_{pc} , ΔT_{pc} , and h_{sf} represent the phase change temperature, temperature window, and latent heat of fusion, respectively. As previously mentioned, the specific heat of solid PCM $c_{p,c,s}$ was assumed to be equivalent to that of liquid PCM $c_{p,c,l}$ (Assumption 3). The heat capacity method for simulating phase change has previously been validated against the exact solution for the one-dimensional Stefan problem [35]. We also showed that the time-dependent thermal behavior of core-shell-matrix composite materials can be accurately predicted by an equivalent homogeneous material with effective thermal properties given by Equations (7.24) to (7.26) [35].

7.2.3 Initial and boundary conditions

The initial temperature was assumed to be uniform throughout the material and equal to T_i , i.e.,

$$T(x, 0) = T_i. \quad (7.27)$$

In the case of a multilayer wall, the temperature and heat flux were continuous at the concrete-insulation ($x = L_c$) and insulation-plaster board ($x = L_c + L_{ins}$) interfaces (Assumption 4), i.e.,

$$\begin{aligned} -k_c \frac{\partial T_c}{\partial x}(L_c, t) &= -k_{ins} \frac{\partial T_{ins}}{\partial x}(L_c, t) \quad \text{and} \\ -k_{ins} \frac{\partial T_{ins}}{\partial x}(L_c + L_{ins}, t) &= -k_{pb} \frac{\partial T_{pb}}{\partial x}(L_c + L_{ins}, t). \end{aligned} \quad (7.28)$$

Convective heat transfer to a constant indoor temperature T_{in} was imposed at the interior wall surface ($x = L_T$), i.e.,

$$-k \frac{\partial T}{\partial x}(L_T, t) = h_i [T(L_T, t) - T_{in}] \quad (7.29)$$

where h_i is the mixed convective heat transfer coefficient accounting for both forced and natural convections and L_T is the total wall thickness (i.e., L_c or $L_c + L_{pb} + L_{ins}$). Convective heat transfer to a periodic sol-air temperature $T_{sa}(t)$ was imposed at the exterior wall surface ($x = 0$) such that,

$$-k \frac{\partial T}{\partial x}(0, t) = h_o [T(0, t) - T_{sa}(t)] \quad (7.30)$$

where h_o is the outdoor convective heat transfer coefficient.

First, the outer wall surface was subjected to a sinusoidal outdoor temperature such that $T_{sa}(t) = T_\infty(t)$, where the outdoor air temperature $T_\infty(t)$ was imposed as a sinusoidal function of time t (in s) given by,

$$T_\infty(t) = \frac{T_{\infty, max} - T_{\infty, min}}{2} \sin \left(\frac{\pi t}{43200} - \frac{2\pi}{3} \right) + \frac{T_{\infty, max} + T_{\infty, min}}{2}. \quad (7.31)$$

Here, $T_{\infty, min}$ and $T_{\infty, max}$ are the minimum and maximum outdoor air temperatures during a day, respectively. A phase shift of $2\pi/3$ placed the peak outdoor temperature $T_{\infty, max}$ at 2:00 pm, as the daily maximum occurred between 1:00 pm and 3:00 pm for more than 80% of the year in California climate zone 9 (Los Angeles, CA) based on weather data [17].

Second, a so-called idealized sol-air temperature was prescribed based on Equation (7.22) using the sinusoidal outdoor air temperature $T_\infty(t)$ given by Equation (7.31) and a solar

radiation flux $q_s''(t)$ expressed as a function of time t (in s) as,

$$q_s''(t) = \begin{cases} q_{s,max}'' \cos\left(\frac{\pi t}{43200} - \pi\right) & \text{for } 6:00 \text{ am} \leq t \leq 6:00 \text{ pm} \\ 0 & \text{for } 6:00 \text{ pm} < t < 6:00 \text{ am} \end{cases} \quad (7.32)$$

where $q_{s,max}''$ is the maximum daily solar radiation heat flux (in W/m²) observed at 12:00 pm and taken as 535 W/m², corresponding to their average value throughout the year in California climate zone 9 [17].

Finally, a realistic sol-air temperature $T_{sa}(t)$ was imposed as a function of time t based on weather data corresponding to January 1st, June 12th, and September 24th for a South-facing vertical wall in California climate zone 9 (Los Angeles, CA) [17].

7.2.4 Accounting for phase change in the admittance method

The decrement factors f_{MW} , f_{AM} , and f_S and their associated time lags defined in Section 7.1.2 are based on the assumption that the wall specific heat capacity c_p is constant. In order to account for phase change in a composite material embedded with microencapsulated PCM, we define the modified specific heat $c'_{p,c,l}$ for the PCM core as,

$$c'_{p,c} = c_{p,c} + \frac{\gamma h_{sf}}{\Delta T_z}. \quad (7.33)$$

Here, ΔT_z is the amplitude of temperature oscillation at the center of the PCM-composite layer and γ is the fraction of PCM within the wall that has undergone phase change during a given diurnal cycle, expressed as,

$$\gamma = \frac{h_{pc}\rho_{eff}}{2\phi_c h_{sf}\rho_c} \quad (7.34)$$

where h_{pc} (in kJ/kg) represents the total thermal energy stored and released as latent heat within the PCM-composite layer during a given cycle per unit mass. The factor γ was approximated as the percentage of the phase change temperature range $T_{pc} \pm \Delta T_{pc}/2$ covered by the range of temperature variation at the center of the PCM-composite layer $\bar{T}_z \pm \Delta T_z/2$, where $\bar{T}_z$ is the daily-averaged temperature at the center of the PCM-composite layer. Figure 7.2 illustrates the six possible scenarios that govern the mathematical approximation of the

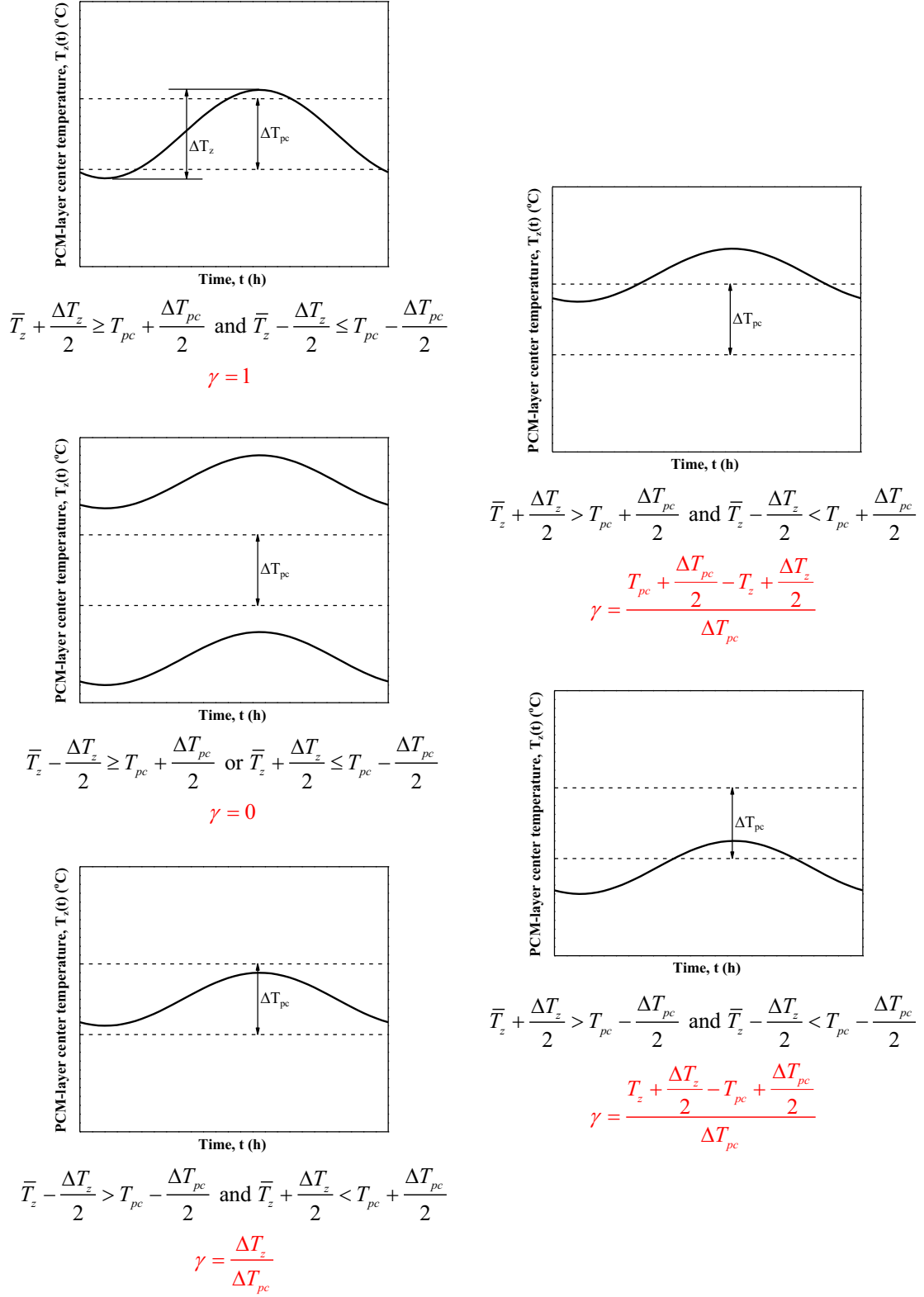


Figure 7.2: Summary of the six cases of wall temperature variation relative to the phase change temperature window and the corresponding mathematical definition of γ for each case.

factor γ . It plots the wall center temperature $T_z(t)$ as a function of time for an arbitrary diurnal cycle along with the phase change temperature window ΔT_{pc} . It

The value of ΔT_z was approximated as a linear interpolation of the amplitudes of temperature oscillation at the inner ΔT_L and outer ΔT_o wall surfaces expressed as,

$$\Delta T_z = \left(1 - \frac{x_{PCM}}{L_T}\right) \Delta T_L + \frac{x_{PCM}}{L_T} \Delta T_o \quad (7.35)$$

where x_{PCM} is the distance from the inner wall surface at $x = L_T$ to the center of the PCM layer. The amplitude of temperature oscillation ΔT_L and ΔT_o at the inner and outer wall surfaces, respectively, can be expressed simply in terms of the decrement factors f_{MW} and f_S based on Equations (7.5) and (7.16).

The daily-averaged temperature at the PCM-composite layer's center $\bar{T}_z$ was approximated as a linear interpolation of the daily-averaged temperatures at the inner $\bar{T}_L$ and outer $\bar{T}_o$ wall surfaces, i.e.,

$$\bar{T}_z = \left(1 - \frac{x_{PCM}}{L_T}\right) \bar{T}_L + \frac{x_{PCM}}{L_T} \bar{T}_o \quad (7.36)$$

where $\bar{T}_L$ and outer $\bar{T}_o$ were expressed in terms of the daily-averaged wall heat flux $\bar{q}_w'' = U(\bar{T}_{sa} - T_{in})$ between the indoor T_{in} and daily-averaged sol-air $\bar{T}_{sa}$ temperatures given by,

$$\bar{T}_L = T_{in} + \frac{\bar{q}_w''}{h_i} \quad \text{and} \quad \bar{T}_o = \bar{T}_{sa} - \frac{\bar{q}_w''}{h_o}. \quad (7.37)$$

In the case when the range of diurnal wall temperature oscillation $T_z \pm \Delta T_z/2$ coincides precisely with the phase change region $T_{pc} \pm \Delta T_{pc}/2$, all of the PCM within the wall undergoes phase change and $\gamma = 1$. By contrast, if the amplitude of diurnal wall temperature oscillation $\bar{T}_z \pm \Delta T_z/2$ does not overlap with the phase change region $T_{pc} \pm \Delta T_{pc}/2$, none of the PCM within the wall undergoes phase change and $\gamma = 0$. Then, the modified PCM specific heat capacity is equivalent to that of solid or liquid PCM.

Note that as the microencapsulated PCM volume fraction ϕ_{c+s} increases, the amplitude of oscillation at the center of the PCM-layer ΔT_z decreases, thus decreasing γ . To account for this effect, ΔT_z and γ was determined for incremental additions $\delta\phi$ of microencapsulated

PCM up to the desired volume fraction ϕ_{c+s} . For example, ΔT_z and γ were first be determined by applying the admittance method to a wall without PCM where $\phi_{c+s} = 0$. These values were then be used to determine the modified PCM specific heat $c'_{p,c}$ and the effective volumetric heat capacity $(\rho c_p)_{eff}$ of the PCM-composite layer with a microencapsulated PCM volume fraction $\phi_{c+s} = \delta_\phi$. The admittance method was then repeated using effective thermal properties to determine new values for ΔT_z and γ . This iterative procedure was repeated, adding an incremental PCM volume fraction PCM δ_ϕ at each iteration, until the desired microencapsulated PCM volume fraction ϕ_{c+s} was reached. In the present study, we considered an incremental PCM volume fraction δ_ϕ of 0.05. Further reducing the incremental PCM volume fraction δ_ϕ had a negligible effect on the predicted thermal load passing through PCM-composite walls in all cases considered.

7.2.5 Constitutive relationships

Table 7.1 summarizes the density, thermal conductivity, and specific heat of the materials considered in this study. Wall materials included concrete [113], wood wool insulation [147],

Table 7.1: Density ρ , specific heat capacity c_p , and thermal conductivity k of PCM, high density polyethylene (HDPE), concrete, insulation, and plaster board.

Material	Subscript	ρ (kg/m ³)	c_p (J/(kg·K))	k (W/(m·K))	Ref.
PCM	c	860	2590	0.21	[111]
HDPE	s	930	2250	0.49	[112]
Concrete	m	2330	880	1.4	[113]
Insulation	ins	500	1000	0.1	[147]
Plaster board	pb	1320	1000	0.5	[147]

and plaster board [147]. The microencapsulated PCM consisted of the commercial organic PCM PureTemp 20 by Entropy Solution Inc. (Plymouth, MN) [111] encapsulated in high density polyethylene (HDPE) [112]. Each microcapsule was assumed to consist of 85% PCM and 15% shell material by mass [133]. Since the PCM and shell had similar densities,

their volume fractions were given by $\phi_c = 0.85\phi_{c+s}$ and $\phi_s = 0.15\phi_{c+s}$, respectively, where $\phi_{c+s} = \phi_c + \phi_s$ is the microencapsulated PCM volume fraction in the PCM-composite. The phase change temperature T_{pc} was taken to be equal to the indoor temperature T_{in} of 20°C in order to maximize the reduction and delay of the thermal load through the PCM-composite wall, as suggested by recent numerical simulations [35]. The phase change temperature window ΔT_{pc} and the PCM latent heat of fusion h_{sf} were taken to be 8°C and 180 kJ/kg, respectively characteristic of PureTemp 20 [111]. The indoor h_i and outdoor h_o heat transfer coefficients were respectively taken to be 7.7 and 25 W/m²·K, in accordance with ISO standard 6946 [156]. The total hemispherical solar absorptivity α_s of the outer wall surface was taken as 0.26, corresponding to the typical value for white paint [113].

When considering a sinusoidal outdoor temperature $T_\infty(t)$, the amplitude of temperature oscillation $(T_{\infty,max} - T_{\infty,min})/2$ was arbitrarily taken to be 7°C and the daily-averaged outdoor temperature $\bar{T}_\infty$ was varied between 10 and 30°C in 5°C increments. In addition, Figure 3.12a plots the sol-air temperature $T_{sa}(t)$ as a function of time on January 1st, June 12th, and September 24th based on realistic weather data covering a broad range of conditions representative of California climate zone 9 (Los Angeles, CA).

7.2.6 Data processing

As previously mentioned, the admittance method [Equations (7.8) through (7.13)] applies to walls exposed to sinusoidal outdoor temperature conditions. In order to determine the decrement factors f_{MW} , f_{AM} , and f_s and their associated time lags for walls exposed to non-sinusoidal conditions, the sol-air temperature $T_{sa}(t)$ was decomposed into a Fourier series with m harmonics expressed as,

$$T_{sa}(t) = \bar{T}_{sa} + \sum_{n=1}^{m/2} [a_n \cos(n\omega t) + b_n \sin(n\omega t)] \quad (7.38)$$

where m is an even number and the coefficients a_n and b_n are defined as,

$$a_n = \frac{2}{P} \int_0^P T_{sa}(t) \cos(n\omega t) dt \quad \text{and} \quad b_n = \frac{2}{P} \int_0^P T_{sa}(t) \sin(n\omega t) dt. \quad (7.39)$$

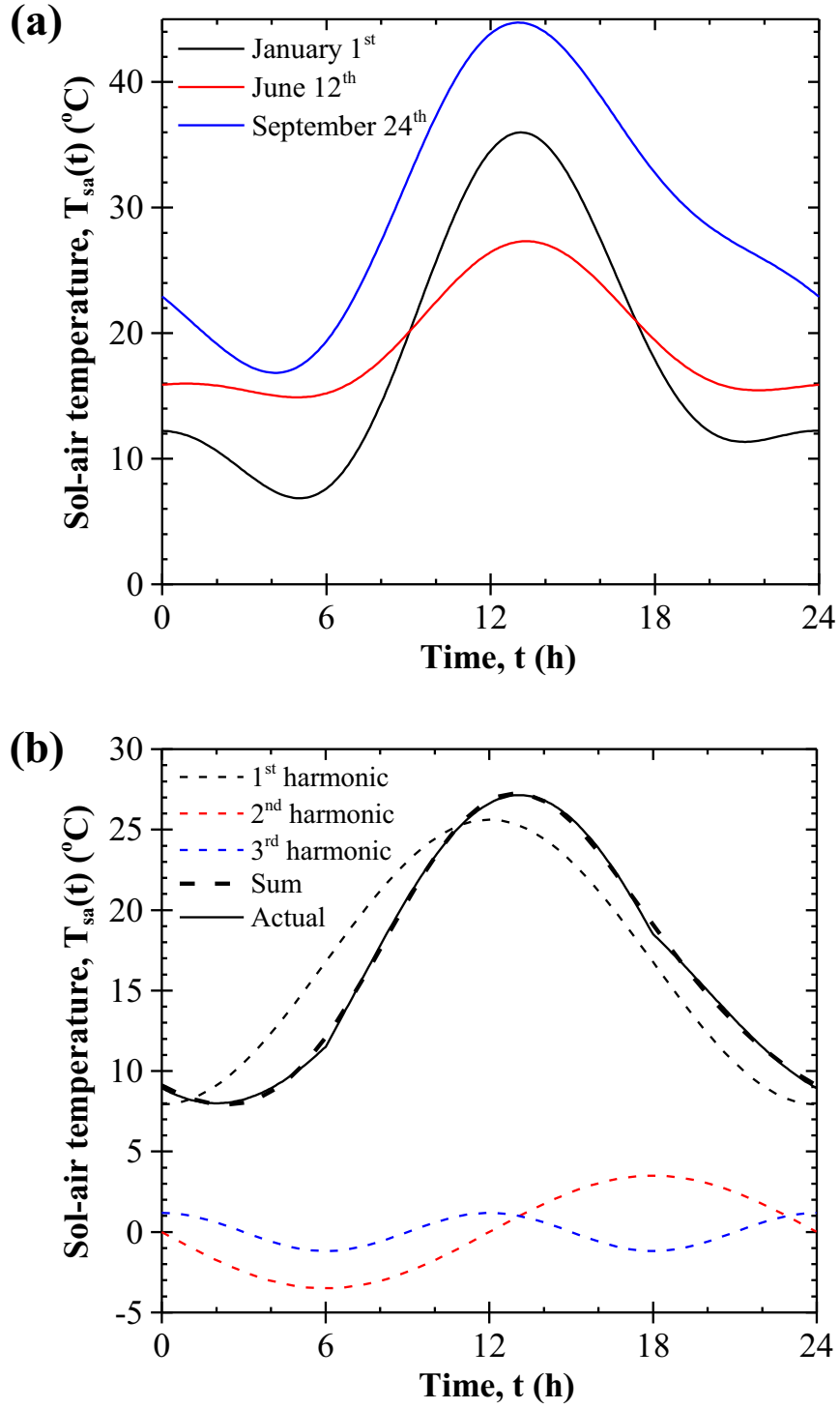


Figure 7.3: (a) Sol-air temperature T_{sa} as a function of time based on weather data for California climate zone 9 (Los Angeles, CA) on January 1st, June 12th, and September 24th and (b) idealized sol-air temperature T_{sa} as a function of time compared with its approximation as the sum of the first three harmonics of a Fourier series.

In the present study, the sol-air temperature $T_{sa}(t)$ was decomposed into up to $m = 4$ harmonics.

Figure 7.3b plots the idealized sol-air temperature $T_{sa}(t)$ as a function of time given by Equation (7.1) where $T_{\infty}(t)$ and $q_s''(t)$ were defined by Equations (7.31) and (7.32), respectively. It also shows each harmonic of the Fourier series decomposition given by Equation (7.38) as well as their sum. The average relative error between the idealized sol-air temperature $T_{sa}(t)$ and its Fourier series decomposition was less than 1%.

Table 7.2 shows the daily-averaged sol-air temperature $\bar{T}_{sa}$ [Equation (7.20)] and the coefficients a_n and b_n [Equation (7.39)] that describe the Fourier series decomposition of the sol-air temperature [Equation (7.38)] for the idealized cases and in California climate zone 9 (Los Angeles, CA) on January 1st, June 12th, and September 24th. The average relative

Table 7.2: Average sol-air temperature $\bar{T}_{sa}$ [Equation (7.20)] and the coefficients a_n and b_n [Equation (7.39)] that describe the Fourier series decomposition of the sol-air temperature in California climate zone 9 (Los Angeles, CA) on January 1st, June 12th, and September 24th.

	$\bar{T}_{sa}$	a_1	b_1	a_2	b_2
Day	(°C)	(°C)	(°C)	(°C)	(°C)
Idealized	$\bar{T}_{\infty} + 1.8$	-8.85	-3.5	1.18	0.0
January 1st	18.07	-11.14	-5.16	5.29	2.46
June 12th	19.25	-5.27	-2.13	1.91	1.44
September 24th	29.73	-10.46	-6.72	3.65	0.0

error between the realistic sol-air temperature $T_{sa}(t)$ and its Fourier series decomposition was less than 6% for all three days considered. Then, the admittance method decrement factor $f_{AM,n}$ and time lag $\phi_{AM,n}$ were determined for a given composite wall configuration subjected to the n^{th} sol-air temperature harmonic using Equations (7.8) through (7.13) and the methodology described in Section 7.2.4. The corresponding inner wall surface heat flux

$q_L''(t)$ was determined by superposition and defined as,

$$\frac{q_L''(t)}{U} = a_0 - T_{in} + \sum_{n=1}^{m/2} \left[f_{AM,2n-1} a_n \cos \left(\frac{2n\pi}{P} (t - \phi_{AM,2n-1}) \right) + f_{AM,2n} b_n \sin \left(\frac{2n\pi}{P} (t - \phi_{AM,2n}) \right) \right]. \quad (7.40)$$

Alternatively, the decrement factor f_{AM} and time lag ϕ_{AM} for a given wall configuration were determined numerically, by solving Equations (7.23) through (7.30) for the wall temperature $T(x, t)$ as a function of space and time. Then, conductive heat flux at the inner wall surface $q_L''(t)$ was determined based on Fourier's law, i.e.,

$$q_L''(t) = -k_j \frac{\partial T_j}{\partial x}(L_T, t). \quad (7.41)$$

The decrement factor f_{AM} and time lag ϕ_{AM} were determined based on Equations (7.14) and (7.12), respectively.

Finally, the diurnal energy flux reduction E_r was defined as the relative difference between the daily energy fluxes (in J/m²) through the wall without $Q_{L,m}''$ and with Q_L'' microencapsulated PCM expressed as,

$$E_r = \frac{Q_{L,m}'' - Q_L''}{Q_{L,m}''} \quad (7.42)$$

where the energy fluxes $Q_{L,m}''$ and Q_L'' were respectively expressed as,

$$Q_{L,m}'' = \int_0^{24 \text{ h}} |q_{L,m}''(t)| dt \quad \text{and} \quad Q_L'' = \int_0^{24 \text{ h}} |q_L''(t)| dt. \quad (7.43)$$

The absolute values of the heat fluxes $q_{L,m}''$ and q_L'' were considered to account for the fact that there is an energy cost associated with maintaining the indoor temperature at T_{in} regardless of the direction of the heat flux across the wall. The energy flux reduction E_r describes the reduction in the daily thermal energy added or removed through a unit surface area of wall achieved by adding microencapsulated PCM.

7.2.7 Method of solution

The governing Equation (7.23) along with the boundary and initial conditions given by Equations (7.27)-(7.30) were solved using the commercial finite element solver

COMSOL Multiphysics 4.3. Numerical simulations were performed for a period of up to five days and the heat flux predictions for the final day were considered. By then, the diurnal heat flux through the wall had reached a periodic steady-state and the maximum relative difference in the inner wall heat flux was less than 1% when extending the simulation period by one day. Numerical convergence was considered to be reached when the maximum relative difference in the inner wall surface heat flux $q_L''(t)$ was less than 1% when reducing the mesh size or time step by a factor of 2. In practice, converged solutions were obtained by imposing a time step of 300 s. The minimum mesh element edge size and maximum growth rate for converged solutions were 2 mm and 1.2, respectively. The number of finite elements needed to obtain a converged solution was 50.

7.3 Results and discussion

7.3.1 Sinusoidal outdoor temperature

We first considered the case of a single layer concrete wall containing microencapsulated PCM and subjected to a sinusoidal outdoor temperature $T_\infty(t)$ described by Equation (7.31). Figures 7.4a and 7.4b plot the admittance method decrement factor f_{AM} and time lag ϕ_{AM} , respectively, as functions of microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0 to 0.2 predicted numerically and using the admittance method. The time-averaged outdoor temperature $\bar{T}_\infty$ ranged from 10 to 30°C in 5°C increments. Figure 7.4a shows that the numerically predicted admittance method decrement factor f_{AM} decreased with increasing microencapsulated PCM volume fraction ϕ_{c+s} for all outdoor temperature conditions. The addition of microencapsulated PCM had the most dramatic effect on the decrement factor f_{AM} when the average outdoor temperature $\bar{T}_\infty$ was equal to the indoor temperature T_{in} of 20°C. The numerically predicted decrement factor f_{AM} was identical between cases where the daily-averaged outdoor temperature $\bar{T}_\infty$ was symmetric about the phase change temperature T_{pc} and indoor temperature T_{in} of 20°C (e.g., $\bar{T}_\infty = 10$ and 30°C). This can be attributed to the fact that the outdoor temperature $T_\infty(t)$ was sinusoidal and thus the same fraction of PCM within the wall changed phase during the diurnal cycle in each of these cases.

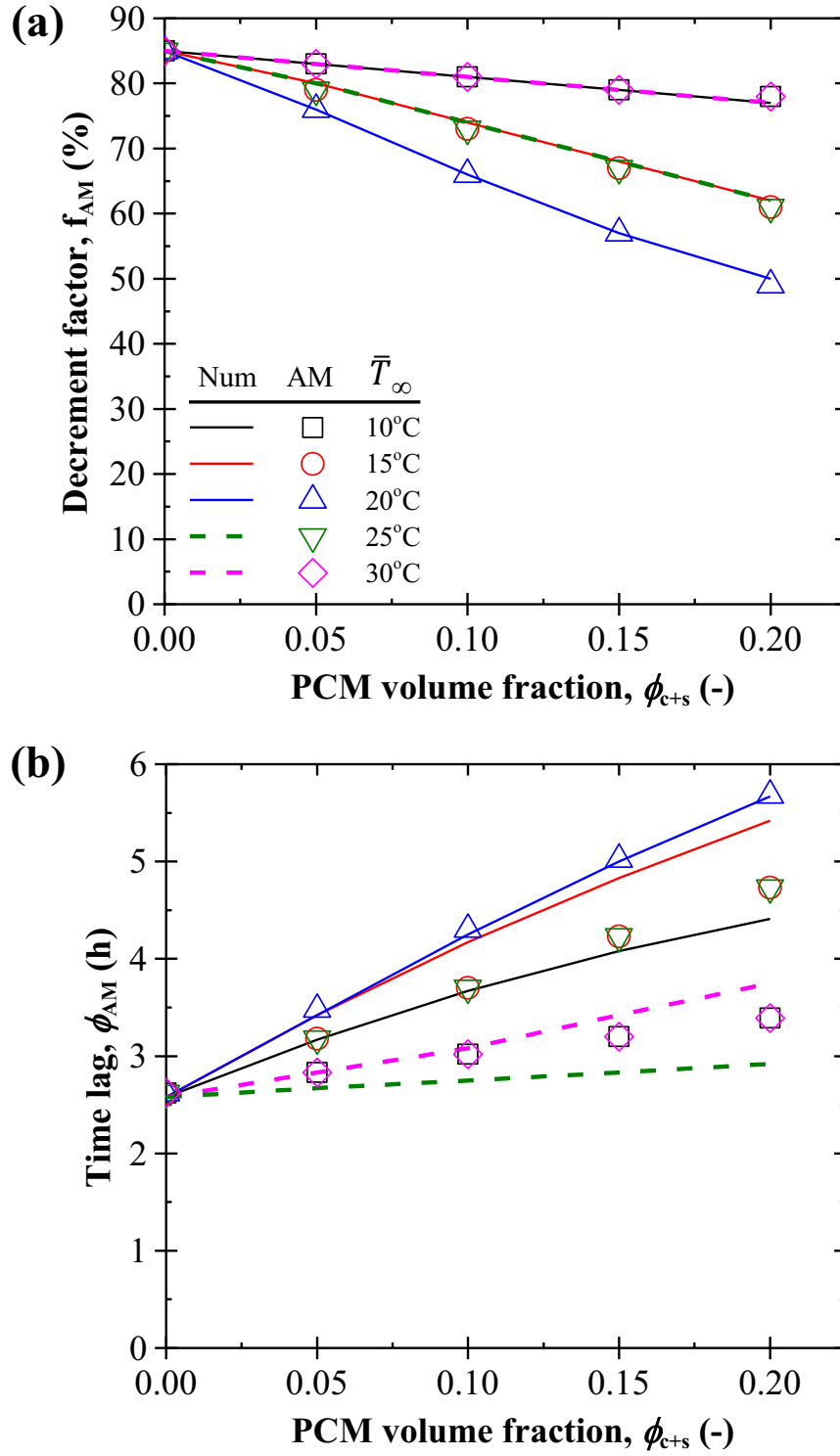


Figure 7.4: (a) Admittance method decrement factor f_{AM} and (b) time lag ϕ_{AM} as functions of PCM volume fraction ϕ_{c+s} predicted numerically and using the admittance method for a composite wall subjected to a sinusoidal outdoor temperature $T_{\infty}(t)$ with an average value $\bar{T}_{\infty}$ ranging from 10 to 30°C.

The decrement factor f_{AM} predicted using the admittance method agreed with numerical predictions within 2% for all outdoor temperature conditions and PCM volume fractions considered.

Figure 7.4b shows that the numerically predicted admittance method time lag ϕ_{AM} increased with increasing microencapsulated PCM volume fraction ϕ_{c+s} for all outdoor temperature conditions. The addition of microencapsulated PCM had the largest effect on the predicted time lag ϕ_{AM} when the daily-averaged outdoor temperature $\bar{T}_{\infty}$ was equal to the indoor temperature T_{in} of 20°C. The numerically predicted time lag ϕ_{AM} was larger when the daily-averaged outdoor temperature $\bar{T}_{\infty}$ was below the indoor temperature T_{in} than when it was above T_{in} . By contrast, ϕ_{AM} predicted using the admittance method was identical between cases when the daily-averaged outdoor temperature $\bar{T}_{\infty}$ was symmetric about the phase change temperature T_{pc} and indoor temperature T_{in} . Despite this discrepancy, the time lag ϕ_{AM} predicted using the admittance method agreed with numerical predictions within 1 hour for all temperature conditions and PCM volume fractions considered.

Figures 7.5a, 7.5b, and 7.5c plot the inner wall surface heat flux $q_L''(t)$ as a function of time predicted numerically and using the admittance method for a single layer PCM-concrete wall subjected to a sinusoidal outdoor temperature $T_{\infty}(t)$ with a daily-averaged value $\bar{T}_{\infty}$ of 10, 20, and 30°C, respectively. In all cases, the addition of microencapsulated PCM decreased the amplitude of oscillation in the inner wall heat flux $q_L''(t)$. As in the case of the decrement factor and time lag, the addition of PCM had the greatest effect on the numerically predicted inner wall heat flux $q_L''(t)$ when the average outdoor temperature $\bar{T}_{\infty}$ was equal to the indoor temperature T_{in} . Figures 7.4a and 7.5 illustrate that a decrease in the decrement factor f_{AM} corresponds to a decrease of the thermal load through a PCM-composite wall.

Figures 7.5a and 7.5c show that, when $\bar{T}_{\infty}$ was smaller or greater than T_{pc} , the addition of microencapsulated PCM delayed the inner wall surface heat flux $q_L''(t)$ during the second or first half of the diurnal cycle, respectively. This is because the temperature within the wall was inside the phase change region ($T_{pc} \pm \Delta T_{pc}$) during the second or first half of the day, respectively. Since the numerically predicted time lag ϕ_{AM} was defined as the time shift in the maximum inner wall surface heat flux $q_L''(t)$, it was larger when phase change coincided

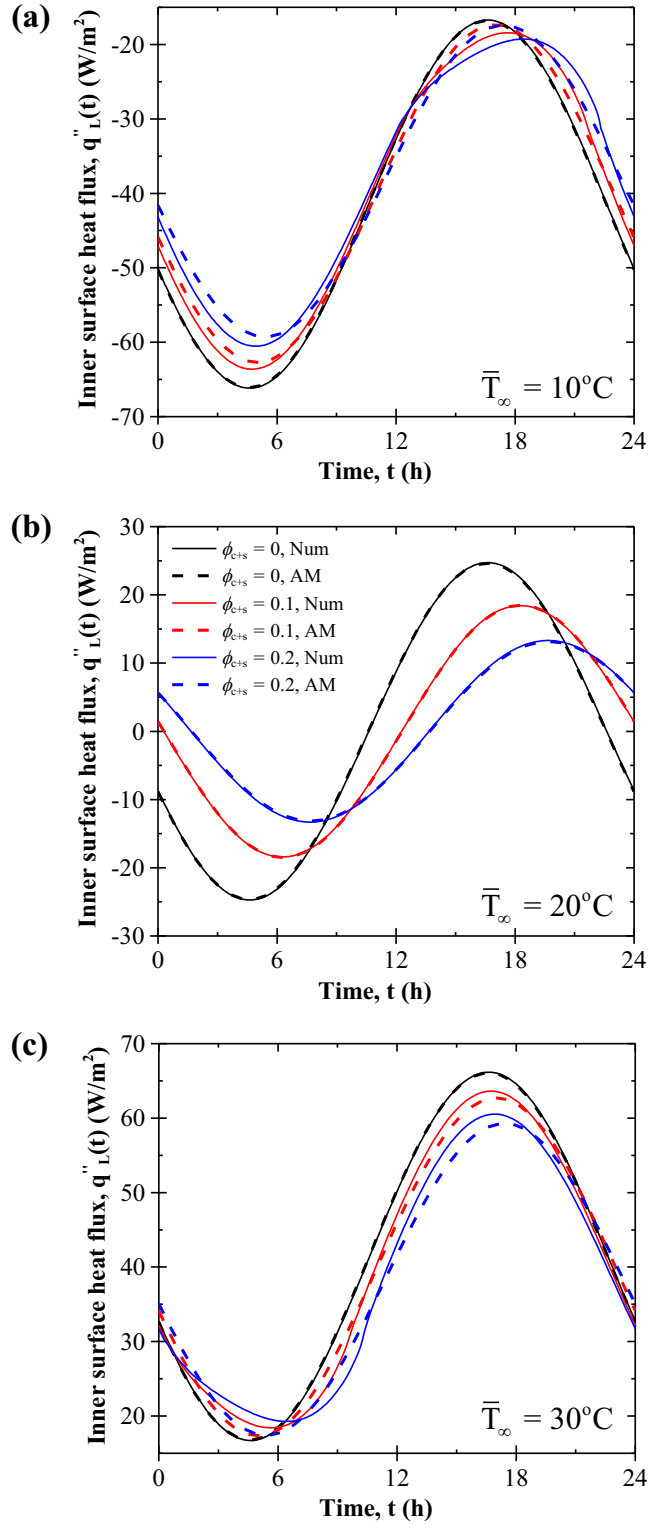


Figure 7.5: Inner wall surface heat flux $q''_L(t)$ as a function of time predicted numerically and using the admittance method for a wall containing up to 20 vol.% PCM and subjected to a sinusoidal outdoor temperature $T_\infty(t)$ with an average value $\bar{T}_\infty$ of (a) 10°C , (b) 20°C , and (c) 30°C .

with the maximum sol-air temperature (Figure 7.5a). On the other hand, the time lag ϕ_{AM} predicted using the admittance method was based on the assumption that phase change was distributed evenly across the entire range of wall temperature variation $T_z \pm \Delta T_z$. Thus, the time lag ϕ_{AM} was equivalent at every time during the day. When the average outdoor temperature $\bar{T}_\infty$ was equal to the phase change temperature T_{pc} (Figure 7.5b), the inner wall surface heat flux $q_L''(t)$ predicted using the admittance method agreed very well with that predicted numerically. In this case, phase change, defined by the effective heat capacity method [Equation (7.26)], occurred much more evenly throughout the diurnal cycle. Thus, the assumption of evenly-distributed phase change described phase change behavior in the numerical model more closely.

Figure 7.6 plots the diurnal energy flux reduction E_r as a function of microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0 to 0.2 predicted numerically and using the admittance method for the same conditions considered in Figures 7.4 and 7.5. For all cases

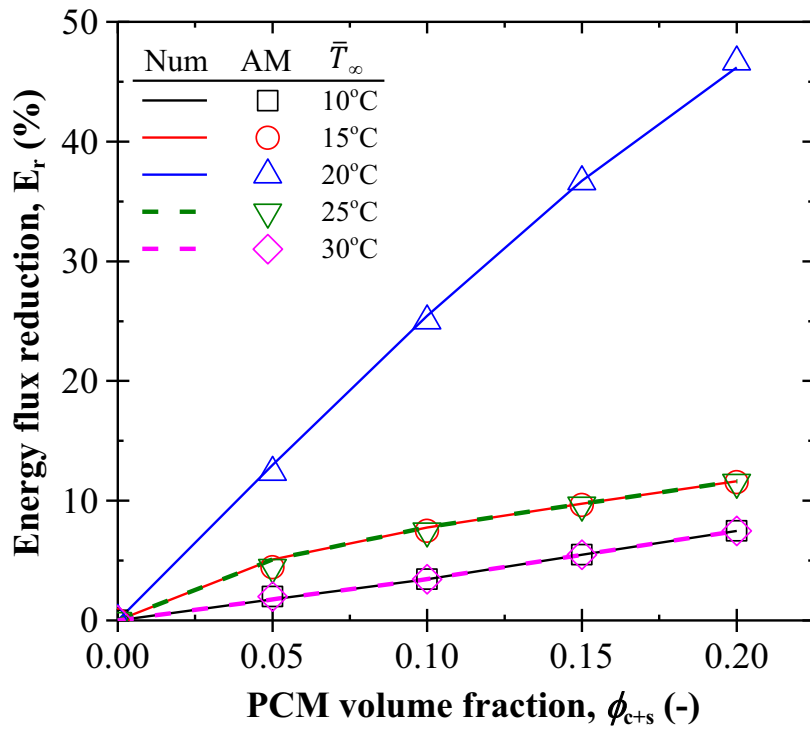


Figure 7.6: Energy flux reduction E_r as a function of PCM volume fraction ϕ_{c+s} predicted numerically and using the admittance method for a wall subjected to sinusoidal outdoor temperature $T_\infty(t)$ with an average value $\bar{T}_\infty$ ranging from 10 to 30°C.

considered, the energy flux reduction E_r increased with increasing microencapsulated PCM volume fraction ϕ_{c+s} . As was the case with the decrement factor f_{AM} , time lag ϕ_{AM} , and inner wall surface heat flux $q_L''(t)$, the addition of microencapsulated PCM had the largest impact on the energy flux reduction E_r when the daily-averaged outdoor temperature $\bar{T}_\infty$ was equal to the indoor temperature T_{in} . The energy flux reduction E_r predicted using the admittance method agreed with numerical predictions within a relative error of less than 4%, even though the predicted time lag ϕ_{AM} differed by up to an hour. This suggests that the energy flux reduction E_r is independent of the time lag ϕ_{AM} . Thus, the admittance method may be used to accurately predict the diurnal energy flux reduction E_r associated with adding microencapsulated PCM to building walls subjected to sinusoidal outdoor temperature $T_\infty(t)$ conditions.

7.3.2 Idealized sol-air temperature

The following section considers a microencapsulated PCM-concrete composite wall subjected to the same set of sinusoidal outdoor temperature $T_\infty(t)$ conditions as in Section 7.3.1 and also to an idealized solar radiation flux $q_s''(t)$ described by Equation (7.32). This non-sinusoidal sol-air temperature $T_{sa}(t)$ was decomposed into a Fourier series as described in Section 7.2.6 in order to assess the thermal response of the wall using the admittance method.

Figures 7.7a through 7.7c plot the inner wall surface heat flux $q_L''(t)$ as a function of time predicted numerically and using the admittance method for a concrete wall containing 0, 10, and 20 vol.% microencapsulated PCM. Here also, the addition of microencapsulated PCM both decreased and delayed the thermal load through the wall, as expected. Figures 7.7a and 7.7c show that the disagreement between inner wall surface heat flux $q_L''(t)$ predicted numerically and using the admittance method in cold and hot climates was more exaggerated than in the case of a sinusoidal sol-air temperature $T_{sa}(t)$. Figure 7.7b shows that $q_L''(t)$ predicted numerically and using the admittance method once again agreed well when the outdoor temperature $T_\infty(t)$ was centered around the indoor temperature T_{in} . Nu-

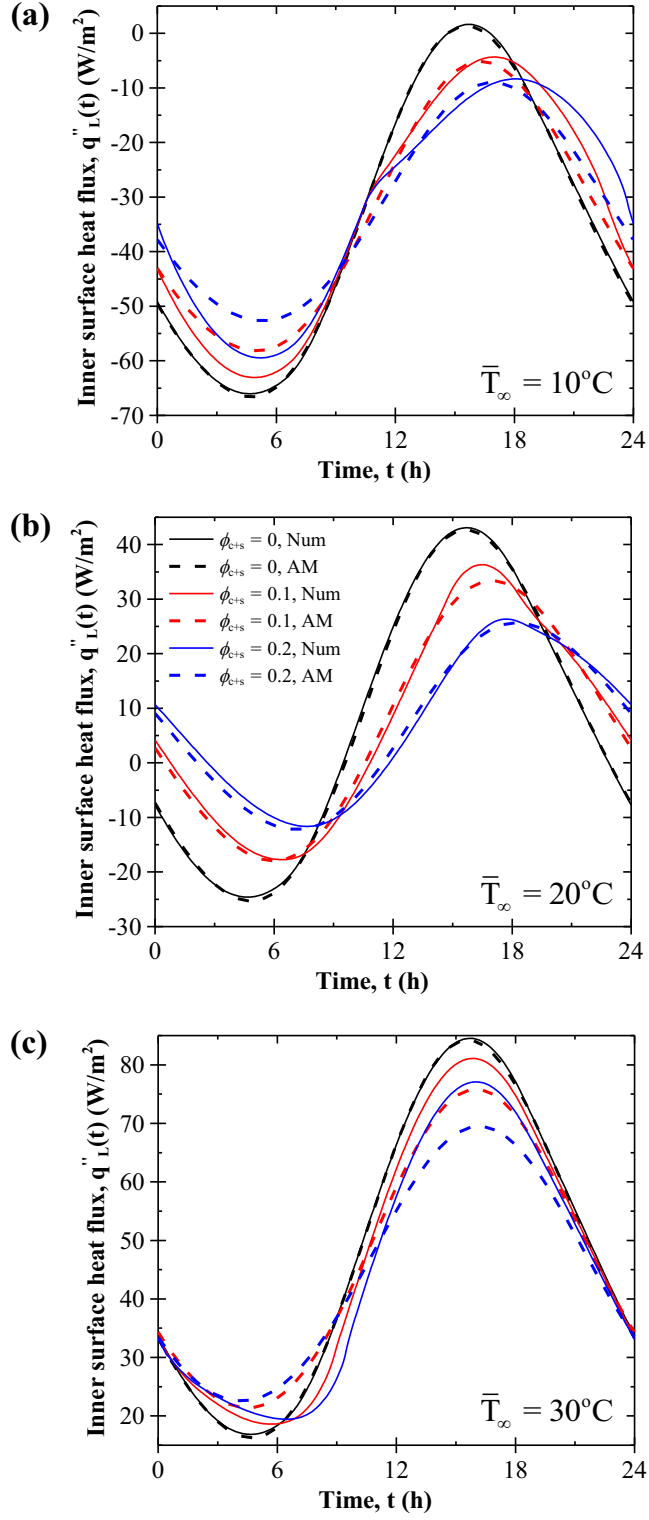


Figure 7.7: Inner wall surface heat flux $q''_L(t)$ as a function of time predicted numerically and using the admittance method for a wall containing up to 20 vol.% PCM and subjected to an idealized sol-air temperature $T_{sa}(t)$ with an average air temperature $\bar{T}_\infty$ of (a) 10°C, (b) 20°C, and (c) 30°C.

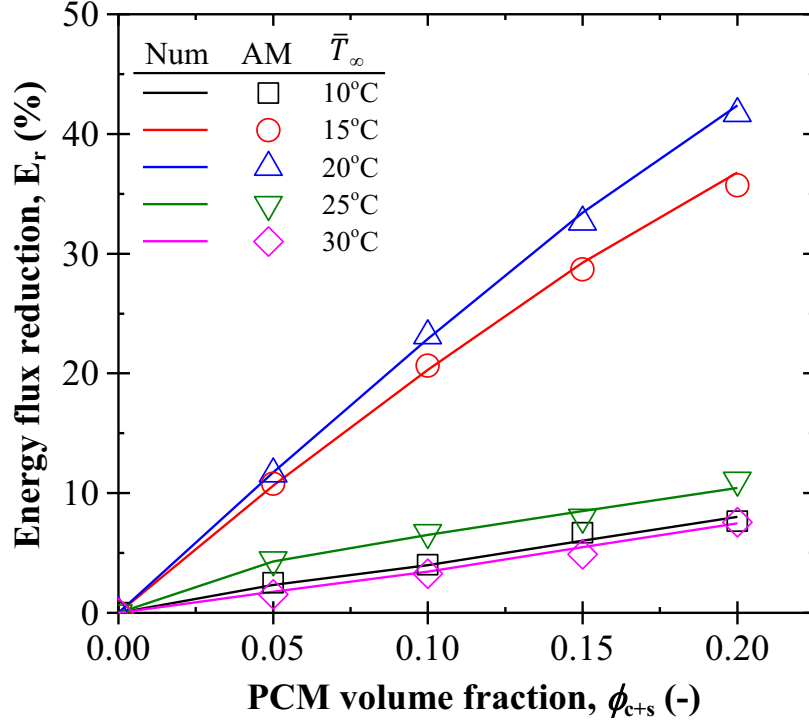


Figure 7.8: Energy flux reduction E_r as a function of PCM volume fraction ϕ_{c+s} predicted numerically and using the admittance method for a wall subjected to an idealized sol-air temperature $T_{sa}(t)$ with an average air temperature $\bar{T}_\infty$ ranging from 10 to 30°C.

merical and analytical predictions also agreed extremely well in the case of walls without microencapsulated PCM. This suggests that the transient response of a wall without PCM to a non-sinusoidal sol-air temperature can be accurately described as the superposition of its responses to each harmonic of a Fourier decomposition.

Figure 7.8 plots the diurnal energy flux reduction E_r as a function of microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0 to 0.2 predicted numerically and using the admittance method for the same set of sol-air temperature conditions considered in Figure 7.7. Here also, the diurnal energy flux reduction E_r increased with increasing microencapsulated PCM volume fraction ϕ_{c+s} . The addition of PCM had the largest effect on E_r when the daily-averaged outdoor temperature $\bar{T}_\infty(t)$ was equal to the indoor temperature $T_{in} = 20^\circ\text{C}$. Despite significant disagreement between the inner wall surface heat flux $q''_L(t)$ predicted numerically and using the admittance method (Figure 7.7), the diurnal energy flux reduction E_r agreed within an average relative error of 5% for all cases considered.

7.3.3 Realistic sol-air temperature

7.3.3.1 Single-layer wall

Figures 7.9a, 7.9b, and 7.9c plot the inner wall surface heat flux $q_L''(t)$ as a function of time predicted numerically and using the admittance method for a microencapsulated PCM-concrete wall containing 0, 10, and 20 vol.% microencapsulated PCM and subjected to a realistic sol-air temperature representative of January 1st, September 24th, and June 12th, respectively. Figures 7.9a and 7.9c show that the inner wall surface heat flux $q_L''(t)$ predicted numerically and using the admittance method agreed very well throughout most of the day for both January 1st and June 12th. These cases were similar to those represented in Figures 7.5b and 7.7b in that the sol-air temperature $T_{sa}(t)$ was centered near the phase change temperature T_{pc} . By contrast, 7.9b shows that the inner wall surface heat flux $q_L''(t)$ predicted numerically and using the admittance method for the case of September 24th agreed very poorly when PCM was included in the wall. In this case, the sol-air temperature $T_{sa}(t)$ only coincided with the phase change temperature range $T_{pc} \pm \Delta T_{pc}/2$ during a short period of the diurnal cycle. In Figures 7.9a-7.9c, the admittance method also accurately predicted the inner wall surface heat flux $q_L''(t)$ for cases without PCM.

Figure 7.10 plots the diurnal energy flux reduction E_r as a function of microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0 to 0.2 predicted numerically and using the admittance method for the same set of realistic sol-air temperature conditions considered in Figure 7.9. The diurnal energy flux reduction E_r increased with increasing microencapsulated PCM volume fraction ϕ_{c+s} . It was slightly larger on June 12th than on January 1st. This can be attributed to the fact that the sol-air temperature $T_{sa}(t)$ had a smaller amplitude of oscillation on June 12th [35]. Predictions of E_r using the admittance method agreed with those based on the numerical model within an average relative error of 6%.

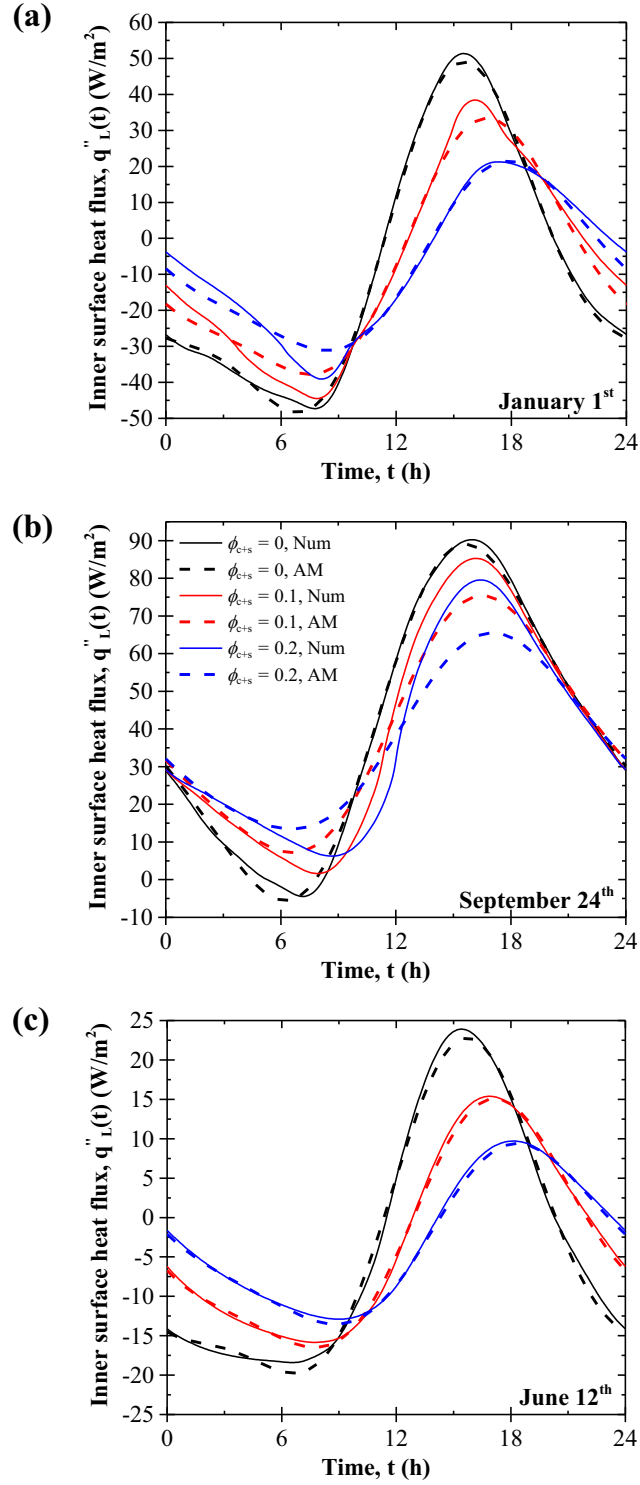


Figure 7.9: Inner wall surface heat flux $q''_L(t)$ as a function of time predicted numerically and using the admittance method for a wall containing up to 20 vol.% PCM and subjected to a realistic sol-air temperature $T_{sa}(t)$ representative of (a) January 1st, (b) September 24th, and (c) June 12th in California climate zone 9 (Los Angeles, CA).

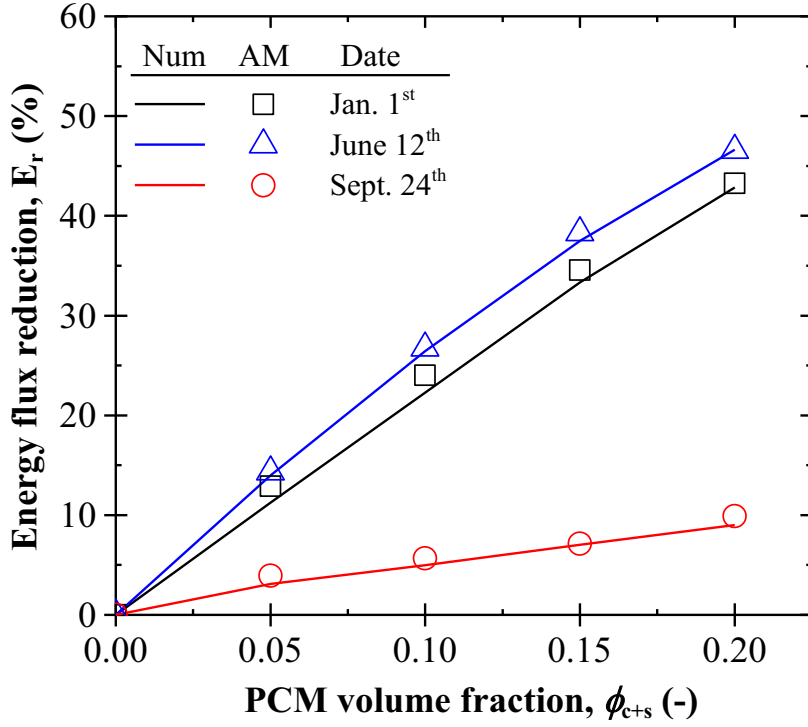


Figure 7.10: Energy flux reduction E_r as a function of PCM volume fraction ϕ_{c+s} predicted numerically and using the admittance method for a wall subjected to a realistic sol-air temperature $T_{sa}(t)$ representative of January 1st, September 24th, and June 12th in California climate zone 9 (Los Angeles, CA).

7.3.3.2 Multilayer wall

Figures 7.11a and 7.11b plot the inner wall surface heat flux $q_L''(t)$ as a function of time predicted numerically and using the admittance method for a multilayer wall containing 0, 10, and 20 vol.% microencapsulated PCM embedded within the concrete or plaster layers, respectively (see inset schematics). The wall was subjected to a realistic sol-air temperature representative of June 12th. Note that the microencapsulated PCM volume fraction ϕ_{c+s} was defined with respect to its matrix layer. Thus, the PCM-concrete configuration (Figure 7.11a) contained a much larger volume of PCM than the PCM-plaster configuration (Figure 7.11b), due to the greater thickness L_c of the concrete layer. Figures 7.11a and 7.11b show again that the addition of microencapsulated PCM reduced and delayed the inner wall surface heat flux $q_L''(t)$. Similar to Figure 7.9c, Figures 7.11a and 7.11b featured very close agreement between the inner wall surface heat flux $q_L''(t)$ predicted numerically and using

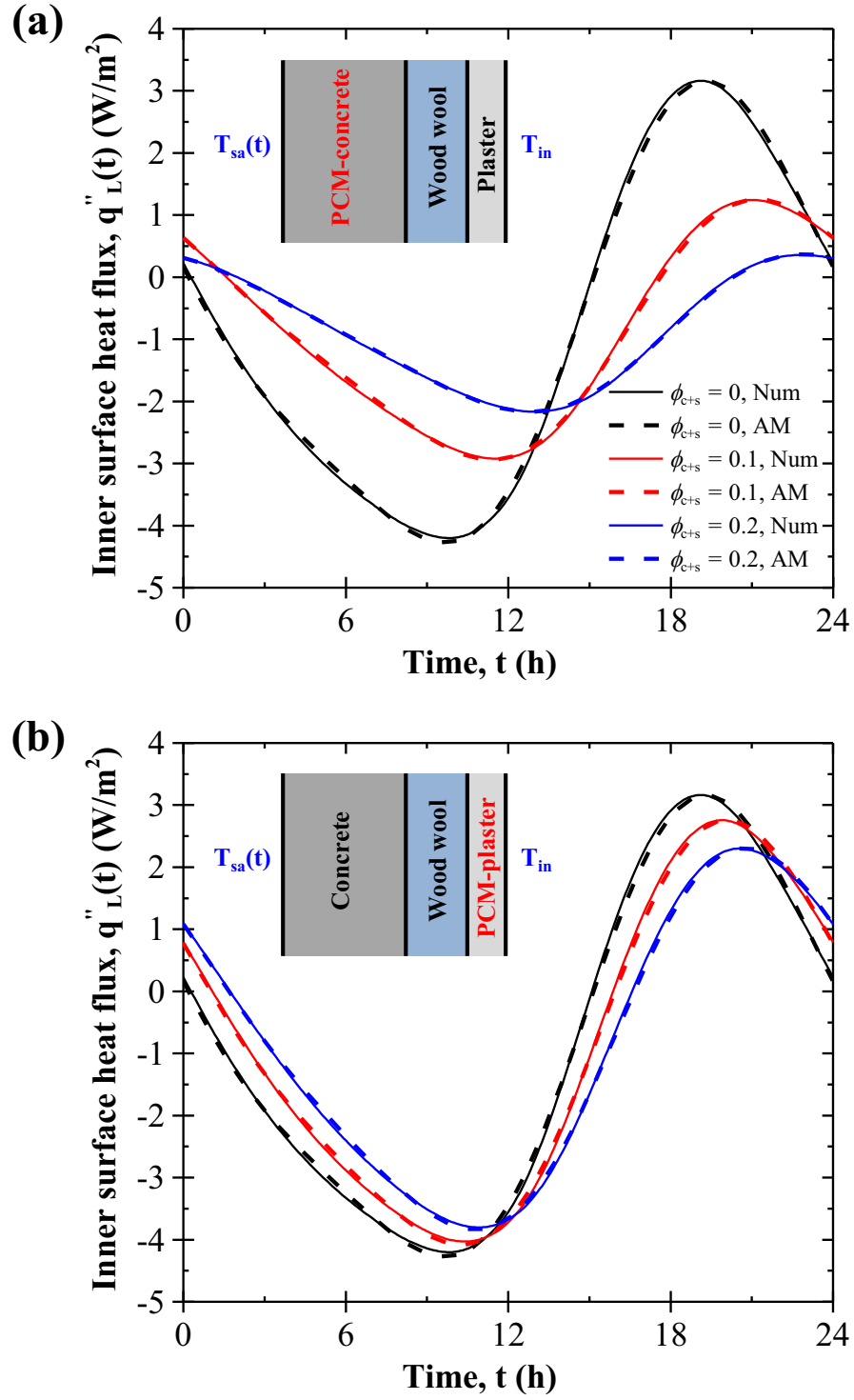


Figure 7.11: Inner wall surface heat flux $q''_L(t)$ as a function of time predicted numerically and using the admittance method for a multilayer wall containing up to 20 vol.% PCM within (a) the concrete (outside) layer or (b) the plaster (inside) layer and subjected to a realistic sol-air temperature $T_{sa}(t)$ representative of June 12th in California climate zone 9 (Los Angeles, CA).

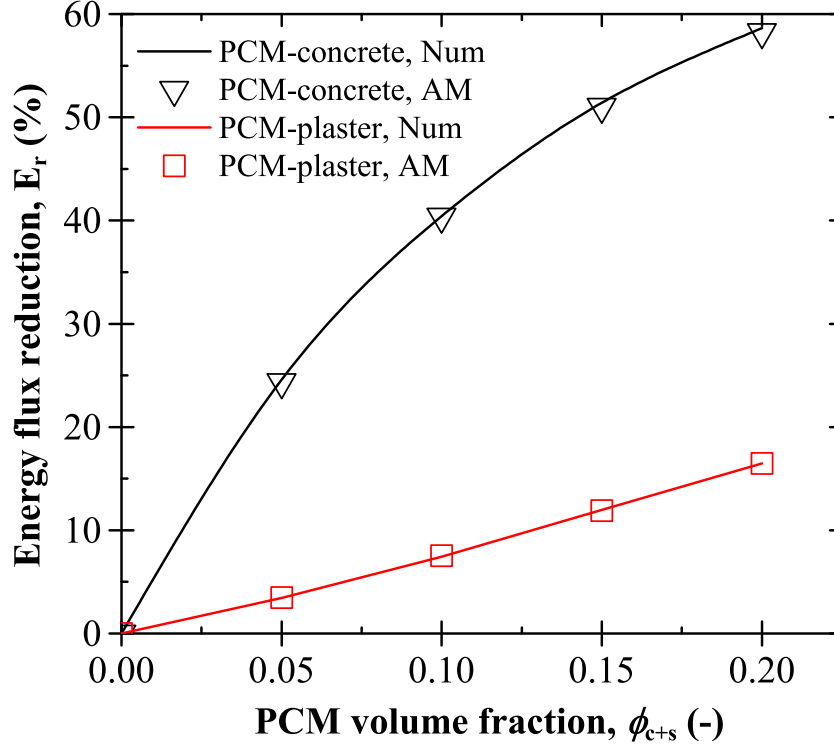


Figure 7.12: Energy flux reduction E_r as a function of PCM volume fraction ϕ_{c+s} predicted numerically and using the admittance method for a multilayer wall containing up to 20 vol.% PCM distributed throughout the concrete (outside) layer or the plaster (inside) layer and subjected to a realistic sol-air temperature $T_{sa}(t)$ representative of June 12th in California climate zone 9 (Los Angeles, CA).

the admittance method, regardless of which layer contained the PCM.

Figure 7.12 plots the diurnal energy flux reduction E_r as a function of microencapsulated PCM volume fraction ϕ_{c+s} ranging from 0 to 0.2 predicted numerically and using the admittance method for the same multilayer wall configurations considered in Figure 7.11. The diurnal energy flux reduction E_r was much larger when the PCM was embedded in the concrete layer than in the plaster layer. This was expected, as the former case included a larger volume of PCM. The predictions of E_r using the admittance method agreed with those based on the numerical model within a relative error of about 1%.

The results of the admittance method illustrated in the preceding sections obey several previously established design rules for microencapsulated PCM-composite walls: (i) adding microencapsulated PCM reduces and delays the thermal load through building walls [35],

(ii) the diurnal energy flux reduction associated with PCM-composite walls is largest in moderate climates with sol-air temperature $T_{sa}(t)$ centered near the indoor temperature T_{in} [35, 36], and (iii) the diurnal energy reduction increases as the amplitude of oscillation in the sol-air temperature $T_{sa}(t)$ decreases [35]. Across all cases considered, the admittance method accurately predicted the diurnal energy flux reduction E_r . In a previous study [36], we showed that adding microencapsulated PCM to building walls could also offer electricity cost-savings. This was a result of shifting the maximum thermal load through a building wall to a later time when electricity was offered at a cheaper rate. The admittance method did not accurately predict the transient inner wall surface heat flux $q_L''(t)$ in cases where the sol-air temperature $T_{sa}(t)$ was not centered near the indoor temperature T_{in} . This suggests that the admittance method may only be capable of accurately predicting cost savings associated with using microencapsulated PCM to take advantage of time-of-use electricity pricing in moderate climates.

7.4 Conclusion

This study presented a novel extension of the admittance method and illustrated its use in the assessment of (i) the dynamic thermal response of a building wall to realistic sol-air temperature conditions and (ii) the energy benefits of adding microencapsulated PCM to a single or multilayer building wall. The proposed method predicted the diurnal energy flux reduction E_r associated with adding PCM to single or multilayer walls subjected to idealized or realistic sol-air temperatures to within 6% of numerical predictions. The results observed several previously established design rules for PCM-composite building materials. By setting up a computational loop, this procedure may be used to determine the annual energy flux reduction associated with PCM-composite materials. It could also be used to evaluate PCM-composite walls featuring alternative PCM incorporation methods such as shape-stabilized PCM (SSPCM) layers. The extended admittance method offers a faster and simpler alternative to traditional finite element methods for evaluating the energy benefits of PCM-composite building materials.

CHAPTER 8

Summary, Conclusions, and Future Work

8.1 Summary

This study was focused on the thermal evaluation of microencapsulated PCM-composite materials as a smart multifunctional building envelope to reduce peak and total energy consumption and to temporally shift the peak electricity loads associated with HVAC in residential and commercial buildings. The following section summarizes the conclusions drawn from this work.

Steady-state numerical simulations were used to predict the effective thermal conductivity of core-shell-matrix composite materials. It was established that: (i) The effective thermal conductivity was independent of the capsules' spatial distribution and size distribution. (ii) The effective thermal conductivity depended solely on the core and shell volume fractions and on the core, shell, and matrix thermal conductivities. (iii) The Felske model [Equation (3.17)] predicted the effective thermal conductivity of the composite material within numerical uncertainty for the wide range of parameters considered.

Diurnal transient numerical simulations were performed on microencapsulated PCM-composite walls subjected to sinusoidal outdoor temperature and solar radiation heat flux. It was established that: (i) A composite wall containing microencapsulated PCMs can be accurately represented by a homogeneous wall with effective volumetric heat capacity and effective thermal conductivity given by Equations (4.10), and (4.12), respectively. (ii) Adding microencapsulated PCM to concrete walls and increasing the latent heat of fusion both substantially reduced and delayed the thermal load on the building. (iii) The phase change temperature leading to the maximum energy savings was equal to the desired indoor tem-

perature regardless of the climate conditions. (iv) In extremely hot or cold climates, the use of PCM delayed the thermal load to take advantage of TOU pricing. However, the energy savings were not significant. Section 4.3.3 suggested that adding microencapsulated PCM to concrete walls could maintain a constant diurnal energy flux while substantially reducing the wall thickness. As an alternative to microencapsulated PCM addition to reduce building energy consumption, this strategy may offer financial savings on concrete material while using less microencapsulated PCM within the wall.

Annual transient numerical simulations were performed on microencapsulated PCM-composite walls subjected to outdoor temperature and solar radiation heat flux based on actual weather data representative of Los Angeles and San Francisco, CA. It was established that: (i) The annual energy and cost savings were maximized when the phase change temperature was near the desired indoor temperature. (ii) The annual energy reduction and cost savings were the largest for the South- and West-facing walls and during the summer in the climates considered. (iii) The annual combined heating and cooling load reduction for an average-sized single family residence ranged from 9-18% and from 17-32% in San Francisco and in Los Angeles, respectively, for PCM volume fraction ranging from 0.1 to 0.3. (iv) The corresponding electricity cost savings ranged from \$37-\$44 in San Francisco and from \$95-\$145 in Los Angeles. (v) The payback period associated with adding microencapsulated PCM to a home in San Francisco was substantially longer than in Los Angeles for a given price of PCM.

An energy indicator was introduced as a novel figure of merit to quantify the thermal performance of PCM-composite materials. It was established that: (i) The energy indicator can be evaluated based on a single heating, hold, and cooling test encompassing the PCM phase change temperature window at any ramp rate. (ii) Numerical predictions of the center-point temperature within cylindrical PCM-mortar composite specimens and the associated predictions of the energy indicator agreed very well with experimental measurements. (iii) The energy indicator was found to (1) increase linearly with increasing microencapsulated PCM volume fraction ϕ_{c+s} and latent heat of fusion h_{sf} , (2) increase quadratically with the specimen radius r_i , and (3) decrease with increasing PCM thermal conductivity k_c . (iv)

The energy indicator measured for small cylindrical specimens was shown to correlate with the diurnal energy flux reduction achieved by adding microencapsulated PCM to a concrete wall.

The widely-used admittance method was extended to account for the effects of phase change on the thermal load passing through PCM-composite building walls subjected to realistic outdoor temperature and solar radiation flux. The analytical results for the thermal load passing through PCM-composite walls agreed very well with those predicted using detailed finite element simulations. The speed and simplicity of the admittance method can enable straightforward evaluation of the energy benefits of PCM-composite walls through user-friendly design software for a wide range of users.

8.2 Conclusions

This study established that there are significant potential energy and financial benefits associated with microencapsulated PCM-composite building envelopes. Moving forward, practical implementation of this technology should be focused on cities with large populations and moderate climates. For example, Los Angeles comprised more than 25% of the population of California in 2014 [157] and was shown to have a favorable climate for microencapsulated PCM-composite building walls. Chapter 5 established that, while increasing the volume fraction of PCM within the building envelope substantially enhanced the annual energy savings in Los Angeles, it also lengthened the payback period. To counteract this, the payback period could be reduced by several mechanisms: (i) reducing the bulk price of microencapsulated PCM, (ii) providing financial incentives such as governmental subsidies, and (iii) increasing the peak and/or base cost of electricity. Chapter 5 suggested that, in the absence of financial incentives and for current electricity prices, the price of microencapsulated PCM will need to fall below about \$1.00/kg in order to achieve a payback period of less than 10 years for a single-family home located in Los Angeles. This value can serve as a target for manufacturers of microencapsulated PCM to encourage use of the material within buildings.

8.3 Future work

The following sections present recommendations for future modeling and simulation efforts to further investigate and exploit the potential benefits of microencapsulated PCM-composite materials in structural concrete elements and energy efficient buildings.

8.3.1 Effective coefficient of thermal expansion of core-shell-matrix composites

The incorporation of phase change materials has been demonstrated as a means to mitigate thermal cracking in restrained concrete elements including pavement and bridge decks [158]. Detailed numerical simulations, such as those presented in Chapters 4 and 5, could support further investigation of PCM addition as a method of crack mitigation. For the sake of computational speed and simplicity, it is useful to simulate microencapsulated PCM-composite materials as homogeneous with effective thermal and mechanical properties. Chapters 3 and 4 identified and validated effective medium approximations (EMAs) which accurately predict the effective thermal conductivity k_{eff} and the effective volumetric heat capacity $(\rho c_p)_{eff}$ of core-shell-matrix composites. Young et al. [1] identified EMAs that accurately predicted the Young's modulus E_{eff} and Poisson's ratio ν_{eff} of core-shell-matrix composites. A similar approach could be used to predict the effective coefficient of thermal expansion CTE_{eff} of core-shell-matrix composites. More specifically, the same core-shell-matrix (a) simple, (b) body-centered, and (c) face-centered cubic unit cell packing arrangements as well as (d) monodisperse and (e) polydisperse microcapsules randomly distributed in a continuous matrix could be used. First, the effects of spatial and size distributions on the effective coefficient of thermal expansion should be elucidated. Second, the effects of the volume fraction and coefficient of thermal expansion of each constituent material should be studied parametrically. Finally, the effective coefficient of thermal expansion CTE_{eff} predicted using detailed numerical simulations of heterogeneous unit cells should be compared with that predicted by EMAs available from the literature [159–161]. The results could be used to identify design and implementation rules to minimize the thermal stress and minimize early age and/or fatigue cracking in concrete pavement. Questions of practical interest in-

clude the following: what is the optimal (i) microencapsulated PCM volume fraction and (ii) phase change temperature, (iii) what is the best season of the year and time of the day to pour concrete, and (iv) how much could microencapsulated PCM addition extend the life of concrete pavement?

8.3.2 Evaluation of buildings with PCM-composite walls using the complete admittance method

The admittance method involves the definition of five so-called “dynamic thermal properties,” namely,

1. The periodic thermal transmittance X is defined as “*the cyclic heat flux released from the inner surface of the wall per unit cyclic temperature variation imposed on the other side of the wall, while holding a constant indoor temperature*” [146].
2. The decrement factor f_{AM} is defined as the periodic thermal transmittance X normalized by the overall heat transfer coefficient U , i.e., $f_{AM} = |X/U|$ [146].
3. The time lag ϕ_{AM} represents the difference between the time (in hours) when the inner wall surface heat flux and the sol-air temperature reached their respective maximum [Equation (7.12)] [146].
4. The thermal admittance Y is defined as “*the cyclic heat flux entering the inner surface of the wall per unit cyclic temperature variation imposed on the same side, while holding a constant outer temperature*” [146].
5. The surface factor F “*quantifies the thermal flux released by a wall to the environmental point per unit heat gain impinging on its internal surface, when the air temperatures on both sides of the wall are held equal*” [146].

All of these parameters can be determined using the transmission matrices of the building envelope components [Equations (7.8) through (7.10)]. In fact, Rees and colleagues provided a thorough qualitative [152] and quantitative [154, 155] discussion of the admittance method

procedure, using these five variables, to predict the indoor air temperature within an entire building. Marletta et al. [146] used all of the dynamic thermal properties to predict the indoor air temperature evolution within an entire room subjected to realistic outdoor sol-air temperature variation.

Chapter 7 extended the admittance method to evaluate the thermal load passing through single or multilayer walls containing microencapsulated PCM. This was accomplished by introducing the modified PCM specific heat $c'_{p,c}$ into the transmission matrices of the building envelope to determine only two dynamic thermal properties, namely, the decrement factor f_{AM} and time lag ϕ_{AM} . This same approach can be used to modify the other dynamic thermal properties mentioned above. This would enable the complete admittance method to predict indoor air temperature within an entire building with a PCM-composite envelope as an alternative to finite element models, which can be time consuming. These results would be useful in elucidating the effects of PCM addition on the energy consumed by the active heating and/or cooling system within the building.

8.3.3 Control strategies for buildings with PCM-composite walls

These outcomes would be achieved through the operation of a building's heating, ventilation, and air conditioning (HVAC) system in response to the thermal loads on the building. The present study demonstrated that microencapsulated PCM addition can reduce and delay the peak passive thermal load through building walls. It remains to be investigated how an active building HVAC system could be used to exploit these effects. An appropriate building HVAC control scheme could optimize energy use and space conditioning and shift electricity consumption to a less expensive time of day by monitoring the thermal load passing through the PCM-composite building envelope. As a result, the energy and/or financial cost associated with heating and cooling residential and commercial buildings could be significantly reduced. It could also help ratepayers save money while enhancing occupant comfort levels.

Knowledge of the indoor air temperature evolution is required to evaluate the efficacy

and energy consumption of heating and cooling control strategies for buildings with PCM-composite envelopes. Indoor air temperature control within buildings with PCM-composite envelopes could be simulated using either (1) a finite element model of a building with PCM-composite walls that accounts for sensible heat storage by the indoor air or (2) a building model based on the five dynamic thermal properties determined using the admittance method to determine the time-dependent indoor air temperature. The study should assess whether the benefits associated with adding PCM to building walls could be augmented by improving upon classical feedback air temperature control schemes, e.g., on-off and proportional-integral-differential (PID) control, most commonly used in buildings [162]. For example, model-predictive control (MPC) has recently received special attention for HVAC control in buildings for several reasons [162]. Most notably, MPC can take anticipatory rather than corrective control actions and is sensitive to time-varying system dynamics, a wide range of operating conditions, and slow-moving processes with time delays [162]. An HVAC system controlled by MPC could anticipate and adjust for the presence of phase change materials, time-dependent indoor air temperature set point, and time-of-use electricity pricing in order to maximize energy and/or cost savings.

8.3.4 PCM-composite Trombe walls for thermal management in hot and cold climates

Chapters 4 and 5 demonstrated that building envelopes containing microencapsulated PCM did not offer significant energy savings via phase change in extremely hot and cold climates. As an alternative, Trombe walls, also known as storage walls or solar heating walls (SHW), can aid in the ventilation, heating, and cooling of buildings [163]. Trombe walls are located within buildings and are composed of a material with a large volumetric heat capacity, such as concrete, brick, or stone [163]. During the day, traditional Trombe walls store thermal energy as they are heated by incident solar radiation flux. Then at night, they release that thermal energy, thus passively heating the building interior. Saadatian et al. [163] discussed the various types of Trombe walls and provided a detailed review of their experimental and numerical evaluation for buildings. Trombe walls containing microencapsulated PCM could

be a promising means to take advantage of phase change materials in buildings located in hot or cold climates. Sharma et al. [7] reviewed several experimental and numerical investigations of PCM-composite Trombe walls for buildings. They concluded that such walls were more convenient than traditional Trombe walls since they require less space for the same thermal energy storage capacity [7]. Castellón et al. [164] experimentally demonstrated that a microencapsulated PCM-Trombe wall reduced the amplitude of temperature oscillation within a small building. Berroug et al. [165] used numerical simulations to evaluate an idealized pure PCM Trombe wall for use in greenhouses to protect plants from extremely cold temperatures .

Detailed numerical simulations of buildings with PCM-composite Trombe walls could be useful to inform their design and implementation. A study should be executed with the aim of evaluating (i) the optimal phase change temperature T_{pc} for PCM-composite Trombe walls as well as their effects on (ii) the thermal comfort of occupants and on (iii) the energy consumption associated with maintaining the desired indoor air temperature. Numerical simulations could be facilitated by comprehensive building evaluation software such as EnergyPlus [68–70] or by simplified methods such as the complete admittance method accounting for phase change, as discussed in Section 8.3.2.

8.3.5 Instructional application for heat transfer through plane-parallel walls

It could be instructive to provide non-specialists with an interactive and user-friendly application that would facilitate the visualization of the impact of thermal properties and design parameters on the periodic thermal load through plane parallel walls. For example, such an application could inform material selection and wall design by home owners, architects, and developers for new or retrofit constructions. In addition, heat conduction through plane-parallel walls is one of the first topics that is covered in introductory heat transfer courses. The application could help students to understand the role that various material choices, arrangements, and dimensions play in transient conduction through walls. More specifically, the application should enable users to explore the effects of adjusting (i) the thermal prop-

erties or (ii) thicknesses of wall layers as well as (iii) the convective heat transfer coefficients at each surface on the periodic temperature and heat flux evolution at the inner and outer wall surfaces. They could also explore the relationship between the temperature and heat flux at each of these surfaces.

The admittance method presented in Chapter 7 offers a computationally simple means to evaluate the one-dimensional (1D) thermal load passing through single or multilayer plane-parallel walls subjected to convective heat transfer to a periodic temperature on one side and to a constant temperature on the other. If this method were coded into an application, the user would provide the (i) thermal conductivity k , (ii) density ρ , (iii) specific heat capacity c_p , and (iv) thickness of each wall layer as well as the (v) convective heat transfer coefficient at each wall surface and (vi) imposed periodic temperature profile. Then, the periodic temperature and heat flux evolution at the inner and outer surfaces would be given as output values.

APPENDIX A

Supplementary material for Chapter 4

A.1 MatLab function to predict the effective thermal conductivity of core-shell-matrix composites using the Felske model

```
function k_eff = felske(phi_c,phi_s,k)

% Computation of the effective thermal conductivity of a composite
% consisting of core-shell particles distributed in a continuous matrix

% Origin of the model:
% J.D. Felske, Int. J. Heat Mass Transfer, vol. 47, 2004

%%Inputs
% phi_c = volume fraction of core material
% phi_s = volume fraction of shell material
% k = thermal conductivity array, i.e., [core shell matrix] [W/(m K)]

Phi = phi_s/phi_c; %ratio of shell to core volume fractions
k_cs = k(1)/k(2); %ratio of core to shell thermal conductivity
k_cm = k(1)/k(3); %ratio of core to matrix thermal conductivity
k_sm = k(2)/k(3); %ratio of shell to matrix thermal conductivity

k_eff = (k(3)*(1-phi_c-phi_s)*(6+4*Phi+2*Phi*k_cs)+(1+2*phi_c+2*phi_s)*...
    ((3+Phi)*k(1)+2*Phi*k(2)))/((2+phi_c+phi_s)*(3+2*Phi+Phi*k_cs)+...
    (1-phi_c-phi_s)*((3+Phi)*k_cm+2*Phi*k_sm)); %effective thermal conductivity
end
```

A.2 MatLab function to predict the effective volumetric heat capacity of core-shell-matrix composites

```
function results = rho_cp_eff(phi_c,phi_s,rho,c_p)

% Computation of the effective volumetric heat capacity of a composite
% consisting of core-shell particles distributed in a continuous matrix

%%Inputs
% phi_c = volume fraction of core material
% phi_s = volume fraction of shell material
% rho = density array, i.e., [core shell matrix] [kg/m^3]
% c_p = specific heat array, i.e., [core shell matrix] [J/(kg K)]

rho_cp_eff = phi_c*(rho(1)*c_p(1))+phi_s*(rho(2)*c_p(2))+(1-phi_c-phi_s)...
    *(rho(3)*c_p(3)); %effective volumetric heat capacity [J/(m^3 K)]
rho_eff = phi_c*(rho(1))+phi_s*(rho(2))+(1-phi_c-phi_s)...
    *(rho(3)); %effective density [kg/m^3]
cp_eff = rho_cp_eff/rho_eff; %effective specific heat capacity [J/(kg K)]
results = [rho_cp_eff rho_eff cp_eff];
end
```

APPENDIX B

Supplementary material for Chapter 5

B.1 MatLab function to integrate inner wall surface heat flux

```
function result = Qflux(A)

%% Calculation of the total, heating, and cooling energy fluxes from heat
%flux data

%%Inputs
% A = array containing inner wall surface heat flux for n cases, i.e.,
%[time qflux_1 qflux_2...qflux_n]
% Units: time [s] and heat flux [W/m^2]

%format long
B = abs(A);
S = size(A); %size of data array
Qflux = zeros(3,S(2)-1); %initialize

%Total energy flux
for j = 1:S(2)-1
Qflux(1,j) = trapz(B(:,1),B(:,j+1)); %integrate over time using the
%trapezoidal rule
end

%Heating energy flux
for j = 1:S(2)-1
```

```

for i = 1:S(1)-1
    if A(i,j+1) <= 0 || A(i+1,j+1) <= 0 %only integrate negative heat flux
Qflux(2,j) = Qflux(2,j) + 0.5*(B(i+1,1)-B(i,1))*(B(i+1,j+1)+B(i,j+1));
%integrate over time using the trapezoidal rule
    else Qflux(2,j) = Qflux(2,j);
    end
end
end

%Cooling energy flux
for j = 1:S(2)-1
for i = 1:S(1)-1
    if A(i,j+1) > 0 || A(i+1,j+1) > 0 %only integrate positive heat flux
Qflux(3,j) = Qflux(3,j) + 0.5*(B(i+1,1)-B(i,1))*(B(i+1,j+1)+B(i,j+1));
%integrate over time using the trapezoidal rule
    else Qflux(3,j) = Qflux(3,j);
    end
end
end
end

result = Qflux;

```

B.2 MatLab functions to integrate inner wall surface heat flux during time-of-use periods

B.2.1 Los Angeles: winter

```

%% Function to calculate the energy flux reduction from heat flux data

function result = Coolflux.Win_LA(A)

%format long
S = size(A); %size of data array

```

```

Coolflux_Win_LA = zeros(2,S(2)-1); %initialize
for d = 1:365
    C = A((72*(d-1)+1):(72*d+1),:); %array containing inner wall
    %surface heat flux for day d
    B = abs(C);
    T = size(C);
    TOU = 3600*[10 20]+86400*(d-1); %time of use periods (in seconds)
for j = 1:T(2)-1
for i = 1:T(1)-1
    if d <= 151 || d >= 274 %if it is winter time
    if C(i,j+1) >= 0 || C(i+1,j+1) >= 0 %if cooling is required
    if C(i,1) < TOU(1) || C(i,1) > TOU(2) %if it is off-peak time
Coolflux_Win_LA(1,j) = Coolflux_Win_LA(1,j) + 0.5*(B(i+1,1)-C(i,1))*...
    (B(i+1,j+1)+C(i,j+1)); %integrate over time using the trapezoidal rule
    else %if it is peak time
Coolflux_Win_LA(2,j) = Coolflux_Win_LA(2,j) + 0.5*(B(i+1,1)-C(i,1))*...
    (B(i+1,j+1)+C(i,j+1));
    end
    else
        Coolflux_Win_LA(1,j) = Coolflux_Win_LA(1,j);
        Coolflux_Win_LA(2,j) = Coolflux_Win_LA(2,j);
    end
end
end
end

result = Coolflux_Win_LA;

end

```

B.2.2 Los Angeles: summer

```

%% Function to calculate the energy flux reduction from heat flux data

```

```

function result = Coolflux_Sum_LA(A)

%format long
S = size(A); %size of data array
Coolflux_Sum_LA = zeros(3,S(2)-1); %initialize
for d = 152:273
    C = A((72*(d-1)+1):(72*d+1),:); %array containing inner wall
    %surface heat flux for day d in summer
    B = abs(C);
    T = size(C);
    TOU = 3600*[10 13 17 20]+86400*(d-1); %time of use periods
    %(in seconds)
    for j = 1:T(2)-1
        for i = 1:T(1)-1
            if C(i,j+1) >= 0 || C(i+1,j+1) >= 0 %if cooling is required
                if C(i,1) < TOU(1) || C(i,1) > TOU(4) %if it is off-peak time
                    Coolflux_Sum_LA(1,j) = Coolflux_Sum_LA(1,j) + 0.5*(B(i+1,1)-B(i,1))*...
                        (B(i+1,j+1)+B(i,j+1)); %integrate over time using the trapezoidal rule
                elseif C(i,1) < TOU(2) || C(i,1) > TOU(3) %if it is mid-peak time
                    Coolflux_Sum_LA(2,j) = Coolflux_Sum_LA(2,j) + 0.5*(B(i+1,1)-B(i,1))*...
                        (B(i+1,j+1)+B(i,j+1));
                else %if it is peak time
                    Coolflux_Sum_LA(3,j) = Coolflux_Sum_LA(3,j) + 0.5*(B(i+1,1)-B(i,1))*...
                        (B(i+1,j+1)+B(i,j+1));
                end
            else
                Coolflux_Sum_LA(1,j) = Coolflux_Sum_LA(1,j);
                Coolflux_Sum_LA(2,j) = Coolflux_Sum_LA(2,j);
                Coolflux_Sum_LA(3,j) = Coolflux_Sum_LA(3,j);
            end
        end
    end
end

result = Coolflux_Sum_LA;

```

```
end
```

B.2.3 San Francisco: winter

```
% Function to calculate the energy flux reduction from heat flux data

function result = Coolflux.Win_SF(A)

%format long
S = size(A); %size of data array
Coolflux.Win_SF = zeros(2,S(2)-1); %initialize
for d = 1:365
    C = A((72*(d-1)+1):(72*d+1),:); %array containing inner wall
    %surface heat flux for day d
    B = abs(C);
    T = size(C);
    TOU = 3600*[8.5 21.5]+86400*(d-1); %time of use periods (in seconds)
    for j = 1:T(2)-1
        for i = 1:T(1)-1
            if d <= 120 || d >= 305 %if it is winter time
                if C(i,j+1) > 0 || C(i+1,j+1) > 0 %if cooling is required
                    if C(i,1) < TOU(1) || C(i,1) > TOU(2) %if it is off-peak time
                        Coolflux.Win_SF(1,j) = Coolflux.Win_SF(1,j) + 0.5*(B(i+1,1)-B(i,1))*...
                            (B(i+1,j+1)+B(i,j+1)); %integrate over time using the trapezoidal rule
                    else %if it is peak time
                        Coolflux.Win_SF(2,j) = Coolflux.Win_SF(2,j) + 0.5*(B(i+1,1)-B(i,1))*...
                            (B(i+1,j+1)+B(i,j+1));
                    end
                else
                    Coolflux.Win_SF(1,j) = Coolflux.Win_SF(1,j);
                    Coolflux.Win_SF(2,j) = Coolflux.Win_SF(2,j);
                end
            end
        end
    end
end
```

```
end
end
```

```
result = Coolflux_Win_SF;
```

```
end
```

B.2.4 San Francisco: summer

```
% Function to calculate the energy flux reduction from heat flux data
```

```
function result = Coolflux_Sum_SF(A)
```

```
%format long
```

```
S = size(A); %size of data array
```

```
Coolflux_Sum_SF = zeros(3,S(2)-1); %initialize
```

```
for d = 121:304
```

```
    C = A((72*(d-1)+1):(72*d+1),:); %array containing inner wall
```

```
%surface heat flux for day d in summer
```

```
    B = abs(C);
```

```
    T = size(C);
```

```
    TOU = 3600*[8.5 12 18 21.5]+86400*(d-1); %time of use periods
```

```
%(in seconds)
```

```
for j = 1:T(2)-1
```

```
for i = 1:T(1)-1
```

```
    if C(i,j+1) > 0 || C(i+1,j+1) > 0 %if cooling is required
```

```
    if C(i,1) < TOU(1) || C(i,1) > TOU(4) %if it is off-peak time
```

```
Coolflux_Sum_SF(1,j) = Coolflux_Sum_SF(1,j) + 0.5*(B(i+1,1)-B(i,1))*...
```

```
(B(i+1,j+1)+B(i,j+1)); %integrate over time using the trapezoidal rule
```

```
elseif C(i,1) < TOU(2) || C(i,1) > TOU(3) %if it is mid-peak time
```

```
Coolflux_Sum_SF(2,j) = Coolflux_Sum_SF(2,j) + 0.5*(B(i+1,1)-B(i,1))*...
```

```
(B(i+1,j+1)+B(i,j+1));
```

```
else %if it is peak time
```

```
Coolflux_Sum_SF(3,j) = Coolflux_Sum_SF(3,j) + 0.5*(B(i+1,1)-B(i,1))*...
```

```

        (B(i+1,j+1)+B(i,j+1));
    end
    else
        Coolflux_Sum_SF(1,j) = Coolflux_Sum_SF(1,j);
        Coolflux_Sum_SF(2,j) = Coolflux_Sum_SF(2,j);
        Coolflux_Sum_SF(3,j) = Coolflux_Sum_SF(3,j);
    end
end
end
end

result = Coolflux_Sum_SF;

end

```

B.3 MatLab code to predict annual total, heating, and cooling energy flux reduction and cost savings

```

%% Annual energy savings for PCM walls %%
clear all
clc

%Computes the heating, cooling, and total relative energy reductions
%% Nomenclature
%Q_flux: energy flux (in J/m^2)
%Q: energy (in J)
%E_r: relative energy reduction (in %/100)
%P: price (in $/---)
%C: cost (in $)
%S: relative cost savings (in %/100)

%Subscripts
%_con: refers to concrete

```

```

_PCM: refers to PCM
_E: refers to electricity
_G: refers to gas
_T: refers to total, i.e. the sum of all four walls
_h: refers to heating energy, i.e. energy added to building to heat
_c: refers to cooling energy, i.e. energy removed from building to cool
_w: refers to winter
_s: refers to summer
_SF: refers to San Francisco
_LA: refers to Los Angeles
_N, _S, _E, _W: refers to North, South, East, and West

%Inputs: .txt files with the format:
%B and C= [Time, q''_North, q''_South, q''_East, q''_West]
%Outputs: Total, heating, and cooling energy consumption (in J) and
%relative reduction (in %)

%Inputs
A = [39.4 37.5 27.9 27.9]; %Wall areas in m^2 [N, S, E, W]
B = importdata(''); %Call text file containing time and heat flux data for
%concrete wall
%format: [Time qflux_N qflux_S qflux_E qflux_W]
C = importdata(''); %Call text file containing time and heat flux data for
%PCM wall
%format: [Time qflux_N qflux_S qflux_E qflux_W]

%format long

%% Annual energy flux (in J/m^2), row[1; 2; 3] = [Total; Heating; Cooling]
Qflux_con = Qflux(B); %concrete walls [N, S, E, W]
Qflux_PCM = Qflux(C); %PCM walls [N, S, E, W]

%% Annual energy (in J), row[1; 2; 3] = [Total; Heating; Cooling]
Q_con = [Qflux_con(1,:).*A; Qflux_con(2,:).*A; Qflux_con(3,:).*A];
%concrete walls [N, S, E, W]

```

```

Q-PCM = [Qflux_PCM(1,:).*A; Qflux_PCM(2,:).*A; Qflux_PCM(3,:).*A];
%PCM walls [N, S, E, W]
Q-T_con = [sum(Q_con(1,:)) sum(Q_con(2,:)) sum(Q_con...
    (3,:))]; %total energy through all four concrete walls
Q-T_PCM = [sum(Q-PCM(1,:)) sum(Q-PCM(2,:)) sum(Q-PCM...
    (3,:))]; %total energy through all four PCM walls

%% Annual relative energy reduction (in %/100) row[1; 2; 3] =
%[Total; Heating; Cooling]
E_r = (Q-T_con - Q-T_PCM)./Q-T_con

%% Time of use cooling energy fluxes (in J/m^2) column[1 2 3 4] =
%[N, S, E, W]
Qflux_c_w-SF_con = Qflux_c_w-SF(B); % row[1; 2] = [off-peak; peak]
Qflux_c_s-SF_con = Qflux_c_s-SF(B); % row[1; 2; 3] =
%[off-peak; partial-peak; peak]
Qflux_c_w-SF_PCM = Qflux_c_w-SF(C); % row[1; 2] = [off-peak; peak]
Qflux_c_s-SF_PCM = Qflux_c_s-SF(C); % row[1; 2; 3] =
%[off-peak; partial-peak; peak]

% Qflux_c_w-LA_con = Qflux_c_w-LA(B); % row[1; 2] = [off-peak; peak]
% Qflux_c_s-LA_con = Qflux_c_s-LA(B); % row[1; 2; 3] =
%[off-peak; partial-peak; peak]
% Qflux_c_w-LA_PCM = Qflux_c_w-LA(C); % row[1; 2] = [off-peak; peak]
% Qflux_c_s-LA_PCM = Qflux_c_s-LA(C); % row[1; 2; 3] =
%[off-peak; partial-peak; peak]

%% Time of use cooling energy (in J)
% column [1 2 3 4] = [N S E W]
Q-c_w-SF_con = [A.*Qflux_c_w-SF_con(1,:); A.*Qflux_c_w-SF_con(2,:)];
% row[1; 2] = [off-peak; peak]
Q-c_s-SF_con = [A.*Qflux_c_s-SF_con(1,:); A.*Qflux_c_s-SF_con(2,:); ...
    A.*Qflux_c_s-SF_con(3,:)];
% row[1; 2; 3] = [off-peak; partial-peak; peak]
Q-c_w-SF_PCM = [A.*Qflux_c_w-SF_PCM(1,:); A.*Qflux_c_w-SF_PCM(2,:)];

```

```

% row[1; 2] = [off-peak; peak]
Q-c-s-SF-PCM = [A.*Qflux_c-s-SF-PCM(1,:); A.*Qflux_c-s-SF-PCM(2,:); ...
    A.*Qflux_c-s-SF-PCM(3,:)];
% row[1; 2; 3] = [off-peak; partial-peak; peak]

%Total through all four walls
Q-c-w-SF-con-T = [sum(Q-c-w-SF-con(1,:)); sum(Q-c-w-SF-con(2,:))];
%row[1; 2] = [off-peak; peak]
Q-c-s-SF-con-T = [sum(Q-c-s-SF-con(1,:)); sum(Q-c-s-SF-con(2,:)); ...
    sum(Q-c-s-SF-con(3,:))];
%row[1; 2; 3] = [off-peak; partial-peak; peak]
Q-c-w-SF-PCM-T = [sum(Q-c-w-SF-PCM(1,:)); sum(Q-c-w-SF-PCM(2,:))];
%row[1; 2] = [off-peak; peak]
Q-c-s-SF-PCM-T = [sum(Q-c-s-SF-PCM(1,:)); sum(Q-c-s-SF-PCM(2,:)); ...
    sum(Q-c-s-SF-PCM(3,:))];
%row[1; 2; 3] = [off-peak; partial-peak; peak]

% % column [1 2 3 4] = [N S E W]
% Q-c-w-LA-con = [A.*Qflux_c-w-LA-con(1,:); A.*Qflux_c-w-LA-con(2,:)];
% row[1; 2] = [off-peak; peak]
% Q-c-s-LA-con = [A.*Qflux_c-s-LA-con(1,:); A.*Qflux_c-s-LA-con(2,:); ...
    A.*Qflux_c-s-LA-con(3,:)];
% % row[1; 2; 3] = [off-peak; partial-peak; peak]
% Q-c-w-LA-PCM = [A.*Qflux_c-w-LA-PCM(1,:); A.*Qflux_c-w-LA-PCM(2,:)];
% row[1; 2] = [off-peak; peak]
% Q-c-s-LA-PCM = [A.*Qflux_c-s-LA-PCM(1,:); A.*Qflux_c-s-LA-PCM(2,:); ...
    A.*Qflux_c-s-LA-PCM(3,:)];
% % row[1; 2; 3] = [off-peak; partial-peak; peak]

%Total through all four walls
% Q-c-w-LA-con-T = [sum(Q-c-w-LA-con(1,:)); sum(Q-c-w-LA-con(2,:))];
% %row[1; 2] = [off-peak; peak]
% Q-c-s-LA-con-T = [sum(Q-c-s-LA-con(1,:)); sum(Q-c-s-LA-con(2,:)); ...
    sum(Q-c-s-LA-con(3,:))];
% %row[1; 2; 3] = [off-peak; partial-peak; peak]

```

```

% Q_c_w_LA_PCM_T = [sum(Q_c_w_LA_PCM(1,:)); sum(Q_c_w_LA_PCM(2,:))];
% %row[1; 2] = [off-peak; peak]
% Q_c_s_LA_PCM_T = [sum(Q_c_s_LA_PCM(1,:)); sum(Q_c_s_LA_PCM(2,:)); ...
%sum(Q_c_s_LA_PCM(3,:))];
% %row[1; 2; 3] = [off-peak; partial-peak; peak]

%% Total, heating, and cooling cost analysis

SEER = 13; %seasonal energy efficiency rating
AFUE = 81; %annual fuel utilization efficiency
D = 1.055e6; %conversion factor

%electricity rates (in $/kWh)
P_E_s_LA = [0.12369; 0.15858; 0.23775]; %summer time of use pricing
P_E_w_LA = [0.14273; 0.12803]; %winter time of use pricing
P_E_s_SF = [0.10074; 0.17528; 0.28719]; %summer time of use pricing
P_E_w_SF = [0.10495; 0.12129]; %winter time of use pricing
%gas rates (in $/J)
P_G_LA = 0.52*9.48043428e-9;
P_G_SF = 0.9099*9.48043428e-9;

%annual heating, cooling, and total cost (in $)
C_h_SF_con = (1/AFUE)*P_G_SF*Q_T_con(2);
C_h_SF_PCM = (1/AFUE)*P_G_SF*Q_T_PCM(2);
C_c_SF_con = (1/(D*SEER)).*(sum(P_E_s_SF.*Q_c_s_SF_con-T) + ...
    sum(P_E_w_SF.*Q_c_w_SF_con-T));
C_c_SF_PCM = (1/(D*SEER)).*(sum(P_E_s_SF.*Q_c_s_SF_PCM-T) + ...
    sum(P_E_w_SF.*Q_c_w_SF_PCM-T));
C_T_SF_con = C_h_SF_con + C_c_SF_con;
C_T_SF_PCM = C_h_SF_PCM + C_c_SF_PCM;

% C_h_LA_con = (1/AFUE)*P_G_LA*Q_T_con(2);
% C_h_LA_PCM = (1/AFUE)*P_G_LA*Q_T_PCM(2);
% C_c_LA_con = (1/(D*SEER)).*(sum(P_E_s_LA.*Q_c_s_LA_con-T) + ...
%sum(P_E_w_LA.*Q_c_w_LA_con-T));

```

```

% C_c_LA_PCM = (1/(D*SEER)).*(sum(P_E_s_LA.*Q_c_s_LA_PCM-T) + ...
%sum(P_E_w_LA.*Q_c_w_LA_PCM-T));
% C_T_LA_con = C_h_LA_con + C_c_LA_con;
% C_T_LA_PCM = C_h_LA_PCM + C_c_LA_PCM;

%annual heating, cooling, and total cost savings (in $)
S_h_SF = (C_h_SF_con - C_h_SF_PCM)
S_c_SF = (C_c_SF_con - C_c_SF_PCM)
S_T_SF = (C_T_SF_con - C_T_SF_PCM)

% S_h_LA = (C_h_LA_con - C_h_LA_PCM)
% S_c_LA = (C_c_LA_con - C_c_LA_PCM)
% S_T_LA = (C_T_LA_con - C_T_LA_PCM)

```

APPENDIX C

Supplementary material for Chapter 7

C.1 MatLab function to predict γ

```
function result = gam(T_z,T_in,DT_z,DT_pc)

if T_z+DT_z/2 >= T_in + DT_pc/2 && T_z-DT_z/2 <= T_in - DT_pc/2
    result = 1;
elseif T_z+DT_z/2 <= T_in - DT_pc/2 || T_z-DT_z/2 >= T_in + DT_pc/2
    result = 0;
elseif T_z+DT_z/2 < T_in + DT_pc/2 && T_z-DT_z/2 > T_in - DT_pc/2
    result = DT_z/DT_pc;
elseif T_z > T_in
    result = (T_in+DT_pc/2-T_z+DT_z/2)/DT_pc;
elseif T_z < T_in
    result = (T_z+DT_z/2-T_in+DT_pc/2)/DT_pc;
end

end
```

C.2 MatLab function to decompose sol-air temperature into Fourier series with four harmonics

```
function result = Decomp(P,A)
t = A(:,1); %time vector
```

```

T_sa = A(:,2); %solair temperature vector
Tsa_cos1 = T_sa.*cos(2*pi*t/P); %product for a1 integral
Tsa_cos2 = T_sa.*cos(4*pi*t/P); %product for a2 integral
Tsa_sin1 = T_sa.*sin(2*pi*t/P); %product for b1 integral
Tsa_sin2 = T_sa.*sin(4*pi*t/P); %product for b1 integral
a0 = 1/P*trapz(t,T_sa); %determine a0: average sol-air temperature
a1 = 2/P*trapz(t,Tsa_cos1); %determine a1: coefficient of 1st harmonic
b1 = 2/P*trapz(t,Tsa_sin1); %determine a2: coefficient of 3rd harmonic
a2 = 2/P*trapz(t,Tsa_cos2); %determine b1: coefficient of 2nd harmonic
b2 = 2/P*trapz(t,Tsa_sin2); %determine b2: coefficient of 4th harmonic
result = [a0 a1 b1 a2 b2];
end

```

C.3 MatLab function to determine decrement factors

```

function A = ADM(n_L,k,rho,c_p,h_i,h_o,L,Pn)

U = 1/(1/h_o+sum(L./k)+1/h_i); %overall heat transfer coefficient
%initialize matrices
p = zeros(1,n_L);
m1 = zeros(1,n_L);
m2 = zeros(1,n_L);
m3 = zeros(1,n_L);
M_wn = zeros(2,n_L*2);
M_w = eye(2,2);
A = zeros(2);

for j = 1:n_L
p(j) = ((pi*L(j)^2*rho(j)*c_p(j))/(Pn*k(j)))^0.5;
m1(j) = cosh(p(j)+p(j)*1i);
m2(j) = ((L(j)*sinh(p(j)+p(j)*1i))/(k(j)*(p(j)+p(j)*1i)));
m3(j) = ((k(j)*(p(j)+p(j)*1i)*sinh(p(j)+p(j)*1i))/L(j));
M_wn(4*j-3:4*j) = [m1(j) m2(j); m3(j) m1(j)];

```

```

end

for x = 1:n_L
M_w = M_w*M_wn(1:2,2*(n_L-x)+1:2*(n_L-x)+2);
end

M_in = [1 (1/h_i); 0 1];
M_out = [1 (1/h_o); 0 1];
M = M_out*M_w*M_in;
M_prime = M(3)-M_w(2)/(h_i*h_o)-M_w(1)/h_o;

%Output
f_c = 1/(U*M(3));
f_AM = abs(f_c);
f_MW = U/h_i*f_AM;
f_w = abs(1/(M_prime)/h_i);
f_o = (U/h_i)*(f_AM/f_w);
if real(f_c) > 0 && imag(f_c) < 0
    phi_AM = abs((Pn/(2*3600*pi))*atan(imag(f_c)/real(f_c)));
elseif real(f_c) < 0
    phi_AM = abs((Pn/(2*3600*pi))*(atan(imag(f_c)/real(f_c))-pi));
elseif real(f_c) > 0 && imag(f_c) > 0
    phi_AM = abs((Pn/(2*3600*pi))*(atan(imag(f_c)/real(f_c))-2*pi));
end

A = [f_AM phi_AM f_MW f_o];
end

```

C.4 MatLab file to determine the daily energy flux reduction associated with adding microencapsulated PCM to single or multilayer walls

```

%% Time lag and decrement factor as a function of PCM volume fraction
clc
clear all

%% Notes
% **Uses the functions Decomp.m, Adm.m, felske.m, rho_cp_eff.m, and gam.m.

% 1. Computes energy flux reduction ratios for single or multilayer
% composite walls containing PCM in 5% increments. This increment may be
% adjusted at line 33. If increment is changed, make sure target volume
% fraction (line 31) is a multiple of the increment.

% 2. Code can be adjusted to accommodate higher numbers of harmonics by
% editing the function "Decomp" accordingly. Also edit the period vector Pn
% (line 38), amplitude vector (line 41), heat flux calculation (lines 82-88
% ), and heat flux plot (lines 98-103)

% 3. In order to adjust for single layer walls, adjust the size of the
% matrices containing thermal properties and thicknesses accordingly (Lines
% 27, 28, 29, 35)

%% Input parameters

%Wall properties and geometry
n_L = 3; %number of layers
n_PCM = 3; %location of PCM (layer 1 is closest to the indoor environment)
k_m = [0.5 0.1 1.4]; %thermal conductivity of each layer
c_p_m = [1000 1000 880]; %specific heat of each layer
rho_m = [1300 500 2330]; %density of each layer
k_comp = [0.21 0.49 k_m(n_PCM)]; %thermal conductivities of
%[pcm shell matrix] [W/m*K]
c_p_comp = [2590 2250 c_p_m(n_PCM)]; %specific heat of [pcm shell matrix]
%[J/kg*K]
rho_comp = [860 930 rho_m(n_PCM)]; %density of [pcm shell matrix] [kg/m^3]
h_sf = 180000; %latent heat of fusion [J/kg]

```

```

DT_pc = 8; %phase change temperature window [C]
L = [0.016 0.05 0.15]; %wall thickness [m]
L_T = sum(L); %total wall thickness
if L_T == L
    L_pcm = L/2;
else
    L_pcm = sum(L(1:n-PCM-1))+L(n-PCM)/2; %distance from inner wall to
    %center of PCM layer
end
T_in = 20; %indoor temperature [C]
h_i = 7.7; %inner surface heat transfer coefficient [W/m2.K]
h_o = 25; %outer surface heat transfer coefficient [W/m2.K]
phi_PCM = 0.2; %desired microencapsulated PCM volume fraction
phi_cs = 0.85; %volume fraction of core wrt shell
phi_inc = 0.05; %increment of PCM volume fraction

%Decompose sol-air temperature into harmonics
nh = 4; %number of harmonics
P = 86400; %period of sol-air temperature
Pn = [86400 86400 43200 43200]; %period of each harmonic
T_solair = importdata(''); %text file containing sol-air temperature
%[time sol-air temp]
a = Decomp(P,T_solair); %vector containing coefficients a0-a3, b1, and b2
A = 2*abs([a(2) a(3) a(4) a(5)]); %peak-to-trough amplitude of each harmonic

%Initialize
f_AM = zeros(nh,phi_PCM/phi_inc+1); %decrement factor matrix
phi_AM = zeros(nh,phi_PCM/phi_inc+1); %time lag matrix
T_sa_avg = a(1); %average temperature of 1st harmonic

for n = 1:nh
    phi_p = 0; %start with no PCM
    phi_s = 0;
    k = k_m; %select matrix properties
    c_p = c_p_m; %select matrix properties

```

```

rho = rho_m; %select matrix properties
for i = 1:phi_PCM/phi_inc+1
Un(i)=(1/h_i+sum(L./k)+1/h_o)^-1; %store overall heat transfer coefficient
ADM_vals = ADM_multi(n_L,k,rho,c_p,h_i,h_o,L,Pn(n)); %determine decrement
%factors
f_AM(n,i) = ADM_vals(1); %admittance method decrement factor
phi_AM(n,i) = ADM_vals(2); %admittance method time lag

DT_L = ADM_vals(3)*A(n); %amplitude of inner wall surface temperature
%variation
DT_o = ADM_vals(4)*A(n); %amplitude of outer wall surface temperature
%variation
DT_z = (1-L_pcm/L_T)*DT_L+L_pcm/L_T*DT_o; %average amplitude of wall
%temperature variation
qflux_avg = Un(i)*(T_sa_avg - T_in); %steady-state heat flux through wall
T_z = (1-L_pcm/L_T)*(T_in + qflux_avg/h_i) + L_pcm/L_T*(T_sa_avg-...
    qflux_avg/h_o);
%average wall center temperature
gamma = gam(T_z,T_in,DT_z,DT_pc); %gamma factor to adjust latent heat of
%fusion

c_p_pc = gamma*h_sf/DT_z+c_p_comp(1); %effective transition range specific
%heat [J/kg*K]
c_p_comp2 = [c_p_pc c_p_comp(2) c_p_comp(3)]; %effective transition range
%specific heats

phi_p = phi_p + phi_inc*phi_cs; %volume fraction of phase change material
phi_s = phi_s + phi_inc*(1-phi_cs); %volume fraction of shell material
k(n_PCM) = felske(phi_p,phi_s,k_comp); %effective thermal conductivity
B = rho_cp_eff(phi_p,phi_s,rho_comp,c_p_comp2); %effective density and
%specific heat
rho(n_PCM) = [B(2)]; %effective density [kg/m3]
c_p(n_PCM) = [B(3)]; %effective specific heat [J/kg.K]
end
T_sa_avg = T_in;

```

```

end

t = T_solair(:,1);
%determine the heat flux for each PCM volume fraction
for i = 1:phi_PCM/phi_inc+1
    qflux_L(:,i) = Un(i)*(a(1)-T_in+f_AM(1,i)*a(2)*cos(2*pi/P*...
        (t-phi_AM(1,i)*3600))+f_AM(2,i)*a(3)*sin(2*pi/P*...
        (t-phi_AM(2,i)*3600))+f_AM(3,i)*a(4)*cos(4*pi/P*...
        (t-phi_AM(3,i)*3600))+f_AM(4,i)*a(5)*sin(4*pi/P*...
        (t-phi_AM(4,i)*3600)));
    Qflux_L(i) = trapz(t,abs(qflux_L(:,i)));
end

%determine the relative energy flux reduction for each PCM volume
%fraction in [%]
for n = 1:phi_PCM/phi_inc
    E_r(n) = (Qflux_L(1)-Qflux_L(n+1))/Qflux_L(1)*100;
end

E_r

%plot the heat flux vs. time for each PCM volume fraction
% figure
% plot(t/3600,qflux_L(:,1),'k',t/3600,qflux_L(:,2),'r',t/3600,...
%qflux_L(:,3),'b',t/3600,qflux_L(:,4),'g',...
%    t/3600,qflux_L(:,5),'m')
% xlabel('Time, t [h]')
% ylabel('Inner wall surface heat flux,  $q_{L}^{\prime}$  [(W/(m2).K)]')
% axis([0 24 -20 25])
% legend('\it{\phi}_{c+s}=0', '\it{\phi}_{c+s}=0.05', '\it{\phi}_{c+s}...
%=0.1', '\it{\phi}_{c+s}=0.15'...
%    , '\it{\phi}_{c+s}=0.2', 'location', 'northwest')

```

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