University of Louisville

ThinkIR: The University of Louisville's Institutional Repository

Electronic Theses and Dissertations

12-2013

Development of concrete incorporating phase change materials for enhanced energy efficiency.

Jeffrey Dee Kiesel
University of Louisville

Follow this and additional works at: <https://ir.library.louisville.edu/etd>

Recommended Citation

Kiesel, Jeffrey Dee, "Development of concrete incorporating phase change materials for enhanced energy efficiency." (2013). *Electronic Theses and Dissertations*. Paper 746.
<https://doi.org/10.18297/etd/746>

This Doctoral Dissertation is brought to you for free and open access by ThinkIR: The University of Louisville's Institutional Repository. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of ThinkIR: The University of Louisville's Institutional Repository. This title appears here courtesy of the author, who has retained all other copyrights. For more information, please contact thinkir@louisville.edu.

DEVELOPMENT OF CONCRETE INCORPORATING PHASE CHANGE
MATERIALS FOR ENHANCED ENERGY EFFICIENCY

By

Jeffrey Dee Kiesel

B.A. Biology, University of Louisville, 1997

B.S. Civil Engineering, University of Louisville, 2001

M. Eng. Civil Engineering, University of Louisville, 2002

A Dissertation

Submitted to the Faculty of the

University of Louisville

J.B. Speed School of Engineering

in Partial Fulfillment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

Department of Civil Engineering

University of Louisville

Louisville, Kentucky

December 2013

DEVELOPMENT OF CONCRETE INCORPORATING PHASE CHANGE
MATERIALS FOR ENHANCED ENERGY EFFICIENCY

By

Jeffrey Dee Kiesel

B.A. (Biology) University of Louisville, 1997

B.S. (Civil Eng.) University of Louisville, 2001

MEng. (Civil Eng.) University of Louisville, 2002

A Dissertation Approved On

November 21, 2013

by the Following Dissertation Committee:

William M. McGinley, Dissertation Director

Ellen G. Brehob

Young Hoon Kim

Thomas D. Rockaway

ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. William Mark McGinley for supporting my efforts for the last three years through expert advice and by obtaining my funding. I would also like to thank my committee members; Dr. Ellen G. Brehob, Dr. Young Hoon Kim and Dr. Thomas D. Rockaway for their support and guidance. In addition, I would like to thank Stephen Zwanzig for his assistance with the numerical modeling aspect of PCMs.

Also, I would like to acknowledge the support provided by the Conn Center for Renewable Energy and Energy Efficiency and the National Concrete Masonry Association. Without their financial support this research would not have been possible.

Finally, I would like to thank my family for supporting my educational endeavors. I truly appreciate the support provided by my mother, father, Jen, Helena, and Grayson. It is with this emotional support and understanding during this difficult process that I have had the opportunity to obtain this merit. I would like to graciously thank all of you and everyone else that has made opportunity come to fruition.

ABSTRACT

DEVELOPMENT OF CONCRETE INCORPORATING PHASE CHANGE MATERIALS FOR ENHANCED ENERGY EFFICIENCY

Jeffrey D. Kiesel

November 21, 2013

Thermal mass incorporated into the building envelope has the ability to attenuate peak interior diurnal temperature fluctuations and energy flow, provide interior thermal phase shifts, and absorb surplus energy from solar gains as well as internal gains created by occupants, lighting, appliances and electronics. Heating and cooling demands can be reduced and delayed by thermally massive building envelopes.

Historically, thermal mass has been achieved using thick, dense building envelopes such as stone, adobe, and mass concrete. These massive walls absorb heat during the day keeping the interior cool, then release the stored heat during the night maintaining interior comfort. The thermal mass of a building envelope, in this case concrete, can be further increased with the incorporation of Phase Change Materials (PCMs).

PCMs increase the effective thermal mass of a structure without increasing the size or significantly changing the weight of the structure. PCMs store energy as they change phase from a solid to a liquid state during a nearly isothermal process. This occurs when

the material reaches the transition temperature of the PCM. Once melting of the PCM is completed, the temperature of the material can once again rise. When the material cools and returns to the transition temperature, the PCM solidifies releasing the stored thermal energy.

In this research Concrete Masonry Units (CMUs) were examined for improved thermal energy performance using the enhanced thermal properties provided by PCMs. PCMs can be incorporated into concrete to form CMUs with higher energy storage capability than standard CMUs. CMUs were chosen for this application because of their extensive use in the construction industry which has the potential to contribute to commercial acceptance.

The work represented in this dissertation indicates that Phase Change Materials can be successfully incorporated into concrete mixes appropriate for use in CMUs. CMUs incorporating PCM will look and function structurally like standard units while also having improved thermal storage performance. In some climates and building configurations, CMUs with improved energy storage via PCMs may have the ability to compete with mainstream insulation technologies.

TABLE OF CONTENTS

APPROVAL PAGE	ii
ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
LIST OF TABLES	viii
LIST OF FIGURES	x
CHAPTER ONE: INTRODUCTION	1
1.1 Overview	1
1.2 Conventional Construction Practices	4
1.3 Research Objectives and Scope of Research Work	5
1.4 Background on Thermal Mass and Phase Change Materials (PCMs)	9
1.5 PCM Characteristics and Types	22
1.6 Encapsulation Methods	27
1.7 Transient Energy Storage Theory	32
1.8 Mathematical Modeling of Latent Heat of PCMs	34
CHAPTER TWO: PCM CONCRETE DEVELOPMENT AND TESTING	40
2.1 PCM Concrete Development	40
2.1.1 Aggregate Analysis	42
2.1.2 PCM Choice and Preparation	44
2.1.3 PCM Encapsulation	48
2.1.4 Concrete Mix Design	55
2.2.1 PCM Content	64
2.2.2 Concrete Density	65
2.2.3 Compression Testing	67
2.2.4 PCM Concrete Mix Optimization	69

CHAPTER THREE: THERMAL CHARACTERIZATION OF PCMS AND PCM CONCRETES	73
3.1 Thermal Testing	73
3.2 Digital Scanning Calorimetry.....	75
3.2.1 DSC Methods.....	78
3.2.2 DSC Analysis.....	80
3.2.3 Enthalpy Measurement Results.....	81
3.3 Dynamic Hot Box Apparatus	104
3.3.1 Development and Fabrication.....	105
3.3.2 Sensor Calibration.....	108
3.3.3 Thermal Conductivity	116
3.3.4 Heat Capacity.....	118
3.3.4 Diurnal Cycling.....	123
CHAPTER FOUR: PCM MODELING.....	143
4.1 One-Dimensional Finite Difference Model.....	143
4.2 Holistic Building Energy Model	148
4.2.1 CODYBA and EnergyPlus	151
4.2.2 CODYBA Analysis Results.....	154
Figure 4.8: 7432 m ² (80K ft ²) Louisville, KY (4A)	155
Commercial Building Energy Use (kWh)	155
Figure 4.9: 7432 m ² (80K ft ²) Louisville, KY (4A)	155
Commercial Building Energy Savings (\$).....	155
4.2.3 EnergyPlus Analysis Results	156
4.3 Economic Analysis.....	175
CHAPTER FIVE: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS	186
5.1 Summary and Conclusions.....	186
5.2 Recommendations	189
REFERENCES	192
APPENDIX A: NOMENCLATURE.....	199
APPENDIX B: SIEVE ANALYSIS RESULTS	200
APPENDIX C: HEAT FLUX SENSOR CALIBRATION	207
CURRICULUM VITAE.....	211

LIST OF TABLES

Table 1.1	24
Table 1.2	25
Table 1.3	26
Table 1.4	27
Table 2.1	43
Table 2.2	43
Table 2.3	44
Table 2.4	54
Table 2.5	57
Table 2.6	65
Table 2.7	66
Table 3.1	82
Table 3.2	85
Table 3.3	99
Table 3.4	99
Table 3.5	101
Table 3.6	115
Table 3.7	117
Table 3.8	131
Table 3.9	139
Table 4.1	159
Table 4.2	159
Table 4.3	160
Table 4.4	169
Table 4.5	178
Table 4.6	179

Table 4.7	179
Table 4.8	180
Table 4.9	180
Table 4.10	181
Table 4.11	181
Table 4.12	182
Table 4.13	182
Table 4.14	183
Table 4.15	183
Table 4.16	185

LIST OF FIGURES

Figure 1.1	2
Figure 1.2	3
Figure 1.3	4
Figure 1.4	6
Figure 1.5	17
Figure 1.6	18
Figure 1.7	19
Figure 1.8	21
Figure 1.9	28
Figure 1.10	30
Figure 1.11	30
Figure 1.12	31
Figure 1.13	31
Figure 1.14	38
Figure 2.1	46
Figure 2.2	46
Figure 2.3	46
Figure 2.4	46
Figure 2.5	47
Figure 2.6	50
Figure 2.7	51
Figure 2.8	52
Figure 2.9	57
Figure 2.10	58

Figure 2.11	58
Figure 2.12	59
Figure 2.13	61
Figure 2.14	61
Figure 2.15	63
Figure 2.16	68
Figure 2.17	68
Figure 2.18	69
Figure 2.19	70
Figure 3.1	75
Figure 3.2	77
Figure 3.3	79
Figure 3.4	79
Figure 3.5	80
Figure 3.6	83
Figure 3.7	87
Figure 3.8	87
Figure 3.9	88
Figure 3.10	88
Figure 3.11	89
Figure 3.12	89
Figure 3.13	90
Figure 3.14	90
Figure 3.15	91
Figure 3.16	91
Figure 3.17	92
Figure 3.18	92

Figure 3.19	93
Figure 3.20	93
Figure 3.21	94
Figure 3.22	96
Figure 3.23	96
Figure 3.24	97
Figure 3.25	97
Figure 3.26	102
Figure 3.27	102
Figure 3.28	103
Figure 3.29	103
Figure 3.30	106
Figure 3.31	106
Figure 3.32	107
Figure 3.33	108
Figure 3.34	110
Figure 3.35	111
Figure 3.36	112
Figure 3.37	114
Figure 3.38	119
Figure 3.39	119
Figure 3.40	120
Figure 3.41	120
Figure 3.42	121
Figure 3.43	121
Figure 3.44	124
Figure 3.45	125

Figure 3.46	125
Figure 3.47	126
Figure 3.48	126
Figure 3.49	127
Figure 3.50	127
Figure 3.51	128
Figure 3.52	128
Figure 3.53	129
Figure 3.54	129
Figure 3.55	130
Figure 3.56	134
Figure 3.57	134
Figure 3.58	135
Figure 3.59	135
Figure 3.60	137
Figure 3.61	137
Figure 3.62	138
Figure 3.63	138
Figure 3.64	140
Figure 3.65	141
Figure 3.66	141
Figure 4.1	144
Figure 4.2	145
Figure 4.3	147
Figure 4.4	147
Figure 4.5	150
Figure 4.6	152

Figure 4.7	154
Figure 4.8	155
Figure 4.9	155
Figure 4.10	160
Figure 4.11	161
Figure 4.12	161
Figure 4.13	161
Figure 4.14	162
Figure 4.15	162
Figure 4.16	162
Figure 4.17	162
Figure 4.18	163
Figure 4.19	164
Figure 4.20	164
Figure 4.21	165
Figure 4.22	165
Figure 4.23	166
Figure 4.24	170
Figure 4.25	170
Figure 4.26	171
Figure 4.27	171
Figure 4.28	172
Figure 4.29	172
Figure 4.30	176
Figure 4.31	177

CHAPTER ONE: INTRODUCTION

1.1 Overview

As readily available sources of energy are depleted and energy costs increase, alternative energy sources and ways to reduce our current demand must be sought. This is an issue which has been debated for years but is now coming to a cusp. Increased use of renewable energy has been at the forefront of arguments with geothermal, biofuels, solar, wind, and hydropower being viable alternatives to fossil fuels. While these sources help to meet our energy demand, alternatively, efforts must also be addressed to examine ways to decrease our energy consumption. Reducing energy consumption not only reduces the resources required for human comfort but also decreases resources required for additional energy infrastructure and power sources; such as resources for new power plants, transmission lines, and the transportation systems for energy sources.

Residential and commercial building energy use accounts for almost 40% of total energy use in the U.S., while transportation and industrial processes make up the rest as can be seen in Figure 1.1 (EIA 2010). Hydrocarbon energy sources such as oil, natural gas, and coal require transportation such as pipelines, tanker ships, barges, or haul trucks. Thus reducing building energy use has the potential to further reduce total energy consumption by additionally reducing energy related transportation uses.

Figure 1.1: Sources and Usage Sectors in the U.S. (EIA 2010)

A substantial portion of energy consumption in the U.S. is devoted to conditioning the interior environment of buildings, whether residential or commercial. As shown in Figure 1.2, heating loads account for 41% of residential energy consumption while cooling loads account for 8% of the total energy use in a typical home (EIA 2005). The remaining 51% of residential energy consumption is due to water heating as well as electronics and appliances.

Figure 1.2: Residential Energy Usage (eia.gov 2005)

As shown in Figure 1.3, heating and cooling account for 5% and 14% of energy used respectively in commercial construction while lighting is the single largest use. As can be inferred from differing proportions of heating versus cooling, residential and commercial buildings behave differently due to differences in the interior air mass, electronics, lighting, refrigeration loads, as well as occupancy patterns. However, for both uses, improving the energy performance of the building envelope has the potential to significantly reduce energy demand which has a cascading effect on energy use.

Figure 1.3: Commercial Energy Usage (eia.gov 2013)

Currently, there are two philosophies used for building envelope design. The first uses highly insulated lightweight construction with minimal air infiltration, the second method uses thermally massive construction with optimized window location and shading to allow solar gain in the winter months and mitigate solar gain in the summer. While highly insulated structures minimize heat penetration, they lack the ability of thermally massive materials to absorb surplus energy, dampen interior temperature fluctuations, and offset peak energy consumption. In addition, once thermal energy has penetrated a highly insulated structure with low thermal mass, it meets the same resistance when the temperature differential reverses.

1.2 Conventional Construction Practices

Conventional construction practices typically use thermal insulation to control energy movements in building envelopes. These configurations typically are prescriptively

defined by building codes for different building climates and building configurations. Some allowance for thermal mass is made in defining these prescriptive limits but in general these allowances are small (ASHRAE 2010).

Currently, single-wythe masonry walls have been used in many industrial and institutional applications. These walls have been traditionally used without insulation but the newer more stringent building codes and standards require that insulation be applied to the walls to meet the higher energy efficiency requirements. This insulation requirement negatively impacts the economics of the wall system and can impact its long-term durability. Research into alternative ways of ensuring adequate energy performance of single-wythe walls is needed.

1.3 Research Objectives and Scope of Research Work

The objective of this research is to develop a concrete mix for use in Concrete Masonry Units (CMUs) that will enhance the energy performance of a CMU wall sufficiently to allow its use in single-wythe applications without insulation. As part of the objective, the concrete mix must meet compressive strength requirements of the ASTM C90 Standard Specification for Loadbearing Concrete Masonry Units (ASTM Standard C90-13 2013). This standard governs the structural use of Concrete Masonry Units allowing a minimum compressive strength of 13.1 MPa (1900 psi).

As shown in Figure 1.4, Phase Change Materials (PCMs) are to be incorporated into CMUs which can be used to construct single-wythe concrete masonry walls with

improved thermal energy storage properties. By maintaining the bare masonry wall configuration, current construction practices can be maintained and improve the likelihood of commercialization of the Phase Change Material Concrete Masonry Units (PCM CMUs).

Figure 1.4: Development of PCM CMU Wall System Objective

Analyses of the effects of enhanced thermal energy storage characteristics on the energy performance of structures constructed with these PCM CMUs were conducted. These analyses were performed to evaluate the relative energy efficiency performance of single-wythe PCM concrete masonry as compared to standard configurations comprised of insulation and conventional concrete masonry.

In order to develop a viable PCM CMU, a series of steps must be completed. First, a viable concrete mix design must be developed that meets the ASTM C90 Standard Specification for Loadbearing Concrete Masonry Units while also allowing significant

volumes of PCM to be incorporated. This must be done while also retaining the PCM while it is in its liquid state. Therefore, proper mix design and PCM containment are essential. In addition, proper PCM selection is critical for energy storage as well as minimal chemical reactivity with the cement matrix, reinforcement, and wall coatings.

Characterization of the PCM thermal properties is necessary to quantify the thermal performance of the PCM concrete mix. The latent heat and transition temperatures are required to understand the energy storage properties so that the mix can be optimized. Optimum transition temperature depends on the climate, interior gains, and HVAC set points since the PCM must cycle through its transition temperature regularly in order to effectively utilize the latent heat.

After PCM selection and successful mix development, the composite PCM concrete thermal properties must be quantified to evaluate thermal performance. Thermal conductivity must be determined in order to evaluate the steady state R-value. R-value is a steady-state value quantifying a material's one-dimensional thermal resistance to heat flux for a temperature differential applied to the bounding surfaces. High R-value can be an attribute during prolonged periods of cold weather, when the PCM remains frozen. Also, high R-value helps to prevent thermal penetration during hot summer periods when the PCM may remain in a liquid state. On the other hand, during cold periods with solar gain, conductivity must be high enough to allow solar thermal energy storage of the PCM during sunny days for release at night. In addition, in cooling climates with large diurnal

temperature swings, higher conductivity can allow cooler nighttime temperatures to penetrate the envelope and thus precool the building envelope for daytime comfort.

The transient thermal mass properties must also be evaluated to quantify the energy storage properties of the PCM CMUs since thermal mass is only effective when accompanied by diurnal fluctuations. To study the transient properties, a Dynamic Hot Box Apparatus was constructed. The device is capable of applying steady state as well as dynamic temperature profiles to a material test sample. The apparatus can perform steady state R-value testing as well as simulate diurnal climate cycling, in addition to performing ramp and step profiles. This allowed testing configurations that emulate both prolonged temperature extremes, temperature cycling, as well as other dynamic profiles needed for thermal testing.

An analytical model was developed and applied to evaluate the performance of PCM CMU walls. A one-dimensional transient conduction finite difference model was used to examine the response of PCMs in a layered building envelope. The Dynamic Hot Box diurnal cycling results were used to validate the model beyond simplified theoretical comparisons.

Two holistic building analyses software programs were used to examine the potential energy savings provided by PCM in the building envelope. These were a modified version of CODYBA and EnergyPlus 8.0. The programs were used to simulate building envelopes using PCM CMU walls and compare these responses to conventional

wall configurations. Whole building energy analyses were performed for wall configurations in varying climates

Finally, an economic analysis was performed. The initial additional upfront cost associated with inclusion of PCM was compared to that of standard configurations. From this comparison the required cost of PCM was determined for which economic viability can be achieved.

This dissertation is presented in five chapters; Introduction (Chapter 1), PCM Concrete Development and Testing (Chapter 2), Thermal Characterization of PCMs and PCM Concretes (Chapter 3), PCM Modeling (Chapter 4), and finally Summary, Conclusions and Recommendations (Chapter 5).

1.4 Background on Thermal Mass and Phase Change Materials (PCMs)

Historically thermal mass has been achieved with a thick, dense building envelope. An example is adobe construction. The massive walls absorb penetrating heat during the day keeping the interior cool, then release the stored thermal energy during the cool nights and thus maintain interior comfort. Alternatively, significant thermal mass can be incorporated into lightweight construction through the use of PCMs. Lightweight frame wall construction can incorporate PCMs as a thin layer, placed in pouches, packets or cylinders, or be suspended in insulation. PCMs can also be incorporated into thermally massive materials such as concrete to further increase the thermal mass, thus improving transient thermal performance.

PCMs can be used to increase the effective thermal mass of a structure without significantly increasing the actual weight of the structure. PCMs store energy as they change phase from a solid to a liquid during a nearly isothermal process. This occurs when the material reaches the transition temperature of the PCM. Energy is stored until the latent heat storage potential is fully utilized. Once melting is completed the temperature of the material can once again rise. When the material cools and returns to the transition temperature, the PCM solidifies releasing the stored thermal energy, again in a nearly isothermal process. Once the latent heat is released, the material can begin to cool again.

PCMs can be used to enhance building energy performance. This can be achieved by placing the PCM in the floor so that solar gain through windows is absorbed and stored. PCM can also be placed in the building envelope to absorb excess solar gains (Athientis et al. 1997, Drake 1987, Neeper 2000) as well as to slow thermal penetration (Richardson and Woods 2008). In addition, energy storage tanks utilizing PCM can be an effective way to store excess solar thermal energy for release at night or to store thermal energy produced in other ways until needed.

PCM impregnated wallboard has seen the widest research and application since it is easy to apply as a retrofit and is non-structural. Other PCM composite materials such as floor tile, concrete flooring, brick, and concrete walls have also been studied (Khudhair et al. 2004). Flooring with PCM has been utilized for solar gain applications. Wallboard, brick, and concrete walls incorporating PCM have also been studied for solar gain applications, as well as for their building envelope performance improvement capabilities.

Further, all of these PCM composites have the ability to buffer internal temperature fluctuations for improved occupant comfort.

PCM composite flooring can be placed in an area of a structure with good fenestration exposure on the southern face. During the winter, the PCM flooring will absorb and store daytime solar gains. The stored thermal energy is released at night to maintain a regulated temperature until daybreak. During summer it can help attenuate peak interior temperatures and prevent overheating. A study was performed to examine the passive use of PCM floor tile in a south facing sunspace for mitigation of overheating and for energy savings. It was found that PCM floor tile in that application has the potential of at least 24% annual heating energy savings (Hittle 2002). PCM concrete flooring was also studied by Entrop et al. (2011). It was found that with southern solar exposure, PCM concrete flooring provides evening and nighttime heating by utilizing the solar thermal energy stored during the day.

PCM wallboard in contact with the interior environment has the ability to absorb interior thermal gains which can be solar, occupant, or from electronics and appliances. Like PCM floor tiles, wallboard can be thermally charged during the winter days in order to maintain nighttime comfort and can buffer interior temperatures in the warm months (Athientis et al. 1997, Drake 1987, Neeper 2000).

There are two favored methods of incorporating PCM into the wallboard; mixing micro-encapsulated PCMs with the gypsum matrix during manufacturing and immersing

finished wallboard in molten PCM. Immersion is more economical while micro-encapsulation provides stability to the liquid state of the PCM. Both methods have their advantages and disadvantages. Immersion requires submerging the wallboard in liquid PCM in order to imbibe it within the gypsum void space. This may allow long-term stability problems. Micro-encapsulation involves polymer encapsulation of PCM spheres with the benefit of stability at the added cost of the encapsulation process and materials.

Masonry has seen extensive use dating back 1000's of years with cut stone being used in many early European, South and Central America structures, as well as in the Egyptian pyramids of Northern Africa, and finally the adobe brick constructions of southwestern North America as well as the Mesopotamian beehives in Asia to name a few. The thick thermally massive exterior of these structures provided human comfort prior to modern insulation. Remnants of these great masonry structures still stand to this day. Due to the consistent and continued use of masonry, as well as its resilience and thermal dampening, much research has focused upon it. Though masonry's thermal mass is substantial, PCMs can improve it. Thus, researchers have investigated whether modern day masonry such as clay brick and concrete units will have improved thermal performance with the incorporation of PCMs.

Brick incorporating PCM has been studied and has indicated a reduction of thermal penetration, dampening of indoor temperature fluctuations, and improved thermal comfort (Alawadhi 2008, Castell et al. 2010, and Zhang et al. 2011). Since clay brick must be kiln fired, PCM core inserts must be inserted, or pouches must be applied to the exterior or

interior of the envelope after firing. Inserts are an economically difficult solution due to the mechanization that inserts require and the feasibility of internal or external PCM containment.

Prior PCM research in concrete has involved incorporating PCM into mass concrete and concrete masonry units in several ways; micro-encapsulated PCM spheres in the concrete matrix, soaking of the cured porous concrete in liquid PCM, and placement of PCM modules within the cores of CMUs. These methods all have advantages and disadvantages. Micro-encapsulation is effective and has been favored due to its ease of incorporation. It is added as a fine aggregate to the materials during mixing. In addition, the capsules provide retention of the PCM in its liquid phase. However, since the PCM is placed within the cement matrix, significant volumes of PCM cannot be incorporated without displacing substantial quantities of the cement and matrix, thus adversely affecting the concrete compressive strength. Finally, the dispersion coating process that forms the microcapsules adds to costs.

Soaking involves infusing the PCM into a porous concrete matrix (Hawes et al. 1991). However, surface tension and molecular bonds are all that prevents the PCM from seeping from the matrix. Long term stability of the composite is questionable.

PCM modules placed in the cores of concrete masonry units have also been studied (Sayler and Kumar 1995). These modules effectively mitigate the seepage issues. However, a portion of the cores of masonry walls are needed for reinforcement in almost

all structural applications. Thus, rendering the cores unusable has significant structural implications in masonry applications. In addition, using the cores for grout and reinforcement replaces a substantial portion of the PCM, lowering PCM quantities. Further, these large PCM cores can experience the difficulties of lack of nucleation sites and incomplete phase change commonly associated with macro-encapsulation.

Some research has focused on vacuum impregnation of porous aggregates. The primary porous aggregates that have been examined are perlite and vermiculite due to their large volume of voids and interconnected pore structure. However, the low strength of perlite and vermiculite is deleterious to concrete in structural applications. Diatomaceous earth has also been examined as a supporting aggregate (Karaman et al. 2011). However, it has a similar negative effects as micro-encapsulated PCM in that it displaces cement and thus reduces concrete strength with increased PCM content.

Expanded clay aggregates have been studied as a porous PCM media (Zhang et al. 2003). The expanded clay provides interconnected pore space for retention of the PCM. Like the PCM immersed concrete, the PCM is retained by surface tension. However, since the PCM aggregates are then used to make PCM concrete, the cement matrix encapsulates the aggregates thus preventing leakage of the PCM.

The energy storage capacity of PCMs is substantial and thus its use has been extended to many uses beyond building applications. PCMs have been studied in fabrics, bridges, dams, space craft, as well as buildings for temperature regulation.

Fabrics have been examined for temperature regulating clothing as well as tents that maintain occupant comfort. This research has largely been facilitated by the military in an effort to provide thermal comfort for soldiers. Ultimately this research has led to PCM clothing being commercialized with socks, shirts, and other clothing items for sale to the public.

Bridges have been studied to see if the incorporation of PCM in road decks can reduce freeze / thaw cycles (Stoll et al. 1996). The repetitive freezing and thawing of concrete bridge decks causes cracking over time. These cracks then allow water to penetrate. With each additional freeze cycle, the water expands and thus enlarges existing cracks as well as developing new cracks due to water in the pore space. This process increases maintenance costs as well as shortening the time before replacement is required. PCM concrete shows promise in minimizing bridge deck maintenance and maximizing life span due to its thermal stabilization properties.

Concrete dams involve placement of mass concrete. The heat of hydration minimizes the volume of concrete that can be placed at a given time in order to allow for dissipation of the heat. Otherwise, large temperature differentials within the concrete mass would cause thermal stresses and thus cracking of a material that is to be impervious to large hydraulic pressures. PCMs may be able to absorb excess thermal energy from the exothermic reaction, providing a thermal buffer to allow for placement of larger volumes of mass concrete at a given time. This has the potential to speed construction and improve economics of mass concrete work (Hunger et al. 2009).

The National Aeronautical Space Administration (NASA) performed a significant amount of research on PCMs in the 1960s to regulate the interior temperature of spacecraft (Bannister 1967). Being in space, a capsule is exposed to solar radiation when in direct sunlight. When shadowed by the earth or moon, the capsule radiates the thermal energy back out to space. PCMs have the ability to store the excess solar thermal energy and release it during periods of radiative cooling, thus maintaining occupant comfort.

The vast variety of uses for energy storage and temperature regulation for which PCMs have been studied make it evident that they have significant potential for these applications. While other uses have been studied, it seems that the most practical application may be for the building environment. PCMs can be used either in energy storage tanks or in the building envelope itself, in both passive and active applications.

The term thermal mass is used to signify the ability of a material to store large quantities of thermal energy and delay thermal penetration through the building envelope. It is related to the heat capacity of the material which refers to the quantity of heat required to raise the temperature of a given mass by one degree (ASHRAE 1997), hence the term thermal mass. Thus, it is related to mass and specific heat of the building envelope material. Increasing mass and/or density increases the thermal mass of a structure.

Thermally massive structures have the ability to attenuate and delay peak interior temperatures in relation to the exterior climatic driving temperatures. This is demonstrated in Figure 1.5. Thermal mass helps to maintain consistent interior temperatures and reduces

temperature differential across the building envelope thus reducing thermal transmittance. In addition, the peak amplitude phase shift has the potential to shift peak energy use to off-peak energy generation times. This shift can help to buffer peak energy generation by power plants, therefore mitigating the need for new peak related generation plants.

In nonresidential buildings, thermal mass is often more effective in reducing cooling loads than heating loads. In some climates, thermally massive buildings can perform significantly better than low mass building regardless of their insulation levels (Wilcox et al. 1985).

Figure 1.5: Thermal Mass Delay and Attenuation (educate-sustainability.eu 2013)

Kosny et al. (2009) have demonstrated that in comparison to materials with low thermal mass and high thermal resistance, comparably resistive materials with high thermal mass have the ability to improve the thermal performance of the building envelope through transient energy storage via specific heat, or in the case of PCMs, latent heat. Thermal mass energy storage has the potential to significantly reduce heating, ventilation, and air-conditioning (HVAC) energy use in many climates. This has led to the development of a Dynamic Benefit for Massive Systems (DBMS) factor that when multiplied by the steady-state R-value, provides the Dynamic R-value Equivalent (DRE) (Kosny et al. 2001) rating which relates the dynamic equivalent of massive structures to the steady-state R-value of lightweight construction. As shown in Figure 1.6 this value provides a measure of the required insulation that a low mass, frame construction structure would need to provide the same energy savings of a massive structure with equivalent steady-state insulation. It is a function of the material configuration and the climatic conditions (Kosny et al. 2009).

Figure 1.6: Relationship between Attic R-Value and Energy Consumption in Bakersfield, CA (Kosny et al. 2009)

Efficiency of thermal mass depends on; building configuration, type of building structure, amount of thermal mass in the building, internal heat sources, climate, steady-state wall R-value, and wall materials configuration. Thermal mass in contact with the conditioned interior is most effective while thermal mass placed on the exterior is the least effective as shown in Figure 1.7 (Kosny et al. 2001).

Figure 1.7: Dynamic Benefit for Massive Systems (DBMS) for House in Washington D.C. (Kosny et al. 2001)

Incorporation of PCMs into the building envelope effectively increases the thermal mass of the structure. As with sensible energy storage, PCM latent heat storage has the benefit of reducing energy consumption, decreasing temperature fluctuations, as well as shifting peak energy use to off-peak hours. However, the PCM must go through the transition temperature and change phase in order to provide energy storage and release.

Theoretically, with a thick enough wall and/or enough PCM, energy from the exterior would never fully penetrate the building envelope during diurnal cycling. However, this would require an uneconomical envelope thickness and/or quantity of PCM. Instead, a more economical use of PCM is one that delays the penetration of heat into the building envelope. This has the effect of lowering the peak interior and exterior wall temperature amplitudes.

In a study by Castellón et al. (2007) in Lleida, Spain, 2.64 meter (8.67 foot) square concrete cubicles were constructed. One cubicle had walls of concrete while the other had walls of concrete incorporating the commercial product, BASF Micronal PCM at 5% mass fraction. Air temperature, interior wall surface temperatures, and heat flux were monitored in each cubicle. Under free floating interior temperatures, it was found that interior wall temperatures for the PCM cubicle were up to 4°C (7°F) cooler than the concrete control cubicle during summer. In addition, a phase lag of approximately two hours was observed in the PCM cubicle.

Further studies by Castellón et al. (2009) involved construction of additional cubicles constructed of brick and alveolar brick with and without insulation as well as with and without PCM. All of the cubicles had sensors measuring interior air temperature, interior wall temperatures, and interior wall heat flux along with an outside weather station and pyrometer. Free floating temperatures were tested for all cubicles; concrete, brick, alveolar brick, brick with insulation, along with all aforementioned material types with PCM. Heat pumps with metering of energy usage were installed for all but the concrete

cubicles. Winter configurations included trombe walls while summer did not. For the winter trombe wall cases, it was found that thermal energy could be stored at lower wall temperatures. The significance of this is that a lower wall temperature produces lower heat transfer losses with the exterior environment during cold weather, thus providing a more efficient system. Under controlled temperature settings in the summer, it was found that alveolar brick with PCM performed better than an insulated brick cubicle. A 14.8% improvement in energy efficiency in contrast to insulated brick was found (Castellón et al. 2009). Reduced peak interior temperature and phase lag is shown in Figure 1.8.

Figure 1.8: Wall Temperature with and without PCM (Castellón et al. 2007)

Finally, thermal mass and thus PCMs have the ability to shift peak cooling loads. This has the potential to improve HVAC performance as well as shift peak energy usage to off-peak hours. Since peak cooling energy consumption can be shifted to nighttime,

condensing unit performance can be improved due a larger temperature differential between the condensing unit and the ambient air temperature as compared to the warmer daytime differential. Further, shifting peak energy consumption to off-peak hours helps to buffer peak energy use and thus can mitigate the need for new power plants built for peak hour demand.

1.5 PCM Characteristics and Types

Ideal PCMs store and release large quantities of thermal energy in a nearly isothermal process in addition to their sensible heat storage. Significant thermal energy is stored and released at the transition temperature via latent heat. Latent heat has much larger energy storage compared to the typical sensible heat values associated with temperature change. A measure of latent heat as compared to the sensible heat of a PCM is the Stephan number, Ste . It provides a ratio of energy storage of sensible heat for a given temperature range divided by the latent heat. A lower Stephan Number indicates higher latent heat storage.

$$Ste = \frac{C_p \Delta T}{L} \quad (1.1)$$

Ste : Stephan Number (unitless)

C_p : Specific Heat ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

ΔT : Temperature Change ($^\circ\text{C}$ or $^\circ\text{K}$)

L : Latent Heat (kJ kg^{-1})

PCMs must provide certain characteristics for effective building envelope applications. These characteristics include significant latent heat energy storage, adequate thermal conductivity with respect to the confining medium, a transition temperature in the range of human comfort, transition range must be reasonably narrow, low reactivity, and the ability to nucleate (Baetens et al. 2010).

There are two main categories of PCMs. These are organic and inorganic PCMs. Organic PCMs include linear alkanes, carboxylic acids (fatty acids), polyethylene glycol (PEG) and other carbon based molecules that provide a change of phase between solid and liquid state (as is the case in typical building envelope applications). Inorganic PCMs typically include hydrated salts of various chemical compositions.

Overall, inorganic PCMs are cheaper, have higher latent heat storage, are more conductive, and are not flammable. On the converse, they have a large volume change and are highly corrosive which causes them to be detrimental to building materials. In addition, they are prone to undercooling and phase separation which affects the long-term efficacy (Baetens et al. 2010).

Although organic PCMs are more costly, flammable, and have poorer thermal performance than inorganic PCMs, their long-term stability and consistent thermal properties throughout the life cycle hold promise for their use in building materials (Baetens et al. 2010). An added benefit of organic PCMs is that their transition temperature can be tailored to the application. With adequate encapsulation or fire retardant treatments,

flammability can be controlled. Thus organic PCMs have potential in the building envelope energy storage sector. The properties of a number of organic and inorganic PCMs are shown in Tables 1.1 and 1.2, respectively. The advantages and disadvantages of organic and inorganic PCMs are in Table 1.3 and 1.4, respectively.

Table 1.1: Organic Phase Change Materials (PCMs)

Organic PCMs		
PCM Compound	Transition Temp. (°C)	Latent Heat (kJ/kg)
Hexadecane	18	200
Octadecane	28	200
Hexadecane / Octadecane Blends	18 to 28	< 200
Capric Acid / Myristic Acid Eutectic	21	200
Capric Acid / Stearic Acid Eutectic	25	180
Butyl Stearate	19	140
PEG 600	22	130
PureTemp 23	23	200

Table 1.2: Inorganic Phase Change Materials (PCMs)
Adapted from (Cabeza and Heinz 2004)

Inorganic PCMs		
PCM Compound	Transition Temp. (°C)	Latent Heat (kJ/kg)
KF 4 H ₂ O	18.5	231
Mn(NO ₃) ₂ 6 H ₂ O	25.8	126
CaCl ₂ 6H ₂ O	29.7	192
LiNO ₃ 3H ₂ O	30	296
51-55% Cu(NO ₃) ₃ 6 H ₂ O + 45-49% LiNO ₃ 3H ₂ O	16.5	250
45-52% LiNO ₃ 3H ₂ O + 48-55% Zn(NO ₃) ₂ 6H ₂ O	17.2	220
55-65% LiNO ₃ 3H ₂ O + 35-45% Ni(NO ₃) ₂ 6H ₂ O	24.2	230
66.6% CaCl ₂ 6H ₂ O + 35-45% Ni(NO ₃) ₂ 6H ₂ O	25	127
45% Ca(NO ₃) ₂ 6H ₂ O + 33.3% MgCl ₂ 6H ₂ O	25	130
48% CaCl ₂ + 4.3% NaCl + 0.4% KCl + 47.3% H ₂ O	26.8	188
67% Ca(NO ₃) ₂ 4H ₂ O + 33% Mg(NO ₃) ₂ 6H ₂ O	30	136

Table 1.3: Advantages and Disadvantages of Organic Phase Change Materials (PCMs).
Adapted from (Kuznik et al. 2011)

Organic PCMs	
<p><i>Advantages</i></p> <ul style="list-style-type: none"> • availability in a large temperature range • freeze without significant super cooling • ability to melt congruently • self-nucleating properties • compatibility with many conventional construction materials • no segregation • chemically stable • relatively high heat of fusion • safe and non-reactive • recyclable 	<p><i>Disadvantages</i></p> <ul style="list-style-type: none"> • low thermal conductivity (can be amended with graphite) • lower volumetric latent heat storage capacity • flammable (depending on containment)

Table 1.4: Advantages and Disadvantages of Inorganic Phase Change Materials (PCMs).
Adapted from (Kuznik et al. 2011)

Inorganic PCMs	
<i>Advantages</i>	<i>Disadvantages</i>
<ul style="list-style-type: none"> • high volumetric latent heat storage capacity • low cost and easy availability • sharp phase change • high thermal conductivity • non-flammable 	<ul style="list-style-type: none"> • large volume change • undercooling • corrosive (especially to steel) • poor thermal stability • phase separation

1.6 Encapsulation Methods

Due to the changing physical nature of PCMs encapsulation is necessary for stabilization during the liquid state. There are two predominant methods of encapsulation; macro-encapsulation and micro-encapsulation. Macro-encapsulation involves encasement of PCM in metal or plastic containment typically a centimeter or larger in diameter. Pouches or canisters are used to prevent PCM seepage during the liquid phase. While this method is economical to produce, there are issues with the lack of nucleation sites to promote crystallization due to a lower surface area to volume ratio. In addition, the large volume has a tendency to inhibit a full phase change throughout the PCM due to differing thermal conductivities of the solid and liquid states.

Micro-encapsulation provides PCM capsules in the range of 20 μ m to 100 μ m in diameter. These microcapsules are capable of repeated cycling without degradation. As shown in Figure 1.9, the shell becomes smoother with increased cycling due to thermal expansion and contraction. In addition, the small size mitigates the nucleation and conductivity issues. However, typical micro-encapsulation techniques create a spherical polymer coating in a dispersion process which increases associated encapsulation costs. Further, the small size creates a significant volume of encapsulation product as compared to the PCM. Core to shell ratio tends to fall in the range of 80% PCM core to 20% shell. Thus a significant portion of the PCM is replaced by the shell. Finally, when mixed into a structural material such as concrete, micro-encapsulated PCMs displace the cement matrix, thus, causing a reduction of strength with increased PCM content.

Figure 1.9: Micro-encapsulated PCM at Different Cycles under SEM (Khudhair et al. 2004)

Another process which has been the focus of this research is vacuum impregnation of the PCM within porous aggregate. This process is attractive because it encapsulates the PCM within the confinement of the aggregate pore space. When utilized in concrete the vacuum impregnated PCM aggregates can be used as lightweight concrete aggregate. In this application the PCM does not displace the cement matrix. The cement matrix surrounds the PCM impregnated aggregates thereby encapsulating them so that retention is not left to surface tension within the pore space. Finally, the microscopic surface irregularities of the pore space provide nucleation sites for PCM crystallization.

Zhang et al. (2004) studied vacuum impregnation of expanded clay and shale. They found that pore diameter and connectivity are essential for absorption of PCM. While expanded shale was capable of incorporating and retaining PCM, expanded clay held significantly larger quantities of PCM. They were able to achieve a significant mass fraction of PCM in the “superlight” expanded clay aggregate up to 68%, 15% for the “normal” expanded clay aggregate, and 6.7% for expanded shale. While the 68% mass fraction uptake is quite significant, the aggregate density is low at 0.76 gm/cm^3 and porosity is 75.6%. Thus it is uncertain whether this aggregate can be used for structural concrete applications. Further, compression testing results were not provided. This is most likely due to the choice of butyl stearate as a PCM. Butyl stearate is a fatty acid and thus deleteriously reacts with cement thereby significantly reducing concrete strength.

Figure 1.10 shows macro-encapsulated PCMs. Figure 1.11 shows micro-encapsulated PCMs. Figures 1.12 and 1.13 compares micro-encapsulated PCMs to vacuum impregnated PCMs in a concrete matrix.

Figure 1.10: Macro-Encapsulated PCM

Figure 1.11: Micro-Encapsulated PCM

Figure 1.12: Representation of Micro-Encapsulated PCM in Cement Matrix
(Not to Scale)

Figure 1.13: Representation of Vacuum Impregnated PCM in Aggregate Pores
(Not to Scale)

1.7 Transient Energy Storage Theory

The fundamental equation for energy storage in building materials is the transient heat flow equation. The equation relates energy storage to the material conductivity and for the case of PCMs, latent heat storage, as a function of time and position. The rate of storage of energy of a material is equal to the sum of the differential of heat entering through the bounding surfaces with respect to position and the rate of energy generation as shown in the following equation (Ozisik 1992). For the rectangular coordinate system (x, y, z) the equation is described as;

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + E \quad (1.1)$$

Where;

C_p : Specific Heat Capacity ($\text{kJ kg}^{-1} \text{K}^{-1}$)

ρ : Density (kg m^{-3})

E : Energy Generation (kJ)

k : Thermal Conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

T : Temperature ($^{\circ}\text{K}$)

x : X Coordinate (m)

y : Y Coordinate (m)

z : Z Coordinate (m)

For the assumption of one-dimensional heat flow this equation simplifies to;

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + E \quad (1.2)$$

For the case of PCM, energy storage, E, is equal to the product of the latent heat, L, the density, ρ , and the fraction, g, of the PCM in liquid state with respect to time;

$$E = -L \rho_{pcm} \frac{\partial g_l}{\partial t} \quad (1.3)$$

Thus the transient heat equation becomes;

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) - L \rho_{pcm} \frac{\partial g}{\partial t} \quad (1.4)$$

Where;

C_p : Specific Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

ρ : Density (kg m^{-3})

ρ_{pcm} : Density of PCM (kg m^{-3})

g : Liquid Phase Fraction

k : Thermal Conductivity ($\text{W m}^{-1} \text{ } ^\circ\text{K}^{-1}$)

L : Latent Heat of Fusion (kJ)

t : Time (s)

T : Temperature ($^\circ\text{K}$)

x : X Coordinate (m)

The equation is non-homogeneous. For a simple case an exact solution can be obtained through separation of variables. For complicated scenarios a numerical solution method is required. Typically a conduction finite difference approximation is used to solve the equation.

1.8 Mathematical Modeling of Latent Heat of PCMs

As stated above, the exact solution to phase change problems is obtainable for only a few idealized situations. These cases are mainly one-dimension infinite and semi-infinite regions with simple boundary conditions. Exact solutions are obtainable only if a similarity solution can be developed allowing the two independent variables x and t to merge into a single similarity variable $x/t^{1/2}$ (Ozisik 1992).

The geometric configuration and boundary conditions of building envelope analysis do not allow exact solutions. Thus numerical methods must be used to solve these phase change problems. The transient heat equation is discretized in order to obtain a solution. Strong form solutions allow determination of the phase change boundary. However, this process is quite complex. Weak form solutions avoid the explicit nature of the moving boundary. These weak solution methods are the apparent capacity method, the effective capacity method, the heat integration method, the source based method, and the enthalpy method to name a few (Hu and Argyropoulos 1996). The following are explanations of the above referenced solution methods presented by Hu and Argyropoulos (1996).

The Apparent Heat Capacity method accounts for phase change by varying the heat capacity of the material. The heat capacity is provided for three regions; the solid phase, the transition from solid to liquid, and the liquid phase as follows;

$$C_{app} = \begin{cases} C_s & T < T_s & \text{Solid Phase} \\ C_{in} & T_s < T < T_l & \text{Solid/Liquid Phase} \\ C_l & T > T_l & \text{Liquid Phase} \end{cases} \quad (1.5)$$

Where;

C_{app} : Apparent Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

C_s : Solid Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

C_{in} : Solid / Liquid Transition Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

C_l : Liquid Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

T : Temperature ($^\circ\text{K}$)

T_s : Solid Phase Transition Temperature ($^\circ\text{K}$)

T_l : Liquid Phase Transition Temperature ($^\circ\text{K}$)

Then;

$$C_{in} = \frac{\left\{ \int_{T_s}^{T_l} C(T) dT + L \right\}}{(T_l - T_s)} \quad (1.6)$$

Where;

C : Specific Heat Capacity ($\text{kJ kg}^{-1} \text{ K}^{-1}$)

L : Latent Heat (kJ kg^{-1})

Thus;

$$C_{app} \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \quad (1.7)$$

Where;

k : Thermal Conductivity ($\text{W m}^{-1} \text{ }^\circ\text{K}^{-1}$)

x : X Coordinate (m)

t : Time (s)

The Effective Capacity method improves upon the apparent capacity method. The temperature profile is assumed between nodes. An effective capacity is calculated based on integration through the control volume as show below.

$$C_{eff} = \frac{\left(\int C_{app} dV \right)}{V} \quad (1.8)$$

Where;

C_{eff} : Effective Heat Capacity ($\text{kJ kg}^{-1} \text{ K}^{-1}$)

C_{app} : Apparent Heat Capacity ($\text{kJ kg}^{-1} \text{ K}^{-1}$)

V : Control Volume (m^3)

The Heat Integration method is performed by monitoring the temperatures of the control volumes. For the melting case, when the temperature of a control volume exceeds the melting temperature, the material in that control volume is assumed to undergo phase

change. The temperature of that control volume is then reset to the melting temperature and the amount of heat due to resetting the temperature is added to an enthalpy account for that control volume. Once the enthalpy account equals the latent heat, the temperature is allowed to rise.

The Source Based method allows the latent heat to be modeled as an additional term representing a source or sink. This allows existing codes to be easily adapted to include latent heat. The heat equation with the source term is as follows;

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + E \quad (1.9)$$

Where;

C_p : Specific Heat Capacity ($\text{kJ kg}^{-1} \text{ }^\circ\text{K}^{-1}$)

ρ : Density (kg m^{-3})

E : Energy Generation (kJ)

k : Thermal Conductivity ($\text{W m}^{-1} \text{ }^\circ\text{K}^{-1}$)

T : Temperature ($^\circ\text{K}$)

t : Time (s)

x : X Coordinate (m)

The Enthalpy method is based on the relationship between enthalpy and temperature. An enthalpy-temperature curve is created such as is shown below in Figures 1.14 (a) and (b).

Figure 1.14: Enthalpy as a function of temperature for (a) isothermal phase change; (b) Non-isothermal phase change (Hu and Argyropoulos 1996)

For isothermal phase change, $T_s = T_l$;

$$h = \begin{cases} C_s T & T \leq T_s & \text{Solid Phase} \\ C_l T + L & T > T_l & \text{Liquid Phase} \end{cases} \quad (1.10)$$

For non-isothermal, linear phase change;

$$h = \begin{cases} C_s T & T < T_s & \text{Solid Phase} \\ C_{in} T + \frac{H_f (T - T_s)}{(T_l - T_s)} & T_s < T < T_l & \text{Solid/Liquid Phase} \\ C_l T + L + C_{in} (T_l - T_s) & T > T_l & \text{Liquid Phase} \end{cases} \quad (1.11)$$

Where;

C_s : Solid Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

C_{in} : Solid / Liquid Transition Heat Capacity ($\text{kJ kg}^{-1} \text{ K}^{-1}$)

C_l : Liquid Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

L : Latent Heat (kJ/kg)

T : Temperature ($^\circ\text{K}$)

T_s : Solid Phase Transition Temperature ($^\circ\text{K}$)

T_l : Liquid Phase Transition Temperature ($^\circ\text{K}$)

All of the above described methods allow the formulation of latent heat in the transient heat conduction equation. The equation developed in the Apparent Heat Capacity method can be easily discretized and solved numerically. The Effective Heat Capacity method was developed to improve upon the Apparent Heat Capacity method. However, it is computationally intensive. The Heat Integration method, also called the post-iterative method is simple and computationally efficient. However, accuracy depends on the time step. The Source Based method allows a heat source or sink to be added to the general form of the transient heat equation as an additional term. Therefore, existing numerical code can be easily adapted. In addition, it provides good accuracy and is computationally efficient. Finally, the Enthalpy method is accurate and the solution is independent of the time step. However, it is complex and computationally intensive (Hu and Argyropoulos 1996).

CHAPTER TWO: PCM CONCRETE DEVELOPMENT AND TESTING

2.1 PCM Concrete Development

Since the objective of this research was to develop a concrete mix that can be used to create Concrete Masonry Units (CMUs), a commercial lightweight concrete masonry mix design was obtained from a local block manufacturer. The aggregate gradation, cement types, proportions and mix water were examined for this mix. Although mix design was based on this local manufacturer's mix, other lightweight aggregates and proportions (following recommended ESCSI standards) were needed to enable PCM incorporation.

Sieve analyses of all of the aggregates that could be used in the PCM concrete mix were conducted. ASTM standard, round, 20 cm (8 inch) diameter sieves were used for all of the sieve analyses. The standard sieve sizes for concrete masonry gradation are 3/8 inch (9.50 mm), #4 (6.35 mm), #8 (3.18 mm), #16 (1.59 mm), #30 (0.85 mm), #50 0.51 mm), and #100 (0.25 mm).

The next step in mix development was the identification of potential PCMs for incorporation into concrete mixes. Initial PCM choices were determined according to their latent heat and transition temperature. This entailed selecting PCMs with a reasonably large latent heat value typically ranging from 150 kJ/kg to 250 kJ/kg, and a transition temperature within $\pm 5^{\circ}\text{C}$ (9°F) of room temperature ($\sim 20^{\circ}\text{C}$, 68°F). Though, several PCMs

that exceeded the $\pm 5^{\circ}\text{C}$ (9°F) from room set point limits were also studied. Next, PCMs were examined for reactivity and thus salt hydrates were excluded. The prime focus of the PCM evaluation was therefore restricted to organic PCMs.

Once a variety of PCMs were selected, encapsulation methods were studied. Three encapsulation methods were studied including micro-encapsulation, form-stabilized diatomaceous earth, and form-stabilized vacuum impregnated porous expanded aggregates. Micro-encapsulation and form-stabilized diatomaceous earth PCMs are commercially available while vacuum impregnation of aggregates was done in the laboratory. Micro-encapsulation is the most common of the PCM encapsulation methods due to its ease of use, although it does add to cost. Diatomaceous earth form-stabilization is less common than micro-encapsulation. However, the use of earthen materials is less expensive than other forms of micro-encapsulation. The downside of this is that the diatomaceous earth encapsulation has a large volume in comparison to other forms of PCM encapsulation. Vacuum impregnation reduces costs by also using earthen materials, and there is a significant volume of the PCM incorporated into the aggregate for little or no additional volume in the mix. The vacuum impregnated aggregates can be incorporated as a structural constituent of the PCM concrete mix if the aggregates are significantly strong. Thus vacuum impregnation holds significant promise for PCM Concrete Masonry Unit development.

Having examined the aggregates, chosen the PCMs, and the encapsulation types, the next step was designing mixes that used all three forms of encapsulation and a variety

of PCMs. All mixes began with a standard block mix modified to incorporate micro-encapsulated PCMs, the diatomaceous earth form stabilized PCMs and finally, vacuum impregnated PCM aggregates.

A total of 24 PCM concrete mixes were developed and prepared. The physical and mechanical properties of the aggregates and concrete mixes were examined and density was measured for the cast concrete samples. Finally, compressive strength was determined for the cast PCM concrete samples.

2.1.1 Aggregate Analysis

The initial step in the PCM concrete mix design was to determine gradation and bulk density of all of the aggregates that could be used in concrete masonry block mixes. The local block manufacturer mix aggregates included crushed limestone, crushed expanded shale, and dredged river sand. A sieve analysis was performed for each of the aggregate types. The bulk density for each aggregate sieve fraction was determined for all of the aggregates. These are summarized in Tables 2.1 and 2.2.

In addition to the provided mix aggregates, other lightweight aggregates were obtained and analyzed. These included several expanded clay blends of varying gradations, several vermiculite blends, expanded perlite, zonolite, and graphite. Sieve analysis and bulk density were determined for each aggregate type. These results are also shown in Tables 2.1 and 2.2.

Table 2.1: Aggregate Sieve Analysis Results

Sieve	Percent Retained					
	Limestone	Expanded Shale	Sand	Expanded Clay (Fines)	Expanded Clay (Intermediates)	Expanded Clay (10% Blend)
3/8	0.00%	0.00%	0.00%	0.00%	0.00%	0.04%
#4	2.65%	1.88%	2.20%	0.11%	37.92%	7.69%
#8	23.12%	25.22%	9.46%	13.87%	34.59%	12.03%
#16	33.41%	26.55%	14.41%	32.77%	16.64%	30.21%
#30	21.90%	17.37%	27.83%	21.78%	6.53%	19.73%
#50	11.39%	11.28%	37.73%	15.96%	2.62%	17.98%
#100	4.98%	6.86%	7.37%	10.94%	1.15%	7.34%
Pan	2.55%	10.84%	0.99%	4.58%	0.54%	4.99%

Table 2.2: Additional Aggregate Sieve Analysis Results

Sieve	Percent Retained					
	Ottawa Sand	Vermiculite (Fine)	Vermiculite (Medium)	Vermiculite (Coarse)	Perlite	Zonolite
3/8	0.00%	0.00%	0.00%	3.11%	0.00%	0.00%
#4	0.00%	0.00%	2.68%	59.33%	5.54%	0.00%
#8	0.00%	3.55%	31.77%	26.89%	43.24%	0.00%
#16	0.00%	42.45%	49.66%	7.55%	28.82%	0.67%
#30	0.97%	41.33%	11.86%	1.55%	9.98%	54.53%
#50	84.74%	9.33%	2.68%	0.45%	5.10%	34.21%
#100	13.89%	2.00%	0.67%	0.45%	2.88%	7.28%
Pan	0.40%	1.33%	0.67%	0.67%	4.44%	3.31%

Individual sieve results for each aggregate can be found in Appendix B.

Aggregate density test results are shown in Table 2.3.

Table 2.3: Aggregate Density Results

Sieve Size	Limestone		Expanded Shale		Expanded Clay		Sand		Vermiculite		Perlite		Graphite	
	gm/ml	lb/ft ³	gm/ml	lb/ft ³	gm/ml	lb/ft ³	gm/ml	lb/ft ³	gm/ml	lb/ft ³	gm/ml	lb/ft ³	gm/ml	lb/ft ³
#4	1.29	80.50	0.61	37.86	0.55	34.23	1.52	94.54	0.11	6.69	0.12	7.24	n.a.	n.a.
#8	1.39	87.03	0.64	39.78	0.58	36.25	1.53	95.47	0.15	9.32	0.15	9.20	n.a.	n.a.
#16	1.47	91.57	0.66	41.27	0.59	36.59	1.51	94.52	0.15	9.53	0.13	8.24	0.169	10.55
#30	1.48	92.57	0.69	42.98	0.60	37.44	1.54	95.81	0.14	8.68	0.11	6.86	0.165	10.28
#50	1.51	94.15	0.77	47.91	0.62	38.87	1.56	97.14	0.16	9.98	0.15	9.54	0.135	8.43
#100	1.43	89.14	0.81	50.60	0.63	39.43	1.55	96.56	0.25	15.39	0.19	12.11	0.183	11.40
Pan	1.11	69.26	0.95	59.39	0.64	40.01	1.64	102.34	0.38	23.71	0.17	10.31	0.247	15.39

From the density results, it can be seen that sand has the highest bulk density. This is logical since sand is typically formed from quartz. Limestone also has a higher density than expanded shale and expanded clay. Expanded vermiculite and expanded perlite are much lower in density than the other aggregates. Graphite has a slightly higher density than vermiculite in the #16 and # 30 sizes while lower for the # 50, #100 and pan sizes.

2.1.2 PCM Choice and Preparation

A variety of PCMs were evaluated during the development of a viable PCM concrete mix. These included linear alkanes, as well as fatty acids. Encapsulation systems included commercial micro-encapsulation, commercially available PCM form stabilized in diatomaceous earth, and bulk PCM vacuum impregnated into porous aggregate in our lab.

Three micro-encapsulated PCMs were evaluated. The first PCM studied was micro-encapsulated BASF Micronal 5001 which is a proprietary organic PCM with a transition temperature of 26°C (79°F). Next were the commercial micro-encapsulated PCM products, Microtek 18d and 28d. Microtek 18d is comprised of pure n-Hexadecane

and has a transition temperature of approximately 18°C (64°F). Microtek 28d consists of n-Octadecane and has a transition temperature of approximately 28°C (82°F). Finally, two products from Entropy Solutions were examined. These were bulk PureTemp 23 (PT23) as well as PureTemp 23 form-stabilized in diatomaceous earth. Both of the PureTemp 23 PCMs have a transition temperature of approximately 23°C (73°F).

Several other bulk linear alkane PCMs were evaluated during the PCM concrete development. As shown in Figures 2.1 and 2.2 these were n-Hexadecane, n-Octadecane, and a proprietary linear alkane blend from Microtek Laboratory with a transition temperature of 24°C (75°F). These linear alkanes consist of a chain of saturated carbon atoms with the associated single bonded hydrogen atoms. In addition, bulk Capric acid (Decanoic acid) and Myristic acid (Tetradecanoic acid) were also examined (See Figures 2.3 and 2.4). These are both fatty acids (carboxylic acids) consisting of saturated carbon chains and a carboxyl group. All of the bulk PCMs were encapsulated using the vacuum aggregate impregnation method. Graphical representations of these PCMs are shown in Figures 2.1 through 2.4.

Figure 2.1: n-Hexadecane
 $\text{CH}_3 (\text{CH}_2)_{14} \text{CH}_3$ (3DChem 2013)

Figure 2.2 n-Octadecane
 $\text{CH}_3 (\text{CH}_2)_{16} \text{CH}_3$ (3DChem 2013)

Figure 2.3: Capric Acid (n-Decanoic Acid)
 $\text{CH}_3 (\text{CH}_2)_8 \text{COOH}$ (3DChem 2013)

Figure 2.4 Myristic Acid
 $\text{CH}_3 (\text{CH}_2)_{12} \text{COOH}$ (3DChem 2013)

The Capric acid (Decanoic Acid) and Myristic acid (Tetradecanoic Acid) PCMs were blended to a 74% Capric acid and 26% Myristic acid ratio by mass according to Figure 2.5. As shown in Figure 2.5, this is the eutectic point for the two PCMs with a melting point of 21°C (70°F) (Karaipekli and Sari 2008). Proportioned quantities of Capric acid and Myristic acid were weighed and combined. The solid PCM flakes were slowly heated and stirred until both materials had melted. The mixture was then stirred for approximately 10 minutes to ensure complete blending of the eutectic mixture.

Figure 2.5: Eutectic Proportioning of Capric acid and Myristic acid (Karaiekli and Sari, 2008)

Organic PCMs were used because inorganic PCMs are typically hydrated salts which are inclined to react strongly with metals. Since the goal of this research is to develop a viable PCM concrete mix that can be used in concrete masonry units (CMUs), salt related corrosion with metal is a significant concern since most masonry structures are reinforced with steel reinforcing bars. Furthermore, even if a salt hydrate PCM concrete that does not react with metals could be developed, the conservative construction industry would likely still not adopt it due to the negative past experience with corrosion of reinforcement.

2.1.3 PCM Encapsulation

Several methods of encapsulation were used during the PCM concrete mix development process. These were micro-encapsulation, diatomaceous earth form stabilization, and vacuum impregnation of expanded porous aggregate form stabilization. Micro-encapsulated PCM was used in the initial trials due its commercial availability, and ease of use, with PCM contained within polymer spheres. Micro-encapsulation allowed the PCM to be incorporated as part of the mix aggregates.

Initially, viable micro-encapsulated PCM mixes were difficult to obtain. This was because the micro-encapsulated PCM spheres are very small, being less than 100 μ m in diameter. This created a large surface area due to the micro-encapsulated PCM which in turn required significant quantities of mix water to obtain a workable mix. The resultant water to cement ratios were initially around 1.0, which is quite high. In addition, the mechanical agitation of the concrete mixer had a tendency to rupture the PCM capsules. Thus between excess mix water and PCM from ruptured capsules entering the cement matrix, initial mixes had poor strength. With the addition of a water-reducing superplasticizing agent and the delayed addition of the micro-encapsulated PCMs to the final stages of mixing, a viable mix was developed. This mix contained 9% micro-encapsulated PCM by mass. It should be noted that 20% of the PCM is the encapsulation, so only approximately 7% PCM was incorporated in the mix by mass fraction.

Because of the added cost of micro-encapsulation and the relatively low PCM percentages possible with micro-encapsulated PCMs, alternative encapsulated methods

were examined. One alternative was presented by Entropy Solutions. This was a fatty acid form stabilized PCM in diatomaceous earth with a mass fraction of approximately 40% PCM. Like micro-encapsulated PCM, the diatomaceous earth form stabilized PCM also displaced the cement in the concrete mix. This PCM composite was mixed within the concrete matrix in a similar fashion to the micro-encapsulated PCM. Surface tension maintains stability of the product prior to mixing. Due to the significant cement matrix displacement and introduction of unconfined PCMs, a viable mix was not obtained using this form of PCM.

Focus was then placed on vacuum impregnation of porous aggregates. This process has the benefit of placing the PCM within the aggregate pore space and not in the cement matrix. Cement is not displaced by the PCM, thus reducing the amount of cement needed to achieve a mix that has the potential to meet ASTM C90 strength requirements while also containing significant quantities of PCM.

Several expanded porous aggregates were examined for potential use in vacuum impregnation. These included expanded vermiculite, expanded perlite, expanded shale, and expanded clay. Due to their compressibility, expanded vermiculite and perlite did not provide the strength needed to create a structural mix. Expanded shale did not provide adequate PCM uptake, most likely due to the unconnected nature of its pore space. However, expanded clay was found to have considerable PCM retention capabilities. Thus, expanded clay aggregates were used for the vacuum impregnation process in all subsequent mix designs.

Expanded clay is manufactured by heating pellets of clay at high temperatures. As shown in Figure 2.6, this causes the moisture trapped in the pore space to expand creating a lightweight ceramic aggregate with a large volume of interconnected pore space. Interconnected pore space is important for the vacuum impregnation process since the PCM must be able to penetrate deeply within the aggregate and the aggregate must be able to retain a significant quantity of PCM. In addition, expanded clay is already used as an aggregate in many commercial lightweight concrete and CMU mixes. Figure 2.6 shows a typical expanded clay aggregate section.

Figure 2.6: Section of Porous Expanded Clay Aggregate

The process of vacuum impregnation involves drawing the air from the aggregate pore space and then replacing it with PCM. In order to do this a vacuum impregnation

device was developed. As shown in Figures 2.7 and 2.8 the principle components of this device were a vacuum pump, a pressure vessel to hold the aggregate, a vacuum regulated funnel to hold the PCM under vacuum pressure prior to impregnation, and a water-filled vacuum trap to protect the vacuum pump from fumes. In addition, a hotplate kept the pressure vessel and the aggregate warm. A heat lamp kept the PCM molten in the funnel. Initially a 2000 ml flask was used as the pressure vessel during initial development. In order to increase production, a stainless steel pressure vessel was constructed to achieve a larger yield for PCM concrete production.

Figure 2.7: Initial Vacuum Impregnation Apparatus

Figure 2.8: View of Enlarged Vacuum Impregnation Apparatus

The vacuum impregnation procedure was as follows;

- (1) The PCM was heated to a liquid state.
- (2) The PCM was then introduced into the vacuum regulated funnel with the PCM temperature maintained via a heat lamp.
- (3) Dry aggregate was placed in the pressure vessel and warmed with the hotplate.

- (4) A vacuum was applied to the sealed system for 10 minutes with the aggregate and PCM separate in order to remove the air from the aggregate pores. Heating of the aggregate and PCM combined during the air removal process would have blocked the pore openings at the surface and thus would have inhibited removal of air from the pore space. Ten minutes was deemed appropriate since the air bubbles filtering through the vacuum trap had substantially dissipated indicating that the air in aggregate pores had been removed.
- (5) The liquid PCM was introduced into the pressure vessel and mixed with the aggregate. An additional 10 minutes of vacuum was maintained to remove any air that may have been introduced with the PCM in solution.
- (6) The vacuum was released and the PCM was allowed to penetrate the pore space. Again, 10 minutes was allowed for impregnation into the pore space.
- (7) The pressure vessel was opened, the extra PCM was decanted, and the PCM impregnated aggregate was allowed to drain on a sieve.

After draining, the PCM aggregates were rinsed in a solution of 50% water and 50% ethanol to remove the PCM from the surface of the aggregate to facilitate bonding with cement during concrete mixing. This solution was considered strong enough to remove the PCM surface coating but not remove substantial PCM from the pores. The PCM aggregate was then placed on drying pans and allowed to dry under forced

convection. Excellent PCM retention was achieved. It is believed, however, that with additional study, this process could possibly be improved to increase PCM retention.

In order to determine the amount of PCM retained, the dry aggregate was weighed prior to vacuum impregnation. The PCM aggregate was again weighed after impregnation and drying. The difference in weight after impregnation divided by the pre-impregnation weight provided the mass ratio of PCM retained in the aggregate. The impregnation process was performed on the aggregates retained on the #4 (6.35 mm), #8 (3.18 mm), #16 (1.59 mm), and #30 (0.85 mm) sieves. Multiple samples with the exception of PureTemp 23 were examined for impregnation efficiency. The average PCM impregnation results for each sieve size are listed in Table 2.4. Smaller sized aggregates were found to hold little PCM and were difficult to handle, especially when sieving and rinsing, and thus were not used. Further research may identify an economical way to impregnate all of the aggregates and thus improve total PCM in the mix.

Table 2.4: Average Vacuum Impregnation Results

Sieve	PCM Type				
	Capric/ Myristic Acid Blend	n- Hexadecane	n- Octadecane	Linear Alkane Blend	PureTemp 23
#4 (6.35mm)	24%	23%	27%	24%	41%
#8 (3.18 mm)	17%	25%	25%	25%	25%
#16 (1.59 mm)	20%	30%	34%	32%	26%
#30 (0.85 mm)	17%	23%	36%	31%	37%

Impregnation percentages were similar for all of the PCMs. The linear alkanes were consistent with the exception of the #30 (0.85 mm) sieve fraction. The values of impregnation for n-Octadecane, the Linear Alkane Blend, and PureTemp 23 ranged from 31% to 37% while the Capric/Myristic Acid Blend and n-Hexadecane had retentions of 17% and 23% respectively. The discrepancies for this sieve fraction are likely due to the small aggregate size creating difficulties in the decanting and rinsing process for that size. The small diameter #30 (0.85 mm) sieve fraction aggregates caused a situation where close aggregate proximity created small aggregate interstices and thus allowed surface tension to dominate. This made it difficult to fully rinse the aggregates. Higher uptake percentages likely indicate excess surface PCM on the aggregate which was not removed during washing.

Beyond the #30 (0.85 mm) aggregates, the Capric acid / Myristic acid eutectic provided similar results to the linear alkanes. However, PureTemp 23 retention was quite high for the #4 (6.35 mm) and #30 (0.85 mm) sieve sizes. The PureTemp 23 was the last PCM evaluated during testing and only one vacuum impregnation was performed for this PCM. Additional, impregnations may provide an average that is closer to the other PCMs. It is likely that PCM viscosity plays a significant role in the retention values.

2.1.4 Concrete Mix Design

The initial concrete mix design was based upon a mix developed by a local concrete masonry unit manufacturer which is shown in Table 2.5.. The mix contained limestone, dredged river sand, and expanded shale aggregates along with Type III Portland cement

and Slag cement as well as a waterproofing admixture, all of which were constituents in the manufacturers mix. As shown in Figures 2.9 and 2.10, the mix was proportioned according to aggregate weights. By mass, the manufacturers mix did not remain in the bounds of the Expanded Shale, Clay, and Slate Institute (ESCSI) gradation limits as is common for masonry block mixes (Holm 1997). Due to the significant variations of density between different aggregates, the mix gradation was examined according to volumetric fractions rather than by weight. Using typical aggregate densities, the mix volume fractions did fall within the ESCSI gradation as shown in Figures 2.11 and 2.12.

For the micro-encapsulated PCM concrete, the commercial mix was altered by removing the fines (sieve size #50 (0.5 mm, 1/50th of an inch) and lower) in the limestone, expanded clay, and sand aggregates. These sieve fractions were replaced with the micro-encapsulated PCM capsules. Two micro-encapsulated PCM percentages were examined; approximately 9% and 17% by mass. These values include the mass of the PCM and the polymer capsules, and thus, provided lower actual percentages of PCM. Type III Portland cement proportions were varied in the mix to optimize strength. A viable mix with 9% micro-encapsulated PCM was obtained by increasing the Type III Portland cement weight by 150% of the original mix and by using a water-reducing superplasticizer. This mix provided approximately 7% PCM by mass after correction for the polymer capsule mass.

Figure 2.9 shows the ESCSI gradation limits. Figure 2.10 shows the commercial lightweight concrete masonry block mix gradation by mass. Figure 2.11 shows the commercial lightweight concrete masonry block mix gradation by volume. Finally, Figure

2.12 shows the proportion of the commercial lightweight block mix replaced by micro-encapsulated PCMs.

Table 2.5: Commercial Block Mix Proportions by Weight

Mix Component	Percent Weight (%)	Density (kg/m ³)	Density (pcf)
Type III Cement	9.89%	1505.7	94
Grade 100 Slag Cement	1.77%	1505.7	94
Expanded Shale	31.80%	789.7	49.3
Manufactured Limestone	24.95%	1525.0	95.2
Concrete Sand	31.58%	1499.3	93.6
M.P. Additive	0.01%	1000.0	62.4

Figure 2.9: ESCSI Minimum and Maximum Gradation Limits

Figure 2.10: Commercial Block Mix by Mass

Figure 2.11: Commercial Block Mix by Volume

Figure 2.12: Commercial Block Mix w/ Volume Replaced by Micro-encapsulated PCM

A similar concrete mix was utilized with the form stabilized PureTemp 23 PCM in diatomaceous earth. Instead of just the coarse fractions the entire aggregate range was used. For this mix 20% form stabilized PCM composite by mass was added to the standard mix.

Initially the diatomaceous earth PCM clumped. This occurred because during transport it had exceeded 23°C (73°F) causing melting, and then cooled and solidified. Removal of the PCM from the container provided large chunks that could not be used in the mix. In order to remove the clumps, the PCM material was warmed and then mixed with the coarse aggregates. This mitigated the clumping. Finally, the remainder of the

aggregates, cement and water were added to the mix. These difficulties caused abandonment of this PCM incorporation method.

In an effort to improve the PCM concrete mix economics, mixes incorporating vacuum impregnated aggregates were developed. These mixes used a variety of PCMs including n-Hexadecane, n-Octadecane, a linear alkane blend with a transition temperature of 24°C (73°F), a eutectic mixture of Capric acid and Myristic acid, and liquid PureTemp 23.

Due to the significant differences in the aggregate densities, the mixes were developed using volume fractions rather than the traditional mass proportions. The bulk density values of the aggregates were used to convert the original mix fractions to volumes. This conversion is necessary when mixing heavy aggregates, such as sand and limestone with lightweight aggregates such as expanded clay and expanded vermiculite.

The ESCSI gradation limits were used as bounds to create a mix that maximized PCM incorporation but maintained workability. PCM was incorporated in the expanded clay aggregate #4 (6.35 mm), #8 (3.18 mm), #16 (1.59 mm), and #30 (0.85 mm) sizes. A new mix was designed by sieve fractions incorporating expanded clay with and without PCM, crushed limestone, and sand as shown in Figure 2.13. This mix had significant PCM content and provided a workable mix for both the controls and PCM mixes.

Figure 2.13: Vacuum Impregnated Expanded Clay PCM Concrete Mix by Volume

A concrete mix was also designed using PCM impregnated expanded clay and expanded vermiculite aggregates. Figure 2.14 shows gradation for this mix.

Figure 2.14: Vacuum Impregnated Expanded Clay and Vermiculite PCM Concrete Mix by Volume

Initially, there was considerable difficulty creating a vacuum impregnated PCM concrete mix that met the compressive strength requirements. At the time, a PCM blend of Capric acid and Myristic acid was being used. Surface cracking of the test cylinders at 2 to 3 weeks after casting suggested a possible cause for the low compressive strengths for the Capric acid and Myristic acid mixes.

At first, the cracking was thought to be caused by hydration related thermal stress. A thermocouple was placed in the center of a sample after casting to determine if this might be the cause. It was found that the interior temperature of the PCM concrete test cylinder raised only slightly during curing. This is probably due to energy storage capacity of the PCM. Further investigation found that there is a reaction between fatty acids and Portland cement. The fatty acid glycerides are broken down by hydrolysis in their constituent acid and alcohol components. This is mainly brought about by the action of aqueous solutions of mineral acids or hydroxides. In alkaline hydrolysis the metal of the hydroxide forms a salt with the fatty acid. This is the process where solutions of sodium or potassium hydroxide act on fats and oils and is used to produce salts, or soaps. This process is known as saponification (Lea and Desch 1956). Saponification cracking is what can be seen in Figure 2.15.

Figure 2.15: Surface Cracking of Cylinders due to Saponification

Once it was determined that saponification was the cause of poor compressive strengths, alternative PCMs were examined. The linear alkanes such as n-Hexadecane, n-Octadecane, and the Microtek 24°C linear alkane blend were used. Once these PCMs were incorporated into the concrete mixes, strengths in excess of the ASTM C90 requirements were obtained. The PureTemp 23 PCM was also investigated. Although PureTemp 23 is vegetable derived and most likely a fatty acid, it had less of a reaction with the cement matrix likely due to esterification of the carboxyl group, reducing reactivity. This PCM has the advantage of having a high heat of fusion and a relatively low cost.

2.2.1 PCM Content

The PCM content was quantified for all of the PCM mixes. For the micro-encapsulated mixes the PCM / capsule content was the mass of the PCM powder incorporated into the concrete mix divided by the PCM concrete mix mass. The micro-encapsulated PCMs were assumed to be 20% resin capsule and 80% PCM. Thus the PCM for micro-encapsulated mixes was 80% of the mass added to the mix. The 20% value was estimated based on thermal testing of the micro-encapsulated PCMs and their pure forms.

The form stabilized diatomaceous earth PCM content was determined similarly to the micro-encapsulated PCM. The PCM / diatomaceous earth content was calculated as the mass of the material incorporated into the concrete mix divided by the PCM concrete mix mass. The diatomaceous earth was approximately 60% of the form-stabilized PCM. Thus, the PCM for the diatomaceous earth stabilized earth mixes was 40% of the mass added to the mix.

The PCM content of the vacuum impregnated expanded porous aggregate PCM concrete was more difficult to quantify. PCM was incorporated into the #4 (6.45 mm), #8 (3.18 mm), #16 (1.59 mm), and #30 (0.85 mm) aggregates. Each aggregate retained different quantities of PCM. In addition, variations in PCM retention were observed for different vacuum impregnation batches of the same PCM. This was a result of slight variations in liquid PCM temperature and thus viscosity, PCM / aggregate mixing, and rinsing of the PCM aggregates. Therefore each mix had slightly different proportions of PCM for each aggregate size. Thus, PCM content was dependent on the individual

aggregate impregnations for each of the sieve sizes and the proportion of each aggregate incorporated into the PCM concrete mix. Table 2.6 summarizes the estimated PCM contents by mass for each concrete mix and PCM encapsulation method. The designations 1.0X, 1.5X, and 2.0X refer to the ratio of the amount of cement in the vacuum impregnated mix as compared to the initial mix obtained from the local block manufacturer.

Table 2.6: PCM Percentage of Concrete Mixes

Mix	PCM Percent
Microtek Micro-encapsulated PCM (1.5X Cement)	7%
Hexadecane (1.5X Cement)	11%
24°C Alkane Blend (1.0X Cement)	14%
24°C Alkane Blend (1.5X Cement)	13%
24°C Alkane Blend (2.0X Cement)	10%
Octadecane (1.5X Cement)	13%
PureTemp 23 (1.5X Cement)	12%

2.2.2 Concrete Density

The concrete density was determined for the control and PCM concrete mixes. This density is needed to accurately evaluate the transient thermal mass behavior of the material because both specific heat and latent heat are dependent on the material mass.

Density was determined during mixing. Each cylinder was weighed full, after consolidation. The weight divided by the cylinder volume provided the density. Initially the cylinders were weighed a second time after the 28 day curing period. However, very

little deviation was found so further density measurements were only performed at the mixing stage. Density was dependent upon the mix compaction. Due to variability in compaction, the PCM mix design values were adjusted for PCM content as a ratio of the projected yield to the actual volumetric yield. Thus, the volume of the entire batch produced was measured to adjust the PCM content. Table 2.7 summarizes the results of the measured densities for all of the concrete mixes.

Table 2.7: Concrete Densities

Mix	Density (kg/m³)	Density (pcf)
Local Block Mix	1791	112
BASF 9%	1440	90
BASF 17%	1302	81
Microtek 18D 9%	1645	103
Microtek 18D 17%	1398	87
Microtek 28D 9%	1661	104
Microtek 28D 17%	1175	73
PT 23 Diatom. Earth	1469	92
Exp. Clay Vac. Imp. Control (1.5 Cement)	1497	93
Exp. Clay Vac. Imp. Control (2X Cement)	1419	89
Exp. Clay Vac. Imp. CA-MA (2X Cement)	1446	90
Exp. Clay Vac Imp. n-Hexadecane (1.5X Cement)	1561	97
Exp. Clay Vac. Imp. 24C Alkane (1.5X Cement)	1537	96
Exp. Clay Vac. Imp. n-Octadecane (1.5X Cement)	1506	94
Exp. Clay Vac. Imp. 24C Alkane (2X Cement)	1658	103
Exp. Clay Vac. Imp. PT 23 (1.5X Cement)	1769	110

By examining the density data it can be seen that the local block mix had the highest density. This is a result of the large amounts of crushed limestone and sand, both being high in density as was shown in Table 2.3. The mixes incorporating BASF and Microtek

micro-encapsulated PCM decreased in density with increased PCM content. This is because the micro-encapsulated PCM is replacing a portion of the mix matrix.

The expanded clay controls for the vacuum impregnation mixes contained an anomaly. The mix with 1.5X cement had a higher density than the 2.0X cement control mix. This is likely due to variability in the compaction process during casting. While the vacuum impregnated mixes contained significant quantities of lightweight expanded clay aggregate, the PCM impregnated into them increased their density significantly and thus increased the mix density as well.

2.2.3 Compression Testing

Compressive strength testing of all PCM concrete mixes was performed according to the ASTM C39 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens (ASTM 2012). As shown in Figure 2.16, 7.62 cm (3”) diameter by 15.24 cm (6”) height cylinders were tested in a Satec Systems, 270 kN (60 kip), universal testing machine after curing for 28 days in a moist room having a temperature of 20°C (68°F) and a relative humidity of 98% ± 2%. A minimum of three samples were tested until failure with the resulting maximum loading recorded. The maximum load divided by the sample area was calculated to determine the compressive strength. Failed specimens were photographed and failure mechanisms were noted. Typical concrete sample specimens are shown in Figure 2.16. The typical crushing pattern of failure is shown in Figure 2.17. Figure 2.18 shows the average compression test results for each mix as well as the

minimum strength required by ASTM C 90. It can be seen that a number of the mixes meet the compressive strength requirements.

Figure 2.16: Concrete Test Cylinders

Figure 2.17: Failed Concrete Test Cylinder

Figure 2.18: PCM Concrete Compression Testing Results

2.2.4 PCM Concrete Mix Optimization

There is an optimal balance of cement and PCM for economics, maximum PCM incorporation while preserving structural compressive strength and thermal performance. While additional cement increases strength, it also displaces PCM carrying aggregates thus reducing the PCM fraction, which in turn reduces energy storage. In addition, other than PCM, cement is the most expensive component in a PCM concrete mix. Thus reducing cement improves economics in two ways. It is therefore imperative to balance PCM and cement through optimization. To facilitate this optimization, compressive strength and PCM percent were plotted in Figure 2.19 with respect to the percentage of Type III cement in the mixes. These cement proportions were 17%, 24%, and 31% respectively by mass.

The 17% percent value relates to the 1X designation (same amount of type III cement as commercial mix), 24% is 1.5X (50% more type III cement than the commercial mix, and 31% is 2X (twice the type III cement as the commercial mix).

Figure 2.19: Optimization of PCM and PCM Percentage as a Function of Type III Cement Proportion

It was found that vacuum impregnated mixes had PCM percentages that ranged from approximately 10% to 14%. While the 10% PCM mix produced strengths that exceeded 34.5 MPa (5000 psi), the 14% PCM mix did not meet minimum compressive strength requirements.

A second order equation for compressive strength as a function of the Type III cement was developed from the data using a regression analysis.

$$C = -917.02x^2 + 629.87x - 71.995 \quad (2.1)$$

In addition, a linear equation for PCM ratio with respect to Type III cement was developed from the data using a linear regression analysis.

$$P = -0.2587x + 0.1827 \quad (2.2)$$

Where;

C : Compressive Strength (MPa)

P : Ratio of PCM mass to PCM concrete mass

x : Ratio of Type III cement mass to PCM concrete mass

Since the minimum allowed compressive strength allowed by ASTM C90 is 13.1 MPa (1900 psi);

$$C = 13.1 \text{ MPa}$$

Therefore;

$$P = 0.134 \text{ (13.5 \% PCM)}$$

$$x = 0.185 \text{ (18.5\% Type III Cement)}$$

Using a minimum compressive strength of 13.1 MPa (1900 psi) and the solving the two equations simultaneously, a PCM percentage of 13.5% PCM can be provided by a mix containing 18.5% Type III cement. This value can most likely be increased if vacuum impregnation retention can be improved through further process enhancement. At this point, a PCM percentage range between 10% and 15% seems to be the upper working range for PCM mix combinations.

In summary, viable PCM concrete mixes were developed meeting the ASTM C90 structural compressive strength of 13.1 MPa (1900 psi). These mixes included micro-encapsulated PCM as well as vacuum impregnated PCM aggregates. Viable PCM mix incorporation ranged from 7% PCM by mass for the micro-encapsulated PCM to almost 13% PCM by mass for the vacuum impregnated PCM. From regression analysis of the current compression testing and vacuum impregnation results, it appears the 13.5% PCM by mass can be achieved. If the vacuum impregnation method can be improved, it may be possible to exceed 15% PCM by mass in the PCM concrete.

CHAPTER THREE: THERMAL CHARACTERIZATION OF PCMS AND PCM CONCRETES

3.1 Thermal Testing

Thermal testing was performed in order to determine the thermal properties of the PCMs, as well as the thermal properties of the PCM concrete. During this portion of the investigation Digital Scanning Calorimetry was performed on small PCM samples typically ranging in mass from 10 mg to 20 mg. Larger PCM concrete and control samples in excess of 150 gm were tested in the Dynamic Hot Box Apparatus.

Pure PCM, micro-encapsulated PCM powder, and vacuum impregnated PCM aggregates were tested in the DSC since the samples were of small enough size to fit in the 6 mm (1/4 inch) DSC pans. In addition, two PCM concrete mixes with cement paste, fine aggregates, and BASF micro-encapsulated PCM were studied. For small samples, the DSC allows accurate analysis of specific heat, latent heat and transition temperature. Two DSC methods were utilized in these tests. These methods were the dynamic method and the isothermal step method. The two different methods were used because DSC results are dependent on sample size and ramping rate. The dynamic method provides accurate values of latent while the isothermal step method provides improved accuracy for the transition temperatures and the phase fraction curve (Gunter et al. 2009).

Larger samples such as concrete specimens required the use of the Dynamic Hot Box Apparatus. This testing device is large enough to test concrete samples. Due to the composite nature of concrete having relatively large, varying aggregates sizes, types, and random material distribution, samples must be of substantial enough volume in order to provide a representative sample. Thus, 7.62 cm (3 inch) diameter samples with a thickness of 2.54 cm (1 inch) were the smallest concrete sample size deemed acceptable for thermal testing.

The Dynamic Hot Box Apparatus was used to test the control and composite PCM concrete thermal conductivity. Thermal conductivity is required for simulation models in order to account for steady-state and transient heat conduction. Further characterization performed using the Dynamic Hot Box apparatus involved the determination of heat capacity. By utilizing the isothermal step method, the specific heat, latent heat, and phase transition temperature were determined for PCM concrete samples. This analysis provided composite PCM concrete heat capacity values. The composite latent heat values were compared to the pure PCM latent heat values. This validated the mass fraction PCM incorporation percentages determined during PCM concrete preparation.

In addition, the Dynamic Hot Box Apparatus was used to simulate diurnal cycling of the control and PCM concrete materials. This provided data that could be examined to quantify peak temperature and flux reductions as well as phase shifts provided by the incorporated PCMs. The diurnal cycling provides tangible data as well as the ability to visualize the PCM performance.

3.2 Digital Scanning Calorimetry

Digital Scanning Calorimetry was performed on the PCM samples in order to determine the latent heat, transition temperature, and specific heat of the materials. As shown in Figure 3.1, a TA Instruments Q20 Digital Scanning Calorimeter (DSC) with an RSC400 cooling apparatus was used to perform the measurements. This apparatus is a heat flux DSC. The TA Universal Analysis software provided with the Q20 DSC was used to determine the latent heat and transition temperatures of samples in the case of the dynamic method. For the isothermal step method the software was used to integrate the individual peaks in order to develop enthalpy curves quantifying the specific heat, latent heat, and transition temperature.

Figure 3.1: Digital Scanning Calorimeter (DSC) with Cooling Device

A heat flux DSC determines the amount of heat absorbed by a sample as a function of temperature change. The DSC is calibrated using the enthalpy of a standard reference material prior to testing. In this case, sapphire was used as the reference material for calibration.

In a typical DSC scan, a test sample and a reference are symmetrically placed in the calibrated DSC furnace. A representation of a heat flux DSC is shown in Figure 3.2. The temperature of the sample is compared to the temperature of the reference which in this case was an empty pan. The temperature difference determines the heat flux between the sample and the furnace (Castellon et al 2008). The enthalpy is determined by the integration of the specific heat as a function of temperature according to the following equation;

$$h(T) = \int_{T_0}^T C_p(T) dT \quad (3.1)$$

Where:

$h(T)$: Enthalpy as a Function of Temperature (kJ kg^{-1})

C_p : Specific Heat Capacity ($\text{kJ kg}^{-1} \text{ } ^\circ\text{K}^{-1}$)

T : Temperature ($^\circ\text{K}$)

T_0 : Onset Temperature ($^\circ\text{K}$)

Figure 3.2: Heat Flux DSC Furnace (Castellon et al 2008)

Both the dynamic method and isothermal step method were used in DSC testing. The dynamic method was used to determine the latent heat. The isothermal step method was used to determine the enthalpy curve from which the PCM phase fraction and specific heat were obtained. This is because the dynamic method produces more accurate results for latent heat, while the step method produces a more accurate enthalpy curve profile for development of the phase fraction (Gunter et al. 2009). The latent heat and transition temperature results from the two methods were compared to examine the variation of the results

Initially DSC measurements were performed on micro-encapsulated PCMs. BASF and Microtek PCM powders were tested for latent heat and transition temperature. At the time of the first tests, the DSC was capable of heating only. Samples of powder form BASF Micronal 5001, Microtek 18d, Microtek 28d, as well as PCM / concrete composites of with BASF at 7% and 16% PCM mass fraction were tested under heating only conditions. The samples were initially tested with the dynamic method at a rate of

10°C/minute. It was found that this ramping rate is much larger than is experienced in a building envelope environment. Though the ramp rate was large, the total measured latent heat is valid (Gunter et al. 2009). However, the transition range for fast ramp rates is wider than would be experienced in an actual building application. Thus, lower ramp rate rates were used to provide tighter transition ranges indicative of building envelope applications. A ramping rate of 1°C/minute was used for all subsequent dynamic DSC testing.

3.2.1 DSC Methods

The method of enthalpy measurement has an impact on the accuracy of the DSC results. The dynamic method is the most commonly used method for determining the melting and solidification latent heats (Gunter et al. 2009). This is likely due to its ease of use and simplicity due to the constant ramping rate and integration of a single peak when determining the latent heat. In addition, it provides results relatively quickly. However, the dynamic method suffers complications with increased sample size and faster ramping rates. Smaller sample sizes cause weak signals and thus inaccuracies, while larger sample sizes exhibit temperature differentials across the sample as shown in Figure 3.3. A sample experiencing heating will be warmer at the surface than the interior. A sample experiencing cooling will be cooler at the surface than the interior. This temperature differential creates a shift in measured phase transition temperature range; towards the warmer temperatures for heating, and towards cooler temperatures for cooling. This can be seen in Figure 3.3. The larger the sample, the larger the transition temperature range shift. In addition to sample size, faster ramping rates further the temperature shift (Castellon et al. 2008). For energy storage applications, both the latent heat and sensible heat must be quantified. Thus

sensitivity to small signals and low ramping rates must be addressed for the specific heat measurements. The dynamic method at $1^{\circ}\text{C}/\text{minute}$ ramp rate for both heating and cooling is shown for PureTemp 23 in Figure 3.4. The phase transition shift is quite pronounced.

Figure 3.3: DSC Dynamic Method Sample Temperature Differential (Castellon et al. 2008)

Figure 3.4: Heating / Cooling Analysis with Dynamic Method

One way to address this effect related to sample size is to use the isothermal step method. This method alleviates the issues with ramping rate and sample size related temperature differentials by using a step-wise temperature profile. The temperature is increased and then held constant until equilibrium is achieved for a series of steps. The enthalpy of each step is integrated to create discrete points in a plot of the melting enthalpy curve. The same is done under cooling conditions to create the crystallization enthalpy curve (Castellon et al, 2008). The isothermal step method in heating is shown for PureTemp 23 in Figure 3.5. This figure shows the individual peaks prior to their integration.

Figure 3.5: Heating Analysis with Isothermal Step Method

3.2.2 DSC Analysis

The TA Universal Analysis 2000 software was used for the DSC analyses of latent heat and enthalpy curves. For the dynamic test method the software was used to integrate

the sample latent energy over the total melting / solidification range to determine the latent heat. The melting and solidification transition temperature is determined from a line drawn tangent to onset of the melting or solidification curve respectively. The transition temperature is determined at the point where the tangent line intersects the line representing the specific heat of the sample. For the step method the energy absorbed or released during each step is integrated to create points in the fusion and crystallization enthalpy curves. The latent heat and transition temperatures can be determined in a manner similar to that performed with the dynamic method using numerical methods. The specific heat is provided by integrating the peaks before and after the phase transition.

3.2.3 Enthalpy Measurement Results

As explained previously, enthalpy measurement results were from two different DSC test procedures. The latent heat and transition temperatures were determined via the dynamic method. The relatively quick test procedure allowed multiple test samples to be tested in order to obtain an average latent heat value. The step method provided specific heat values and the latent heat phase fraction curve for energy modeling. The latent heat and transition temperatures of melting and solidification for the dynamic DSC tests on pure PCMs and a composite BASF PCM and fine aggregate concrete mix are shown in Table 3.1. The transition temperatures represent the temperatures where the melting and solidification phase transitions begin. The latent heat of melting and solidification characterize the energy storage capabilities for the PCM during the phase transition. The column showing the latent heat average is an average value of the melting and solidification latent heats.

Table: 3.1: PCM Latent Heat and Transition Temperature from Dynamic Method

PCM Sample	Transition Temp. of Melting (°C)	Latent Heat of Melting (kJ/kg)	Transition Temp. of Solid. (°C)	Latent Heat of Solid. (kJ/Kg)	Latent Heat Average (kJ/Kg)
BASF Micronal 5001	22.3	99.0	24.6	100.0	99.5
Cement/9% BASF	23.4	9.1	N/A	N/A	9.1
Cement/17% BASF	23.0	17.6	N/A	N/A	17.6
Microtek 18D	13.3	158.8	13.8	156.0	157.4
Microtek 28D	23.6	144.4	25.3	147.5	146.0
Capric / Myristic Acid	21.0	138.1	19.3	131.3	134.7
n-Hexadecane	14.6	199.7	13.7	185.9	192.8
25% Octa / 75% Hexa	13.2	114.6	14.6	125.1	119.9
50% Octa / 50% Hexa	14.3	123.0	17.5	120.5	121.8
75% Octa / 25% Hexa	18.3	101.4	20.8	106.9	104.2
n-Octadecane	23.1	198.9	23.9	203.0	200.9
Microtek Alkane Blend	17.1	150.6	20.89	140.9	145.8
PureTemp 23 Liquid	21.6	202.2	~20 (est.)*	202.2	202.2
PureTemp 23 Diatom Matrix	22.4	100.9	~20 (est.)*	99.7	100.3

*The transition temperature of solidification for Pure Temp 23 was estimated due to supercooling of the sample which prevented its determination using the DSC software

The linear alkanes, n-Hexadecane and n-Octadecane were blended in varying proportions to examine the effects on latent heat and transition temperature. The variations in transition temperature and latent were measured using the dynamic method for blend ratios of 25%, 50%, and 75% n-Octadecane along with pure n-Hexadecane and n-Octadecane. As shown in Figure 3.6, the transition temperature varied somewhat proportionally with increased n-Octadecane while latent decreased for blended samples in comparison to pure samples.

Figure 3.6: n-Hexadecane and n-Octadecane Blend DSC Results

Examination of the blends of n-Hexadecane and n-Octadecane shows that blending of these linear alkanes provides a feasible method of tailoring transition temperatures. As shown in Figure 3.6 blending the two alkanes to provide a transition temperature comes at

the cost of reduced latent heat energy storage. From the results it appears that the Microtek linear alkane blend PCM with a stated 24°C (75°F) transition temperature (actually tested to be approximately 21°C (70°F)) is a 25% n-Hexadecane and 75% n-Octadecane alkane blend. The transition temperatures are extremely close. The latent heat was slightly lower for the in-house blend. This may be due to material and measurement variability.

Dynamic DSC testing was also performed on vacuum impregnated expanded clay aggregates. Aggregates of #4 (6.35 mm), #8 (3.18 mm), #16 (1.59 mm), and #30 (0.85 mm) sizes were tested with n-Hexadecane, n-Octadecane and the linear alkane blend. The DSC testing of the expanded clay aggregates provided performance data for the composite PCM and aggregate. In addition, the PCM aggregate data provided confirmation of the amount of PCM impregnation in each of the aggregate sizes. Comparing the PCM aggregate latent heat to the pure PCM latent heat provides data about the PCM impregnation ratios.

Wide phase transition ranges and incongruent phase transition during cooling of the pure linear alkanes also led to further study of these PCMs vacuum impregnated into the porous expanded clay aggregates to see if performance improvements could be obtained with vacuum impregnation. It was hoped that vacuum impregnation of the pure PCMs in the expanded clay aggregate pore space would provide nucleation sites in order to improve PCM performance. The pure n-Octadecane and alkane blend PCMs tended to exhibit two peaks during cooling.

Table 3.2 summarizes the results of the tests of PCM / expanded clay composite samples. Listed in the table are the average latent heat of melting, latent heat of solidification, the average of the latent heats of melting and solidification, and the ratio of the average latent heat of the PCM / expanded clay composite to that of the pure PCM materials.

Table 3.2: Vacuum Impregnated Expanded Clay Aggregate DSC Results

PCM Aggregate	Latent Heat of Melting (kJ/kg)	Latent Heat of Solidification (kJ/kg)	Latent Heat Average (kJ/kg)	Latent Heat of Vacuum Impregnated PCM / Pure PCM (%)
n-Hexadecane #4	26.5	26.2	26.4	14%
n-Hexadecane #8	36.9	36.1	36.4	19%
n-Hexadecane #16	39.6	38.9	39.2	20%
n-Hexadecane #30	43.6	42.6	43.1	22%
Alkane Blend #4	22.4	22.5	22.5	15%
Alkane Blend #8	26.9	25.4	26.2	18%
Alkane Blend #16	31.1	30.5	30.8	21%
Alkane Blend #30	33.2	31.9	32.5	22%
n-Octadecane #4	35.1	35.8	35.4	18%
n-Octadecane #8	39.7	40.5	40.1	20%
n-Octadecane #16	30.8	31.2	31.0	15%
n-Octadecane #30	37.0	37.5	37.3	19%
Average	NA	NA	NA	19%

Examination of Table 3.2 indicates that the average latent heat of the vacuum impregnated expanded clay aggregates ranges from 14% to 22% with an average value of 19%. The standard deviation is 3%. The values shown in Table 3.2 are for averages of 3 or more repeated test results. Higher latent heat percentages indicate higher impregnation efficiency of the aggregates. Considering that the PCM vacuum impregnation by mass fraction in Table 2.4 ranged from 23% to 36% with an average of 28% for the linear alkane impregnated PCM aggregates, it can be determined that the values of 14% to 22% as shown in Table 3.2 are reasonable and validate the mix values. Since the PCM aggregates were stored for several months before DSC testing there was sufficient time for the aggregates to repeatedly cycle through their transition temperatures prior to testing. Immediate incorporation of the PCM aggregates into PCM concrete would likely have mitigated PCM loss and would therefore have provided higher latent heat for the individual aggregates. Thus, it can be determined that immediate incorporation of PCM aggregates into the concrete mix or cold storage of PCM aggregates is essential to long-term stability prior to concrete mixing.

Figures 3.7 through 3.21 show typical behavior observed for this range of samples during DSC testing. The results of each PCM first show typical melting and solidification curves for pure PCM and then curves for the #4 (6.35 mm) through the #30 (0.85 mm) vacuum impregnated aggregates are shown for each PCM. In addition, the latent heat comparisons shown in Table 3.2 are illustrated.

Figure 3.7: Typical Pure n-Hexadecane DSC Test Result (100% PCM)

Figure 3.8: Composite #4 Aggregate / n-Hexadecane DSC Test Result (14% PCM)

Figure 3.9: Composite #8 Aggregate / n-Hexadecane DSC Test Result (19% PCM)

Figure 3.10: Composite #16 Aggregate / n-Hexadecane DSC Test Result (20% PCM)

Figure 3.11: Composite #30 Aggregate / n-Hexadecane DSC Test Result (22% PCM)

Figure 3.12 Typical Pure Alkane Blend DSC Test Result (100% PCM)

Figure 3.13: Composite #4 Aggregate / Alkane Blend DSC Test Result (15% PCM)

Figure 3.14: Composite #8 Aggregate / Alkane Blend DSC Test Result (18% PCM)

Figure 3.15: Composite #16 Aggregate / Alkane Blend DSC Test Result (21% PCM)

Figure 3.16: Composite #30 Aggregate / Alkane Blend DSC Test Result (22% PCM)

Figure 3.17: Typical Pure n-Octadecane DSC Test Result (100% PCM)

Figure 3.18: Composite #4 Aggregate / n-Octadecane DSC Test Result (18% PCM)

Figure 3.19: Composite #8 Aggregate / n-Octadecane DSC Test Result (20% PCM)

Figure 3.20: Composite #16 Aggregate / n-Octadecane DSC Test Result (15% PCM)

Figure 3.21: Composite #30 Aggregate / n-Octadecane DSC Test Result (19% PCM)

Reviewing the above DSC test results for the pure PCMs as well as the composite expanded clay / PCM aggregates, it can be seen that the composite latent heat proportions are consistent with the PCM impregnation mass ratios shown in Table 2.4. Figure 3.7 shows that for the pure n-Hexadecane a single melting and solidification curve without multiple peaks is exhibited. This remains true for the n-Hexadecane / aggregate composites as shown in Figures 3.8 through 3.11.

The pure alkane blend melting and solidification curves both exhibit two peaks as shown in Figure 3.12. This is likely due to the mixture of alkanes with different transition temperatures. Impregnating the alkane blend in the aggregate improves the PCM performance by providing a single melting and solidification peak most likely due to

increased nucleation sites in addition to stabilizing the blend as shown in the above Figures 3.13 through 3.16.

The pure n-Octadecane sample has a second peak during cooling as shown in Figure 3.17. This is likely due to super cooling. While the #4 (6.35 mm) aggregate / PCM composite exhibits a similar DSC curve as compared to the pure n-Octadecane, the smaller #8 (3.18 mm) through # 30 (0.85 mm) aggregates exhibit a smoothed cooling curve as compared with the pure PCM. This is likely due to increased nucleation sites found in the porous aggregate pore space. With smaller aggregate size it is evident that nucleation is improved. Overall, as shown in Figures 3.18 through 3.21, it appears that the performance of n-Octadecane is improved when incorporated into expanded clay aggregates and appears viable for use in PCM concrete production.

The step method data was used to develop the enthalpy curves for n-Hexadecane, n-Octadecane, the Microtek linear alkane blend, and PureTemp 23. The temperature steps were typically 1°C. However 0.5°C steps were also used in the melting region when equilibrium was not reached with the 1°C steps. These smaller step values were summed to create consistent 1°C steps for graphing. From the step method data, the phase fraction curves were determined. Figures 3.22 through 3.25 show typical test results from the step method. The latent heat of fusion and crystallization were determined by integrating the peaks.

Figure 3.22: Pure PureTemp 23 DSC Step Method Results

Figure 3.23: Pure n-Hexadecane DSC Step Method Results

Figure 3.24: Pure n-Octadecane DSC Step Method Results

Figure 3.25: Pure Microtek Alkane Blend DSC Step Method Results

From the step method it can be seen that the PureTemp 23 and n-Hexadecane samples exhibit good melting and solidification performance as shown in Figures 3.22 and 3.23. The phase change region occurs in a reasonably narrow range and the initial transition temperature for melting and solidification are relative close. Further, in comparison to the dynamic method, the PureTemp 23 sample shows cooling and heating transition temperatures that are considerably closer than that measured using the dynamic method. As shown in Figure 3.24, the n-Octadecane appears to either exhibit supercooling or performance issues due to impurities as can be seen by a solidification profile that exhibits two peaks. This may be due to nucleation issues. Though, as noted previously, incorporation into expanded clay aggregates allowed the peaks to merge.

The linear alkane blend exhibits a smeared profile for melting and solidification as shown on Figure 3.25. The transition range for both melting and solidification occurs over a wide temperature range. In addition, the total latent heat is lower than the pure alkane materials. This is confirmed by the results of the blends of n-Hexadecane and n-Octadecane in Figure 3.6. Table 3.3 summarizes the results from the step method tests. Table 3.4 compares the dynamic method to the step method test results.

Table 3.3: PCM Latent Heat and Transition Temperature from Step Method

PCM Sample	Transition Temp. of Melting (°C)	Latent Heat of Melting (kJ/kg)	Transition Temp. of Solid. (°C)	Latent Heat of Solid. (kJ/kg)	Latent Heat Average (kJ/kg)
n-Hexadecane	13.75	195	14.5	180	187.5
n-Octadecane	22.25	200	24.5	190	195
Microtek Alkane Blend	16.25	180	22.5	150	165
PureTemp 23 Liquid	20.5	220	20.5	220	220

Table 3.4: Comparison of Dynamic Method to Step Method

PCM Sample	Transition Temp. of Melting (°C)		Transition Temp. of Solid. (°C)		Latent Heat Average (kJ/kg)	
	Dynamic Method	Step Method	Dynamic Method	Step Method	Dynamic Method	Step Method
n-Hexadecane	14.53	13.75	13.68	14.5	190.1	187.5
n-Octadecane	22.41	22.25	23.77	24.5	183.6	195
Microtek Alkane Blend	18.62	16.25	21.63	22.5	124.1	165
PureTemp 23 Liquid	22.36	20.5	20	20.5	204.5	220

A comparison of the dynamic method values to the step method values indicates that there is fairly good agreement in transition temperatures. Variations in transition temperatures are most likely due to the step method not providing continuous data from

which an accurate tangent can be obtained from. Latent heat values are also fairly close for all but the Microtek Alkane Blend with a 24°C (75°F) transition temperature. However, this blended PCM smeared the latent heat across a large temperature range which creates difficulties in integrating the enthalpy to determine latent heat.

Specific heat from the step method provided data that is consistent with published results (Kuznik et al. 2011). Linear alkanes and fatty acids are documented as having a specific around 2 kJ/kg °C depending on solid or liquid state. All of the PCMs tested produced measurements around this value or slightly higher. However it was difficult to determine a solid phase specific heat for the Microtek alkane blend. This was because the latent heat of the blend continued well into the cooler temperatures of the test procedure. The lowest value measured during the step method test was 2.6 kJ/kg °C and thus, the specific heat lies at or below this value. Starting the DSC test at a lower temperature would likely have provided more accurate specific heat values. Specific heat values are shown in Table 3.5.

Table 3.5: Specific Heat from Step Method

PCM Sample	C _p Solid (kJ/kg °C)	C _p Liquid (kJ/kg °C)
n-Hexadecane	2.5	2.1
n-Octadecane	2.5	2.3
Microtek Alkane Blend	<2.6*	2.2
PureTemp 23 Liquid	2.3	2.4

* Specific heat of the Microtek Alkane Blend in the solid form was difficult to determine due to the latent heat being smeared over a rather large range. This is most likely due to the blended PCM.

The data in Table 3.5 shows the PCM specific heat outside of the transition temperature ranges from 2.1 to 2.6 kJ/kg°C. The average value is 2.36 kJ/kg°C with a standard deviation of 0.17 kJ/kg°C.

The DSC isothermal step method data was used to create enthalpy summation curves. The specific and latent heat capacity for each temperature step was summed to obtain the curves. The enthalpy summation curves are shown in Figures 3.26 through 3.29. These enthalpy summation curves can be used in energy analysis programs such as Energy Plus which require input heat capacity as a function of temperature. In addition, it is possible to develop phase fraction curves that can be utilized in finite difference models analyzing the effects of PCMs using the source term method. Examining the enthalpy summation curves provides insight into the hysteresis effects of the PCMs. Shifts in the cooling enthalpy curve with respect to the heating enthalpy curve indicates PCM hysteresis.

Figure 3.26: Pure n-Hexadecane Enthalpy Summation

Figure 3.27: Pure n-Octadecane Enthalpy Summation

Figure 3.28: Pure Microtek Alkane Blend Enthalpy Summation

Figure 3.29: Pure PureTemp 23 Enthalpy Summation

Examining the enthalpy summation data, it is evident that all of the PCMs experienced a hysteresis effect. This is marked by an enthalpy shift between heating and cooling. While the Microtek blend experienced lower latent heat and a wider transition range, the hysteresis was less severe than that with the pure PCMs

3.3 Dynamic Hot Box Apparatus

In order to study the transient properties related to the effective thermal mass of PCM concrete, a Dynamic Hot Box Apparatus was designed and constructed to test larger samples. The Dynamic Hot Box Apparatus was designed to subject material samples to varying temperature conditions similar to that of a building envelope. This involved exposing one side of the sample to a simulated exterior diurnal climate. The other side of the sample was exposed to a simulated interior environment. The perimeter of the sample was well insulated to prohibit flanking losses.

In addition to transient behavior, the Dynamic Hot Box Apparatus was capable of steady-state testing. Step temperature profiles were applied to the climate chamber side while the other side was held constant. From the temperature differential across the sample and the measured heat flux, the thermal conductivity of the sample could be determined.

Further development of the apparatus controls allowed matching ramping and step-wise profiles to be applied on both sides of the sample simultaneously. This permitted transient thermal properties to be measured in a similar fashion as the DSC. Equal flux entered or exited both faces of the sample simultaneously. This had the benefit of reducing

flux values, which improved flux reading accuracies. From the temperature change of the sample and the flux input or output, an enthalpy curve for the PCM concrete composite could be obtained. Thus, specific heat and latent heat could then be calculated.

3.3.1 Development and Fabrication

Exterior climates were simulated with a climate chamber that provided or removed significant thermal energy. A Tenney Benchmaster BTC-05-C Climate Chamber with a Watlow F4 Temperature Controller capable of custom ramp and step profiles ranging from -60°C (-76°F) to 200°C (392°F) was utilized. Interior environments were simulated within a heavily insulated box in which the temperature was regulated by two, Tellurex A45, 144 Watt thermoelectric units. Thermoelectric units were chosen because they are capable of heating or cooling depending on the direction of current flow, thus simulating an HVAC system with heating and cooling. In addition, they can provide stable temperature regulation and thus maintain a programmed set point.

A thick insulation barrier separated the two chambers and included an area designed to accept test samples. The barrier was sized to test small cylindrical samples and eventually, representative wall sections. The heat flow was measured on both samples faces with Omega HFS-4 heat flux transducers calibrated using a NIST certified Glass Fiberboard Standard Reference Material. The temperature profile across the sample was measured with type K thermocouples placed on both faces as well as with a thermocouple inserted into the middle of the sample specimen. Thermocouples were checked for

accuracy using an Omega CL 134 thermocouple calibrator with hot and cold calibration chambers.

Figure 3.30 shows the Dynamic Hot Box Apparatus. Figure 3.31 provides an explanatory schematic of the assembly. Figure 3.32 shows the PCM concrete sample with heat flux transducer without the Kapton sensor shield.

Figure 3.30: Dynamic Hot Box Apparatus

Figure 3.31: Schematic of Dynamic Hot Box Apparatus

Figure 3.32: PCM Concrete Test Sample with Heat Flux Transducer

Temperature and heat flux data were acquired with a National Instruments (NI) Data Acquisition System (DAQ) and LabVIEW 2012 software. An NI PXI-1052 chassis was connected via an NI PXIe-ExpressCard 8360 communication link. An NI PXI-6251 analogue to digital module converted the analogue sensor input signals to digital data format. An SCXI 1302 terminal was connected to a SCXI 1520 slot for analogue data acquisition. The DAQ system is shown in Figure 3.33.

In addition, temperature in the interior environment chamber was maintained via a Proportional, Integral, Gain, (PID) controller developed in LabVIEW. In response to the thermocouple temperature input from the interior environment chamber, digital output signals were pulsed via an NI SCC-68 unit controlling an H-bridge amp powering the thermoelectric units. This configuration allowed for variable current flow and direction supplied to the thermoelectric devices.

Figure 3.33: Data Acquisition System

3.3.2 Sensor Calibration

When performing experimental work confidence in sensors is essential. Thus validating sensor accuracy is important in the process of setting up an experiment. Type K thermocouples were used to measure temperature profiles in the Dynamic Hot Box apparatus. The thermocouples consist of a Chromel (90% nickel and 10% chromium) wire and an Alumel (95% nickel, 2% manganese, 2% aluminum, and 1% silicon) wire (Thermometrics 2013). Varying temperatures produce a linear response of voltage output. In order to validate the thermocouple sensor accuracy they were placed in calibrated cold and hot chambers of an Omega CL 134 thermocouple calibrator and the registered values were compared with the calibrated chamber set points. Thermocouples that compared well were used for testing.

The HFS-4 heat flux transducers/sensors came factory calibrated via a radiative flux calibration procedure. During this investigation extensive evaluation of these thin-film heat flux transducers revealed inaccuracies at the flux ranges typically experienced in building envelope applications. Sensors with identical factory calibration constants gave significantly different flux readings when placed side by side. In addition, intercept values were not provided for the voltage output at zero heat flux. Initially, the intercept was determined for zero flux. However, even with the intercept value determined, the calibration constants provided by the manufacturer continued to provide erroneous results. This revealed a need to calibrate sensors in their environment at flux levels expected during testing.

In addition, through testing and experience it was found that sensor behavior is highly dependent on not only application but also mounting. The thermal conductivity of the material being tested has a significant effect on application procedure. With testing materials of low conductivity, such as insulating materials, differences in thermal conductivity of the sensor and the tested material are less of a concern. However, since concrete has a fairly high thermal conductivity, sensor conductivity becomes a concern due to the tendency of heat to travel through the path of higher conductivity (van der Graaf 1985). Thus, the sensors provide enough resistance to encourage heat flow around them when attached to concrete. In materials with higher conductivity it is necessary to assure that differences in thermal conductivity between test material and sensor are accounted for. In this investigation, this was accomplished by applying a sensor shield of two laminated layers of Kapton mylar to the sample face around the heat flux transducer, along with a

third laminated layer of Kapton covering the sensor shield and the sensor as shown in Figure 3.34. The transducer is manufactured by sandwiching thermopiles between two layers of Kapton. Thus, the Kapton sensor guard with 2 surrounding layers provided consistent thermal conductivity across the sample face ensuring consistent heat flux through the sample and sensor. The third layer provided a consistent and relatively high conductivity buffer across the sample to minimize convection related fluctuations caused by the fans in the hot box apparatus.

Figure 3.34: Schematic of Kapton Heat Flux Sensor Shield and Cover

A 2.54 cm (1 inch) NIST Certified Glass Fiberboard Standard Reference Material (SRM) 1450d with known thermal conductivity was obtained and is shown in Figure 3.35. This material was in the range of conductivity required for building envelope analysis. The certification provided a linear equation relating average standard reference material temperature to thermal conductivity. Thus with proper installation of heat flux sensors and thermocouples, a temperature differential across the material and voltage output from the

heat flux sensors could be obtained to create a correlation. The calibrated thermal conductivity was related in the following equation:

$$k = 1.10489e^{-4} * T \quad (3.1)$$

Where;

k : Standard Reference Material Thermal Conductivity (W/m²)

T : Average Standard Reference Material Temperature (°K)

Figure 3.35: NIST Certified Glass Fiberboard SRM 1450d

The heat flux sensors were exposed to a series of temperature differentials with the steady state chamber at 20°C (68°F) and the climate chamber varying from -50°C (-58°F) to 85°C (85°F) in 5°C (9°F) increments. In addition, the sensors were placed and sealed

between two, 5.08 cm (2 inch) thick pieces of expanded polystyrene at 20°C (68°F) in the environmental chamber and allowed to reach steady state and thus a state of zero flux. The resulting voltage output from each sensor provided a verification of the intercept value for zero flux. The intercept and linear response at various temperature differentials were used to develop linear equations of heat flux as a function of voltage output in the microvolt range. The calibration equations for a 20°C (68°F) sensor temperature are shown in Figure 3.36 for three sensors.

Figure 3.36: Heat Flux Sensor Calibration Results (20°C Sensor Temperature)

From Figure 3.36, it can be seen that the heat flux reading as a function of voltage is linear with a slope intercept for which a voltage output occurs with no heat flux. The

linearity is a result of maintaining sensor temperature within a fairly narrow range of $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$ ($68^{\circ}\text{F} \pm 9^{\circ}\text{F}$). This was achieved by placing the sensors on the side of the standard reference material exposed to the steady-state (interior) chamber with a constant temperature of 20°C (68°F) maintained by the thermoelectric units. A slight deviation due to temperature dependence can be seen on the left side of the graph. The sensors were around 25°C (77°F) for these readings. Above approximately 20°C (68°F) the sensors begin to experience nonlinear behavior.

As previously stated the heat flux sensors are temperature dependent. The calibrations are based on a sensor temperature of 20°C (68°F). Significant deviations from a sensor temperature of 20°C (68°F) results in inaccurate flux readings. This effect is caused by the Kapton thermal barrier conductivity being a function of temperature and the Seebeck coefficient temperature dependency of the thermopile.

In order to quantify the heat flux sensor temperature dependency, additional calibration tests were performed by varying the temperature in the steady-state (interior) chamber. The chamber was varied from 0°C (32°F) to 50°C (122°F) in order to provide variable sensor outputs as compared to the standard 20°C (68°F) sensor temperature. These additional sensor calibrations are shown in Appendix C. For each sensor, a regression analysis was performed on the slopes obtained at each of the temperature steps. This provided temperature dependent coefficients as shown in Figure 3.37, which can be multiplied by the sensor voltage output to obtain a heat flux value after the slope intercept is taken into account.

Figure 3.37: Heat Flux Sensor Voltage Coefficient as a Function of Temperature

The above data indicates that the calibration factor (voltage multiplier coefficient) is temperature dependent. On average, there is an approximately 8% difference in this factor for the 0°C (32°F) and 50°C (122°F) sensor temperatures as compared to the 20°C (68°F) sensor temperature.

Using the average slope intercept, shown in Table 3.6, obtained from the linear regression analyses, the follow equations were developed to transform voltage output of the heat flux transducers into heat flux for varying sensor temperatures.

Table 3.6: Linear Regression Analysis Results for Varying Sensor Temperature

Sensor Temp (°C)	Sensor G		Sensor H		Sensor K	
	M (Slope)	B (Intercept)	M (Slope)	B (Intercept)	M (Slope)	B (Intercept)
50	0.494	-18.257	0.486	-19.711	0.538	-20.411
40	0.493	-17.949	0.497	-19.932	0.535	-20.155
30	0.505	-18.458	0.516	-20.341	0.540	-19.95
20	0.554	-20.798	0.554	-22.539	0.582	-22.675
10	0.535	-19.558	0.553	-21.549	0.575	-21.248
0	0.576	-21.867	0.589	-24.139	0.627	-24.015

Heat Flux Output for Transducer “G”:

$$q = [2 * 10^{-5} * T^2 - .0024 * T + .573] * V - 19.481 \quad (3.2)$$

Heat Flux Output for Transducer “H”:

$$q = [8 * 10^{-6} * T^2 - .0025 * T + .587] * V - 21.369 \quad (3.3)$$

Heat Flux Output for Transducer “K”:

$$q = [4 * 10^{-5} * T^2 - .0038 * T + .623] * V - 21.409 \quad (3.4)$$

Where;

q : Heat Flux (W m⁻²)

T : Temperature (°C)

V : Voltage (μV)

3.3.3 Thermal Conductivity

The thermal conductivity of the concrete control (no PCM) and PCM concrete samples was determined using the Dynamic Hot Box Apparatus. A constant temperature was applied to one side of the sample while a step profile was applied by the climate chamber side. Steps typically ranged from -60°C (-76°F) to 80°C (176°F) with each step of sufficient length to achieve steady-state. The heat flux and temperature was measured at both sample faces. In addition, temperature was measured at the middle of the sample. From the heat flux and temperature differential, the thermal conductivity was calculated by rearranging the following equation:

$$q = k \frac{dT}{dx} \quad (3.5)$$

as;

$$k = q \frac{dx}{dT} \quad (3.6)$$

Where;

k : Thermal Conductivity ($\text{W m}^{-1} \text{ } ^\circ\text{C}^{-1}$)

q : Heat Flux (W m^{-2})

x : Sample Thickness (m)

T : Temperature Differential ($^\circ\text{C}$)

Table 3.7 provides the thermal conductivity results from the Dynamic Hot Box Apparatus along with the densities of the control and PCM concrete test samples.

Table 3.7 Thermal Conductivity

Concrete Mix	Density (kg/m³)	Thermal Conductivity (W/m°C)
Concrete Control (1.5X)	1497	0.52
Micortek 18D 9% (1.5X)	1645	0.75
n-Hexadecane Concrete (1.5X)	1556	0.64
24C Alkane Concrete (1.5X)	1537	0.59
24C Alkane Concrete (2X)	1658	0.65
n-Octadecane Concrete (1.5X)	1497	0.60
PureTemp 23 Concrete (1.5X)	1769	0.54

Comparing the conductivity data in Table 3.7 indicates that all of the values are within a relatively narrow range of 0.52 to 0.75 W/m °C. The minimum conductivity of 0.52 W/m² was measured for the control and the maximum conductivity of 0.75 W/m² was measured for the micro-encapsulated PCM concrete (18D 9%). These values are reasonable since the control should have a lower conductivity than the similar concretes with PCM vacuum impregnated into the porous aggregate. The PCM displaces the air in the aggregates and slightly increases the conductivity of the porous aggregates and thus the overall conductivity of the concrete. It is also logical that the micro-encapsulated mix has the highest conductivity. This is because the mix has a high proportion of dense aggregates such as sand and limestone. In addition, the micro-encapsulated PCM is incorporated into the cement matrix, thus filling voids in the matrix that may have been devoted to air space.

3.3.4 Heat Capacity

Measurement of heat capacity was performed on the PCM concrete samples. The test method for heat capacity of the concrete samples involved a similar configuration to the thermal conductivity testing. The sample was placed in the sample holder of the Dynamic Hot Box Apparatus. The thermoelectric temperature controller software was reconfigured so that matching temperature profiles could be applied to both faces of the sample. A step temperature profile was applied to the sample ranging from 0°C (32°F) to 35°C (95°F). Each step was held constant until equilibrium was reached and the flux returned to 0 W/m². This provided the energy storage for each step of the profile. The energy storage for each step could then be integrated and used to create discrete points in an enthalpy curve. The method is analogous to the isothermal step method used in the DSC analysis. In a similar fashion to the DSC isothermal step method, this method was capable of quantifying enthalpy according to the following equation;

$$h(T) = \int_{T_0}^T C_p(T) dT \quad (3.7)$$

From the above equation, the specific heat and latent heat of the composite PCM concrete samples was determined. This method determined the specific heat before and after the transition temperature range. Latent heat was determined for the transition range. Figures 3.38 through 3.41 give the latent heat and enthalpy summation of two tests of PCM concrete incorporating vacuum impregnated n-Hexadecane. Figures 3.42 and 3.43 show the latent heat and enthalpy summation of the PCM concrete incorporating PureTemp 23.

Figure 3.38: n-Hexadecane Concrete Enthalpy (Trial 1)

Figure 3.39: n-Hexadecane Concrete Enthalpy (Trial 2)

Figure 3.40: n-Hexadecane Concrete Enthalpy Summation Curve (Trial 1)

Figure 3.41: n-Hexadecane Concrete Enthalpy Summation Curve (Trial 2)

Figure 3.42: PureTemp 23 Concrete Enthalpy Curve (Heating)

Figure 3.43: PureTemp 23 Concrete Enthalpy Summation Curve (Heating)

Figures 3.38 and 3.39 show latent heat values of 13.3 kJ/kg for Trial 1 and 25.3 kJ/kg for Trial 2 of PCM concrete with n-Hexadecane during melting. Considering that n-Hexadecane has an average latent heat of approximately 190 kJ/kg, from Trial 1 it can be estimated that the PCM concrete incorporates approximately 7% PCM while Trial 2 provides an estimate of 13%. Trial 1 is within 36% of the mix calculations of 11% PCM incorporated by mass. Trial two is 18% in excess of the mix calculations. The average of the two trials is 10% which is quite close to the 11% mix estimate. The deviation in results is reasonable considering the unknowns including, the uncertainty of vacuum impregnation values of the porous aggregates, the uncertainty of the proportions of the vacuum impregnated porous aggregates in the concrete mix, any PCM loss due to cycling, and the uncertainty of PCMs in the representative sample. It is expected that a larger sample size would improve the PCM concrete latent heat approximation.

The latent heat values of cooling are approximately 9 kJ/kg for both trials. The lower latent values for cooling may be due to hysteresis of the PCM. In addition, the enthalpy summation curve for Trial 2 shows significant difference between melting and solidification. This may also indicate hysteresis.

Prior to latent heat onset and afterwards, the specific heat of the PCM concrete was found to be approximately between 1.1 kJ/kg and 1.3 kJ/kg. Considering the specific heat of the n-Hexadecane is 2.5 kJ/kg °C in liquid state and 2.1 kJ/kg °C in solid state, at 10% PCM the specific heat of the concrete is approximately ± 1.2 kJ/kg °C which is reasonable. This helps to further validate the results.

Figure 3.42 shows the latent heat for the PCM concrete sample incorporating PureTemp 23. During heating, it was determined that the latent heat of the PCM composite is 31.1kJ/kg. This is compared to the 205 kJ/kg latent heat of PureTemp 23 in pure form examined in the DSC. According to the ratio of the composite latent heat to the pure PCM latent heat it is estimated that the sample is 15.2% PCM which is close to the mix estimate of 12%. Further, the specific heat of the sample ranges from 1.1 kJ/kg °C to 1.3 kJ/kg °C which also falls within the predicted range.

3.3.4 Diurnal Cycling

The concrete samples were subjected to diurnal thermal cycling to simulate an exterior climate. The climate chamber was programmed to perform oscillating temperature profiles with a period of 24 hours. Initially, several temperature profiles were programmed to represent four seasonally representative days developed from TMY3 data for Louisville, KY; Winter, Spring, Summer, and Fall.

A control concrete specimen (no PCM) was modeled using the modified STAR program developed by Zwanzig et al. (2012) using the TMY3 seasonal days. The resulting surface temperature profiles were replicated for the control sample using the climate chamber of the Dynamic Hot Box Apparatus by developing an equation that determined climate chamber temperatures that would provide the required surface temperature. The climate chamber temperatures were then fine-tuned by trial and error to achieve the desired surface temperature profiles. Once developed, these same profiles were then used in further runs of PCM concrete. While these runs give good qualitative results, the apparatus

had deficiencies in the barrier which allowed flanking losses that affected the measured heat flux values. However, behavioral trends of the concrete and PCM concrete can be seen. The graphs in Figures 3.44 through 3.55 show the Dynamic Hot Box surface heat flux and temperature profiles for the control and various PCM concrete samples.

Figure 3.44: Control Concrete (2X) Surface Heat Flux-4 Season

Figure 3.45: Control Concrete (2X) Surface and Midpoint Temperature-4 Season

Figure 3.46: n-Hexadecane Concrete (1.5X) Surface Heat Flux-4 Season

Figure 3.47: n-Hexadecane Concrete (1.5X) Surface and Midpoint Temperature-4 Season

Figure 3.48: Alkane Blend Concrete (1.5X) Surface Heat Flux-4 Season

Figure 3.49: Alkane Blend Concrete (1.5X) Surface and Midpoint Temperature-4 Season

Figure 3.50: Alkane Blend Concrete (2X) Surface Heat Flux-4 Season

Figure 3.51: Alkane Blend Concrete (2X) Surface and Midpoint Temperature-4 Season

Figure 3.52: n-Octadecane Concrete (1.5X) Surface Heat Flux-4 Season

Figure 3.53: n-Octadecane Concrete (1.5X) Surface and Midpoint Temperature-4 Season

Figure 3.54: PureTemp 23 Concrete (1.5X) Surface Heat Flux-4 Season

Figure 3.55: PureTemp 23 Concrete (1.5X) Surface and Midpoint Temperature-4 Season

Examination of the above flux and temperature profiles provides insight into the material behavior for the representative Winter (mid-January), Spring (mid-April), Summer (mid-July), and Fall (mid-October) days. From the above figures, it can be seen that the PCM concrete samples exhibit phase changes. This is shown by the abrupt change in flux and temperature around the PCM transition temperature in PCM concrete graphs.

Table 3.8 provides a comparison of the peak maximum and minimum diurnal cycle temperature values for the control and PCM concrete mixes subjected to the four seasonal temperature profiles representing January, April, July, and October.

Table 3.8: Peak Temp. Values of Concrete Mixes Subjected to 4 Seasonal Days of TMY3

Concrete Sample-Season	Exterior Temp. (°C)		Midpoint Temp. (°C)		Interior Temp. (°C)		Avg. Temp. (°C)	
	High	Low	High	Low	High	Low	High	Low
Control-Winter	30.3*	3.2*	29.1*	5.4	28.0*	7.6	29.1*	5.4
Control-Spring	27.7*	13.0*	26.8*	14.0	26.0	14.8	26.8*	13.9
Control-Summer	40.0	18.7	37.1	19.0	34.6	19.1	37.2	18.9
Control-Fall	41.7	11.7*	38.5	12.8*	35.8	13.8*	38.7	12.8*
n-Hexadecane-Winter	29.6	3.7	28.3	5.7	27.6	7.3	28.5	5.6
n-Hexadecane -Spring	27.6	14.3	26.7	15.2	26.1*	15.5	26.8*	15.0
n-Hexadecane -Summer	40.1*	18.6*	36.9	18.9*	35.5	18.9*	37.5	18.8*
n-Hexadecane -Fall	41.9*	13.5	38.4	14.5	36.7*	15.0	39.0	14.3
Alkane Blend (1.5X)-Winter	29.1	3.9	28.2	5.2	27.2	7.6	28.2	5.6
Alkane Blend (1.5X)-Spring	27.3	13.7	26.7	14.2	26.0	15.0	26.7	14.3
Alkane Blend (1.5X)-Summer	39.9	20.1	37.7*	20.3	35.4*	20.1	37.7*	20.1
Alkane Blend (1.5X)-Fall	41.7	12.7	39.1*	13.4	36.6	14.3	39.1*	13.5
Alkane Blend (2X)-Winter	29.4	4.0	28.4	5.6	27.5	7.1*	28.4	5.5
Alkane Blend (2X)-Spring	27.3	13.9	26.6	14.7	26.0	15.2	26.6	14.6
Alkane Blend (2X)-Summer	39.4	19.7	36.8	20.0	34.9	19.8	37.0	19.8
Alkane Blend (2X)-Fall	41.0	12.5	38.1	13.3	36.0	13.9	38.3	13.2
n-Octadecane-Winter	28.1	3.3	27.2	4.7*	26.3	7.1*	27.2	5.0*
n-Octadecane -Spring	26.8	13.1	26.3	13.7*	25.5	14.5*	26.2	13.8*
n-Octadecane -Summer	39.9	19.8	37.5	20.2	35.1	19.9	37.5	19.9
n-Octadecane -Fall	41.7	12.1	39.0	12.9	36.2	13.8*	39.0	12.9
PureTemp 23-Winter	28.0	5.2	26.9	7.3	25.7	9.4	26.9	7.3
PureTemp 23-Spring	26.1	14.1	25.4	15.2	24.5	15.9	25.3	15.1
PureTemp 23-Summer	38.4	19.1	35.7	19.4	33.3	19.3	35.8	19.3
PureTemp 23-Fall	40.2	13.2	37.2	14.4	34.6	15.3	37.4	14.3

*Peak Maximum and Minimum Diurnal Cycle Values

In Table 3.8, it can be seen that the majority of the peak temperature values occur with the control sample. The n-Hexadecane sample has the second highest occurrence of peak temperature values. These peaks occur mostly during the Summer and Fall cycles. This is due to the low PCM transition temperature of this sample that does not activate the PCM during warmer cycles. Next was the n-Octadecane sample which exhibited extremes

mostly during the Winter and Fall cycles due to this sample's relatively high PCM transition temperature. The alkane blend samples had fewer extremes while the PureTemp 23 sample exhibited less temperature extremes as compared to the other samples. The alkane blend and PureTemp 23 PCM concrete samples had PCM transition temperatures near room temperature and between the seasonal extremes.

The temperature data shows that PureTemp 23 and both linear alkanes with 24°C (75°F) PCM transition temperature provided the smallest temperature differential between the two faces as compared to the control and the other PCM concrete composites. This coincides with typical PCM philosophies which recommend that PCM transition temperature should be close to ambient room temperature.

Further development of the Dynamic Hot Box Apparatus reduced flanking loss for improved performance. This was done by developing a barrier system in which the concrete test sample was tightly fitted in a 30.5 cm by 30.5 cm (12 inch x 12 inch) square sample holder that was 5.1 cm (2 inches) thick. This was constructed by cutting a hole that was tapered from slightly smaller than the sample size to being the sample diameter in each of two 2.54 cm (1 inch) thick pieces of expanded polystyrene (XPS) insulation. The sample was then encased between the two pieces of XPS with smaller diameter of the holes facing the exterior. This provided a tight seal around the test samples. The two pieces of XPS were then sealed around the sample with putty and taped along the perimeter. Finally, the sample holder was placed in a newly constructed barrier for the Dynamic Hot Box Apparatus which contained the sample while minimizing thermal penetration with high R-

value materials along with creating an obstructed and circuitous path around the sample holder edges to minimize air flow around the sample.

With improvement of the sample test barrier it was decided to implement a standard temperature profile with constant amplitude to simplify comparison. The average temperature of this profile was 20°C (68°F) and the amplitude was 25°C (77°F) providing a maximum temperature of 45°C (113°F) and a minimum temperature of -5°C (23°F). This ensured that the PCMs exhibited one complete phase change during each cycle. The interior environment chamber was held constant at 20°C (68°F). Results from the diurnal profile cycling showed trends in the control and composite PCM concrete behavior. Flux and temperature phase shifts as well as peak heat flux values were noted. Results from the control and PureTemp 23 PCM concrete tests are shown in Figure 3.56 through 3.59.

Figure 3.56: Control Concrete (1.5X) Surface Heat Flux (20°C Average)

Figure 3.57: Control Concrete (1.5X) Surface and Midpoint Temp. (20°C Average)

Figure 3.58: PureTemp 23 (1.5X) Surface Heat Flux (20°C Average)

Figure 3.59: PureTemp 23 Concrete (1.5X) Surface and Midpoint Temp. (20°C Average)

While Figures 3.56 and 3.57 indicate consistent heat flux and temperature profiles across the control sample, Figures 3.58 and 3.59 show clear melting regions in both the heat flux and temperature profile data. This melting occurs between 22°C (72°F) and 24°C (75°F) which is the transition temperature range of the PureTemp 23 PCM.

Figure 3.60 shows a comparison of the control concrete (no-PCM) and PureTemp 23 concrete (PCM) temperature differential between the interior and exterior sample faces. Both samples have similar cement ratios, gradation, and aggregates. The only significant difference is the presence of PCM vacuum impregnated within the aggregates. Reviewing the below temperature differentials (dT) for both the control concrete sample and the PureTemp 23 sample, it can be seen that PCM helps to mitigate the peak temperature differential. Both the peak maximum and minimum temperatures are reduced. Thus, peak heat flux is reduced due to the capacitance of PCMs as is shown in Figure 3.61. This validates the finding of others in this field with respect to reduction of peak heat flux. Figure 3.62 and 3.63 show the temperature profiles of the samples across their thickness. The diurnal temperature differentials across the sample for both the high and low forcing temperature applied by the climate chamber are summarized in Table 3.9. These values represent the difference in temperature between the climate face and the interior face.

Figure 3.60: Control and PureTemp 23 Surface Temperature Differential

Figure 3.61: Control and PureTemp 23 Interior Surface Heat Flux

Figure 3.62: Control (1.5X) Temperature Profiles (24 Hours)

Figure 3.63: PureTemp 23 Concrete (1.5X) Temperature Profiles (24 Hours)

Table 3.9: Diurnal Cycle (0°C (32°F) to 40°C (104°F) Maximum Amplitude)
Temperature Differential ($\Delta T = T_{\text{Climate}} - T_{\text{Interior}}$) Data for the High and Low Temperatures
Applied by the Climate Chamber

Concrete Sample/ Statistic	ΔT at Max Climate Chamber Temperature	ΔT at Min Climate Chamber Temperature
Control (1.5X)	5.53 °C (42.0°F)	4.49 °C(40.1°F)
PureTemp 23 (1.5X)	5.15 °C (41.3°F)	4.04 °C (39.3°F)
Peak Reduction of PCM vs. Control	0.38 °C (32.7°F)	0.45 °C (32.8°F)
Avg. Reduction in Peaks for PCM	6.87%	10.02%

The PureTemp 23 temperature profile in Figure 3.63 shows clearly defined melting across the sample. This is in comparison to the control in Figure 3.62 which shows no melting. There is also an amplitude temperature shift due to the PureTemp 23 PCM exhibited. The minimum and maximum peak temperatures are slightly higher ($\sim 1^\circ\text{C}$ higher) for the PureTemp 23 PCM concrete. This is likely due to the PCM capacitance.

The above data in Table 3.9 provides a comparison of temperature differential across the samples for the control and the PureTemp 23 PCM samples. It can be seen that the PCM concrete provides a reduction in the temperature differential across the sample for both the high and low temperature peaks applied by the climate chamber. Peak temperature differential reduction ranged from approximately 7% to 10%. When compared to the heat flux equation, a reduction in temperature differential provides a reduction in heat flux through the material.

The surface temperature profiles shown in Figures 3.64 through 3.66 represent the exterior, midpoint, and interior temperature for both the control and the PureTemp 23 PCM concrete sample. A phase shift and attenuation can be observed. In addition, the phase change regions exhibit increased phase shift with thermal penetration towards the interior. Finally, the tendency of the PCM to provide slightly higher surface temperatures is shown.

Figure 3.64: Climate Side Temperature Profiles (24 Hours)

Figure 3.65: Midpoint Temperature Profiles (24 Hours)

Figure 3.66: Interior Temperature Profiles (24 Hours)

Figures 3.64 through 3.66 above show the temperature of the control and the PCM concrete sample at the climate side face, the midpoint, and the interior face. The significance of these three figures is that they show a consistent temperature profile for the control sample while showing a phase shift for the PCM concrete sample. The phase lag increases and becomes more pronounced during melting from the climate chamber face, to the midpoint, and then to the interior face. This shows the PCM energy storage as a function of the sample depth.

In review, during thermal testing, the thermal properties of PCMs, PCM aggregates, and PCM concrete were quantified. The specific heat, latent heat and transition temperature of the PCMs were determined from DSC and Dynamic Hot Box Apparatus analyses. This quantified the energy storage potential of the PCMs and the PCM concretes. In addition, the thermal conductivity and diurnal transient response was obtained from the Dynamic Hot Box Apparatus.

The thermal analyses provided information for holistic building modeling of PCM concrete masonry envelopes. For building modeling, the significant data obtained from the DSC and Dynamic Hot Box thermal testing included PCM latent heat, PCM transition temperatures, PCM concrete thermal conductivity, and validation of PCM incorporation

CHAPTER FOUR: PCM MODELING

4.1 One-Dimensional Finite Difference Model

A one-dimensional transient thermal conduction finite difference model was developed by Stephen Zwanzig at the University of Louisville Mechanical Engineering Department (Zwanzig et al. 2012). The model is based on the STAR code (Simplified Transient Analysis of Roofs) initially developed by Wilkes (1989). The code was updated from Fortran 77 to Fortran 90 and the source term was added to model the latent heat effects of PCM materials. The program solves the following one-dimensional transient heat transfer equation that has been described earlier;

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) - L \rho_{pcm} \frac{\partial g}{\partial t} \quad (4.1)$$

The one-dimensional transient heat equation is modified to account for latent heat using the source term which is a Source Based method. The program and analysis is described in more detail in Zwanzig et al. (2012) and is capable of transient building envelope analysis of walls and roofs. In this analysis, internal boundary conditions are addressed using interior air temperature and convection coefficients, as well as external boundary conditions that provide excitations via TMY3 climate data utilizing air temperature, diffuse and direct solar radiation, and wind related convection.

PCMs are dealt with by providing latent heat and a phase fraction profile. Thus total latent heat is accounted for and the melting curve is provided by the phase fraction data. The PCM latent heat and phase fraction were determined using the Digital Scanning Calorimeter (DSC). The DSC data can be found in chapter 3. The PCM composite material data was validated by the Dynamic Hot Box Apparatus testing.

The model has been validated against analytical solutions (Zwanzig et al. 2012). The first validation was for heat conduction through a plane wall with finite thickness and infinite width and length. Boundary conditions for the top and bottom surface were assumed to be convective heat transfer according to the one-dimensional analytical solution. Input data included a wall thickness of 27.0 cm (10.6 in.), Biot number of 0.01852, initial wall temperature of 20°C (68°F), and ambient temperature of 60°C (140°F) (Zwanzig 2012). Comparisons are shown in Figure 4.1.

Figure 4.1: Analytical Solution vs. STAR Comparison for Plane Wall with Convection

(Zwanzig et al. 2012)

The second comparison was based on a two-phase Stefan problem developed by Solomon (1979). This problem addressed a semi-infinite PCM slab, with an isothermal phase change, initially at a constant temperature of 21°C (70°F) and in solid phase. A constant temperature boundary condition of 95°C (203°F) was applied to the top of the slab. The slab is adiabatic on the sides and bottom (Zwanzig et al. 2012). The comparison is shown in Figure 4.2.

Figure 4.2: Analytical Solution vs. STAR for 2-Phase Stefan Problem

(Zwanzig et al. 2012)

Figures 4.1 and 4.2 indicate good agreement with the model and the analytical solutions. While the second comparison is for an isothermal phase change, the numerical model requires a phase transition range. A narrow transition temperature range provided

good agreement. Thus, the model appears to give good agreement between its predictions and aforementioned analytical solutions. Due to the good agreement of the model with the analytical solutions, and the use of the source term method which is easily incorporated, this modeled was selected for comparison with experimental results.

A comparison with analytical models provides only a partial validation of the model. A theoretical model should also be experimentally validated if possible. The experimental results from the Dynamic Hot Box Apparatus were used for this purpose.

Experimental heat flux data from the Dynamic Hot Box Apparatus were compared with the numerical model of Zwanzig (2012) using experimental temperature boundary conditions. In addition to validating the model, this comparison helped to validate the accuracy of the experimental work. Eventually, implementation of the code into a holistic building energy software program such as EnergyPlus has the potential to improve PCM behavioral predictions in a software platform that can account for the multi-faceted aspects of holistic building analysis.

Data from the Dynamic Hot Box Apparatus was obtained from small samples of PCM concrete that were approximately 7.62 cm (3 inches) in diameter and 2.54 cm (1 inch) in thickness. The samples were exposed to various temperature excitations. Comparisons were initially made for the diurnal fluctuations based on the 4 seasonal days from TMY3 data. In the following Figures 4.3 and 4.4 are the interior heat flux comparisons for varied temperature excitations on the exterior surface and applied interior surface temperatures

maintained around 20°C (68°F), for two types of PCM concrete with varying transition temperatures.

Figure 4.3: Diurnal Interior Heat Flux Comparison for n-Hexadecane PCM Concrete

Figure 4.4: Diurnal Interior Heat Flux Comparison for Alkane Blend PCM Concrete

Review of the above comparisons indicates that the general trends compare favorably. Peak flux data are reasonably close considering the uncertainties in material properties such as conductivity and latent heat, as well as sensor calibration. These comparisons show that the model is capable of predicting heat flux data trends as well as phase transition related flux variations. The phase transitions are reproduced reasonably well. Inconsistencies may also be attributed to the 1 hour time intervals used in the model time steps that may smear the transition effects in the modeling.

Further comparisons with experimental results obtained by using improved sensor calibrations will provide better comparative data. In addition, smaller modeling time steps may allow transitions to be modeled with higher precision.

4.2 Holistic Building Energy Model

Two Holistic Building Energy Modeling programs with PCM capabilities were utilized to examine the effects of PCM incorporated into the building envelope. The first was a version of CODYBA (Noel et al. 2001) that has been modified to model PCM latent heat effects. The second was EnergyPlus 8.0 (EnergyPlus 2013), which utilizes an enthalpy curve to input heat capacity as a function of temperature.

Typical commercial constructions were examined to see if PCM concrete masonry walls have potential as a cost effective construction material. In order to model the concrete masonry, simplifying assumptions need to be made due to the non-homogeneous structure of concrete masonry blocks. As shown in Figure 4.5, masonry blocks are comprised of

two faces of constant thickness and density as well as an inner zone comprised of cores and webs. The homogenous faces model well, while the web and cores present difficulties in one-dimensional modeling due to their 2-dimensional structure.

Methods have been developed to obtain reasonable results in modeling complicated structures such as concrete masonry units in one-dimensional analysis. A thermally equivalent wall method has been developed by Kosny et al. (2002). This method utilizes a finite element modeling program such as ANSYS to examine the total energy flow through the building element as well as the transient properties. By trial and error, an equivalent 1-dimensional wall section is developed that replicates the thermal behavior of the more complex wall element. This equivalent wall method can then be used in one-dimensional building envelope analysis programs such as CODYBA and EnergyPlus.

While the equivalent wall method can be developed by utilizing a multi-dimensional finite element program, it is a tedious and time consuming process. An alternate method has been developed by Karambakkam et al. (2005). This is the equivalent homogenous layer method. Non-homogenous materials are stratified into similar layers. In the case of a masonry wall, two layers representing the faces enclose a composite section of cores and webs as shown in Figure 4.5. The core and web layer properties are modeled as a smeared layer. The total thickness of the element is maintained while conductivity, specific heat, and density are varied to model the thermal properties of the core / web section.

Figure 4.5: Representation of the Equivalent Homogeneous Layers

As discussed, the faces of the masonry form continuous material sections with homogenous properties. The section making up the web and cores has proportionately lower density and specific heat while the conductivity is a function of the web and core properties according to the parallel path approach (ASHRAE 1997). Thus, the sum of the three layers produces equivalent thermal conductivity, thermal mass, and density to the actual non-homogeneous concrete masonry unit wall structure. There are some inaccuracies introduced with this method in transient response. However, considering the relative nature of the comparisons, the relatively small errors should be similar for all of the configurations being evaluated, as long as they have similar masses.

Further simplifications of the model included using a concrete thermal conductivity of $0.55 \text{ W/m } ^\circ\text{C}$ obtained from Hot Box Apparatus testing, a specific heat of $1.2 \text{ kJ/kg } ^\circ\text{C}$ which was verified in thermal testing of PCM concrete, and a PCM latent heat of 200 kJ/kg

which is a realistic estimate of the pure linear alkanes as well as the PureTemp 23 fatty acid ester as determined from the DSC testing. Proportions of 10%, 15%, and 20% PCM incorporation provided composite PCM concrete latent heat values of 20 kJ/kg, 30 kJ/kg, and 40 kJ/kg respectively which were used in the holistic building analyses.

4.2.1 CODYBA and EnergyPlus

CODYBA (Noel et al. 2001) is a holistic building simulation program that models the energy performance of buildings. The input information for a model includes the building zone geometry and exterior and interior constructions. The driving parameters are the climatic conditions, internal loads, and HVAC inputs. The equations representing the thermal balance of a given area include an air volume, one-dimension finite conduction through the envelope, and the solar heat flux expression for the surfaces where sunlight reaches the walls and floors. The modified version of CODYBA also incorporated PCM modeling capabilities. The one-dimensional transient finite difference conduction model was updated to calculate the heat flux through building envelopes that incorporate PCM latent heat energy storage (Noel 2001). The CODYBA program was used to study the behavior of a 7432 m² (80,000 ft²) one story masonry building. The simplified HVAC models used by CODYBA software limited its application and EnergyPlus was used for more complicated analyses.

EnergyPlus (EnergyPlus 2013) is a holistic building simulation program that has been developed to simulate complex building models. It utilized, updated, and streamlined parts of the code of the well-established EQuest and DOE-2 building analysis programs to

create a building energy modeling platform that incorporates the best aspects of both platforms along with providing a modular interface for independent code. EnergyPlus is capable of modeling the envelope surface heat transfer using TMY3 data as well as the envelope conduction, interior air mass balance, and HVAC calculations simultaneously. This program provides an HVAC plant sizing algorithm that is dependent on exterior climate (EnergyPlus 2013). A schematic of the program components is shown in Figure 4.6.

Figure 4.6: EnergyPlus Program Schematic (EnergyPlus 2013)

For typical wall configurations, EnergyPlus utilizes the conduction transfer function as a default to calculate building envelope energy flow. EnergyPlus uses the state space method for conduction transfer functions and Laplace transformations (used in BLAST) to reach the solution. The program models the wall as a thermal resistance between nodes, and a thermal capacitance at the nodes. For typical thermal mass

configurations, the results have been shown to be within 1% of the analytical solution (EnergyPlus 2013).

For walls that incorporate latent or variable thermal conductivity, the conduction transfer function cannot be used. In this case, the conduction finite difference solution must be used. For these cases EnergyPlus provides two different options for the solution scheme. These are Crank-Nicholson and the fully implicit scheme. The Crank-Nicholson scheme is semi-implicit, is based on an Adams-Moulton solution and is considered second-order in time. The algorithm uses an implicit finite difference scheme coupled with an enthalpy-temperature function to account for phase change energy. The fully implicit scheme is also based on the Adams-Moulton solution approach and is considered first order in time (EnergyPlus 2013).

In addition, the finite difference algorithm can utilize the source / sink layer capability. This option may play a role in future modeling since the ultimate goal of this research is to configure the PCM masonry walls to allow ventilation of the cores with air conditioned using earth tubes or solar radiation. During summer, the air cooled by the ground can be used to remove excess heat. During the winter if the ground temperature is higher than the air temperature, air can be warmed by the ground and then can be used to add heat to the walls. The source / sink capabilities of the model can be used to describe the transfer of excess heat from the cores during the summer and to introduction of the heat during winter (EnergyPlus 2013).

4.2.2 CODYBA Analysis Results

CODYBA was used to evaluate a 7432 m² (80,000 ft²) commercial building in Louisville, Kentucky for the monthly average temperatures shown in Figure 4.7. Analyses were performed for a number of different exterior wall configurations, including 8 inch concrete masonry with core insulation, and then interior insulation and PCM configurations. The baseline configuration used an exterior wall of 8 inch concrete masonry units with core insulation and then insulation of the interior face using 3.18 cm (1.25 inch) of XPS rigid insulation as required by ASHRAE 90.1 provisions (ASHRAE 2010).

Also evaluated were CMU walls with polyurethane insulated foam cores and varying percentages of incorporated PCM in the concrete masonry units. Figure 4.8 shows the yearly energy used by the building for each configuration. Figure 4.9 shows the yearly energy costs for each configuration.

Figure 4.7 Louisville, KY (4A) Monthly Avg. Temperature

Figure 4.8: 7432 m² (80K ft²) Louisville, KY (4A)
Commercial Building Energy Use (kWh)

Figure 4.9: 7432 m² (80K ft²) Louisville, KY (4A)
Commercial Building Energy Savings (\$)

By examining the results of the CODBYBA analysis for Louisville, KY, it can be seen that PCM masonry with core insulation and PCM cannot achieve equivalent energy consumption performance. However, when the yearly energy is translated into energy costs, PCM masonry has the ability to provide energy cost savings at approximately 15% PCM incorporation by mass according to the CODYBA analysis. The associated energy costs used in the analysis were \$0.084/kWh for electricity and \$0.0282/kWh (\$11.6/c.f.) for natural gas as obtained from EIA.gov (2013).

4.2.3 EnergyPlus Analysis Results

For the remaining EnergyPlus analyses a small office building was examined. The small office building is one of the Department of Energy (DOE) commercial reference building models and was used because it has been calibrated and has been recognized as providing a reliable baseline for the analyses (EnergyPlus 2013). The analyses were conducted for several climate zones ranging from ASHRAE Climate Zones 1 through 5. Beyond Zone 5 passive solar strategies are necessary to engage the PCMs by utilizing the daytime solar gains for passive heating. Passive heating and cooling were beyond the scope of this analysis. Standard configurations, thermostat set points, and schedules were used in the analyses to evaluate the effects of PCMs in these conditions. It is expected that further research utilizing passive methodologies will show a significant potential for PCMs to improve building energy performance.

Of the various reference buildings, the small office building was chosen because the model is small enough and has few zones in order to allow the effects of PCM to be

identified more readily. Furthermore, the small office configuration has a commercial occupancy schedule similar to larger “big box” commercial schedules making it representative of typical commercial masonry construction.

The cast concrete mass walls of the small office reference building were replaced with concrete masonry. For the Miami, FL Climate Zone 1A there is no insulation requirement for commercial mass walls. Thus, hollow core masonry was modeled with and without PCMs. ASHRAE Zones 2 through 5 have prescriptive insulation requirements for commercial mass walls. For each of these climate zones, polyurethane masonry foam fill core insulation was modeled to improve the performance of PCM concrete masonry single-wythe wall configurations. Finally, a parametric study was performed to examine how various configurations of PCM masonry units with varying PCM transition temperatures effect performance.

All of the analyses were compared to single-wythe masonry exterior walls with hollow cores. This baseline was used because, uninsulated concrete masonry walls have been the standard in commercial and institutional construction prior to more stringent ASHRAE 90.1 requirements being developed. Hollow core exterior concrete masonry walls with interior insulation is what is currently required for some zones by ASHRAE 90.1 and was analyzed as the prescriptive requirement.

The R-value of the exterior concrete masonry wall units were calculated using the concrete conductivity obtained from the Dynamic Hot Box results. The parallel path

method was used in the calculation for hollow cores and insulated cores. The R-value of the hollow core masonry was found to be $0.4 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($2.5 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$) while polyurethane foam core insulation provided a masonry R-value of $1.2 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($6.8 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$). Standard R-values were used for insulation and other materials (ASHRAE 1997).

Exterior PCM concrete masonry walls with varying transition temperatures along with polyurethane core insulation (note, no core insulation was used for the Miami, FL analysis) was compared to the performance of the exterior walls configured to meet the ASHRAE 90.1 prescriptive requirements. In the analyses, the roofs had an R-value of $4.8 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($27 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$). This was the value provided in the reference building models. For the building analyses in the Atlanta, GA, Albuquerque, NM, and Boulder, CO locations, additional measures beyond core insulation were required to achieve equivalent consumption performance. Increased PCM percentages (up to 20% PCM) were examined in an effort to meet the energy performance equivalent. In addition, the performance of increased roof insulation with 10% PCM incorporation of the masonry walls, as well as non-PCM masonry with an increase in roof insulation were examined

The standard reference building types and representative climates are shown in Tables 4.1 and 4.2 respectively (EnergyPlus 2013). The ASHRAE climate zone map is shown in Figure 4.10. The ASHRAE 90.1 Non-Residential Mass Wall R-value requirements are listed in Table 4.3 (ASHRAE 2010). A schematic of the small office condo configuration is shown below in Figure 4.11 (EnergyPlus 2013). The monthly

average temperatures of the study areas are shown in Figures 4.12 through 4.17 (The Weather Channel 2013).

Table 4.1: Std. Ref. Bldg. Type

Building Type Name	Floor Area (ft ²)	Number of Floors
Large Office	498,588	12
Medium Office	53,628	3
Small Office	5,500	1
Warehouse	52,045	1
Stand-alone Retail	24,962	1
Strip Mall	22,500	1
Primary School	73,960	1
Secondary School	210,887	2
Supermarket	45,000	1
Quick Service Restaurant	2,500	1
Full Service Restaurant	5,500	1
Hospital	241,351	5
Outpatient Health Care	40,946	3
Small Hotel	43,200	4
Large Hotel	122,120	6
Midrise Apartment	33,740	4

Table 4.2: Std. Ref. Bldg. Climate Zones

Climate Zone	Representative City
1A	Miami, Florida
2A	Houston, Texas
2B	Phoenix, Arizona
3A	Atlanta, Georgia
3B-Coast	Los Angeles, California
3B	Las Vegas, Nevada
3C	San Francisco, California
4A	Baltimore, Maryland
4B	Albuquerque, New Mexico
4C	Seattle, Washington
5A	Chicago, Illinois
5B	Boulder, Colorado
6A	Minneapolis, Minnesota
6B	Helena, Montana
7	Duluth, Minnesota
8	Fairbanks, Alaska

Figure 4.10: ASHRAE Climate Zone Map (Energymodeling 2013)

Table 4.3: ASHRAE 90.1 Non-Residential Mass Wall R-Value Requirements

Climate Zone	R (m ² °C/W)	R (ft ² °F hr/btu)
1 (A, B)	No Requirement	No Requirement
2 (A, B)	1.0	5.7
3 (A, B, C)	1.3	7.6
4 (A, B, C)	1.7	9.5
5 (A, B, C)	2.0	11.4
6 (A,B)	2.3	13.3
7	2.7	15.2
8	2.7	15.2

Figure 4.11: EnergyPlus Small Office Standard Reference Building Schematic

Figure 4.12: Miami, FL (1A)
Monthly Avg. Temperature

Figure 4.13: Phoenix, AZ (2B)
Monthly Avg. Temperature

Figure 4.14: Atlanta, GA (3A)
Monthly Avg. Temperature

Figure 4.15: San Francisco, CA (3C)
Monthly Avg. Temperature

Figure 4.16: Albuquerque, NM (4A)
Monthly Avg. Temperature

Figure 4.17: Boulder, CO (5B)
Monthly Avg. Temperature

The yearly HVAC energy consumption for the reference building for each configuration and location was examined for building envelope variations of the small office reference building. The EnergyPlus simulation results shown in Figures 4.20 through 4.25 compare the HVAC energy consumptions of all variations of an exterior wall system meeting the ASHRAE 90.1 prescriptive requirements (standard concrete masonry and interior insulation). A positive percentage change indicates that the given configuration uses less energy than the prescriptive wall configuration, and thus represents better energy performance. A negative percentage value represents a conditions where more energy is used by the configuration being evaluated.

Figure 4.18: HVAC Savings for Small Office Condo in Miami, FL (Zone 1A) for Varying Transition Temperature, No Core Insulation and PCM Masonry

Figure 4.19: HVAC Savings for Small Office Condo in Phoenix, AZ (Zone 2B) for Varying Transition Temperature, Core Insulation and PCM Masonry

Figure 4.20: HVAC Savings for Small Office Condo in Atlanta, GA (Zone 3A) for Varying Transition Temperature, Core Insulation and PCM Masonry

Figure 4.21: HVAC Savings for Small Office Condo in San Francisco, CA (Zone 3C) for Varying Transition Temperature, Core Insulation and PCM Masonry

Figure 4.22: HVAC Savings for Small Office Condo in Albuquerque, NM (Zone 4B) for Varying Transition Temperature, Core Insulation and PCM Masonry

Figure 4.23: HVAC Savings for Small Office Condo in Boulder, CO (Zone 5B) for Varying Transition Temperature, Core Insulation and PCM Masonry

The above data shows the energy performance impact of PCM concrete masonry for ASHRAE Climate Zones 1 through 5 respectively, based upon HVAC energy consumption. The Miami, FL (Zone 1A) comparisons are for concrete masonry with no core insulation since Zone 1 does not have an insulation requirement for mass walls. There is a performance improvement provided by PCM masonry for conventional construction, schedules, and ventilation, however it is small. Further research into night time cooling and shading will likely provide improved results.

The remainder of the analyses (Zone 2 through Zone 5) incorporated polyurethane foam core insulation into the exterior walls. While this core insulated wall configuration does not meet the ASHRAE 90.1 prescriptive R-value requirements it provides improved thermal resistance while maintaining the more economical single-wythe exterior wall

construction. It was found that in Phoenix, AZ (Climate Zone 2B), core insulation with exposed exterior concrete masonry walls exceeds the performance of the ASHRAE 90.1 configuration. Incorporation of PCM masonry further improves the energy efficiency performance of the insulated core wall. Like Miami, FL, night time ventilation has the potential to significantly improve the thermal mass performance of PCM concrete masonry.

Atlanta, GA results show that core insulation and a masonry wall with the PCM percentage of 15% can provide energy performance that equals the energy consumption of the ASHRAE 90.1 interior insulation configuration. Further, with 10% PCM and an additional R-value of $0.35 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($2 \text{ ft}^2 \text{ hr } ^\circ\text{F/btu}$) of roof insulation, equivalent performance can also be achieved. Equivalent performance can also be obtained using exterior walls with standard concrete masonry, core insulation, and an additional R-value of $0.70 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($4 \text{ ft}^2 \text{ hr } ^\circ\text{F/btu}$) of roof insulation.

In San Francisco, CA (Climate Zone 3C, Marine) the standard concrete masonry walls with core insulation exceeded the minimum performance requirements. The addition of PCM into the concrete masonry produced significant additional energy savings. An additional 2% reduction in energy consumption was achieved when 10% PCM concrete masonry with a transition temperature of 19°C was used.

In locations beyond Climate Zone 3, additional roof insulation was also used to achieve equivalent energy consumption performance, when needed. The roof insulation

was incrementally increased by R-value steps of $0.35 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($2 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$) until the performance met or exceeded the energy performance of the ASHRAE prescriptive configurations. For Albuquerque, NM, an additional roof insulation R-value of $1.06 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($6 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$) produced equivalent performance with exterior walls of 10% PCM concrete masonry, while additional roof insulation (R-value $1.41 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($8 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$)) produced equivalent performance with standard masonry and core insulation.

In Boulder, CO (Zone 5B), the addition of PCM concrete and core insulation into single-wythe exterior wall construction did not produce equivalent energy use to the prescriptive requirements. Additional roof insulation was needed. It was found that an exterior wall configuration of 10% PCM concrete masonry, core insulation, and additional roof insulation (R-value of $2.82 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($16 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$)) produced equivalent performance. Without, PCM concrete masonry, the required additional roof insulation R-value is $3.87 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($22 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$). The PCM provides the same effect as an additional roof insulation n R-value of $1.06 \text{ m}^2 \text{ }^\circ\text{C/W}$ ($6 \text{ ft}^2 \text{ hr }^\circ\text{F/btu}$).

Equivalent energy performance based on yearly energy use as compared to prescriptive configurations is a method of design in some building codes such as Canada. Other design codes use alternative methods. Since the ASHRAE code (ASHRAE 2010) defines equivalent energy performance based on cost, additional analyses were performed. The energy consumption was converted into energy costs for electricity and natural gas according to the ASHRAE 90.1 Energy Cost Budget method (ASHRAE 2010). This analysis was done for standard masonry with interior insulation, standard masonry with

core insulation (except Miami, FL), as well as selected PCM concrete masonry and roof insulation configurations. Energy cost data used for the analyses which is shown in Table 4.2 was obtained from EIA.gov (2013). For each configuration a yearly energy cost was determined and compared to the yearly energy used by the building configuration with uninsulated exterior masonry walls. The net energy cost savings for each configuration is shown in Figures 4.26 through 4.31.

Table 4.4: Energy Cost Data (EIA.gov 2013)

City	Electricity (per kWh)	Natural Gas (per kWh)
Miami	\$ 0.0947	\$ 0.0354
Phoenix	\$ 0.1000	\$ 0.0330
Atlanta	\$ 0.0987	\$ 0.0329
San Francisco	\$ 0.1438	\$ 0.0243
Albuquerque	\$ 0.0976	\$ 0.0215
Louisville	\$ 0.0843	\$ 0.0282
Boulder	\$ 0.0981	\$ 0.0254

Figure 4.24: Annual Energy Cost Savings for Small Office Condo in Miami, FL (Zone 1A)

Figure 4.25: Annual Energy Cost Savings for Small Office Condo in Phoenix, AZ (Zone 2B)

Figure 4.26: Annual Energy Cost Savings for Small Office Condo in Atlanta, GA (Zone 3A)

Figure 4.27: Annual Energy Cost Savings for Small Office Condo in San Francisco, CA (Zone 3C)

Figure 4.28: Annual Energy Cost Savings for Small Office Condo
Albuquerque, NM (Zone 4B)

Figure 4.29: Annual Energy Cost Savings for Small Office Condo
Boulder, CO (Zone 5B)

Based on energy costs, a number of wall construction configurations were able to meet or exceed the performance of the ASHRAE 90.1 code prescriptive wall configurations in Climate Zones 3 through 5.

In Miami, FL neither interior insulation nor PCM masonry provided significant performance improvement. As was stated previously, night time ventilation would likely provide improved performance, especially for PCM concrete masonry. In Phoenix, AZ exterior walls with standard concrete masonry and core insulation exceed the ASHRAE 90.1 comparison benchmark and PCM concrete masonry provides marginal energy cost savings. Again night time ventilation may improve this performance.

In Atlanta, GA the exterior concrete masonry wall configuration with 10% PCM was able to provide equivalent energy costs. Additional, roof insulation was not required. Standard concrete masonry walls with core insulation did not provide equivalent performance. However with additional roof insulation, this configuration did show energy cost equivalency, but at lower performance levels than for the PCM concrete masonry.

In San Francisco, CA configurations with both standard concrete masonry walls with core insulation and with 10% PCM concrete masonry showed equivalency to interior insulated standard masonry walls. The PCM concrete masonry configuration provided the most cost savings

In Albuquerque, NM configurations with exterior walls having 10% PCM concrete masonry produced better behavior than the interior insulation configuration without additional roof insulation. The configuration with the insulated core standard masonry walls required additional roof insulation to achieve equivalent performance.

Finally, in Boulder, CO equivalent performance was not met with any of the other wall configurations evaluated, although the configurations with exterior walls with 10% PCM concrete masonry was almost equivalent. It is expected that exterior walls with PCM incorporation between 10% and 15% would likely meet the required energy performance.

Overall, it was found that in Climate Zones 3 through 5, PCM concrete masonry can be used to provide equivalent performance alternatives to the ASHRAE 90.1 prescriptive requirements. For Climate Zones 3 and 4, the energy cost budget method allowed the PCM concrete masonry without additional roof insulation measures. In Zone 5, the PCM concrete masonry with additional roof insulation provided slightly less savings than the interior insulation baseline. However, these configurations with additional roof insulation provide equivalent energy consumption performance in Zone 5.

It should be noted that passive heating and cooling techniques have the ability to improve the performance of the alternative exterior wall configurations. Configuration of windows and eaves to allow solar gain in the winter while minimizing it during the summer can help provide heating in the winter and prevent it during the summer. Further, night

time ventilation can evacuate excess heat introduced into the building during the day to help precool the building prior to occupancy.

4.3 Economic Analysis

Results from the EnergyPlus holistic building simulations were used to analyze the economic implications of using PCM concrete masonry in exterior walls. Costs for PCM masonry single-wythe construction were compared to standard concrete masonry with interior insulation and finishing. As shown in Figure 4.30, the typical interior insulation configuration for a single-wythe masonry wall included a masonry wall section, furring, interior rigid polyurethane insulation, wallboard, and paint finishes. The single-wythe masonry wall shown in Figure 4.31 included standard concrete masonry units as well as PCM concrete units along with polyurethane core insulation and paint. Finally, where required, additional roof insulation was examined for single-wythe construction with and without PCM.

Figure 4.30: Single-Wythe Concrete Masonry Wall Configuration with Interior Insulation, Furring, Wallboard, and Interior Paint (Adapted from NCMA 2013)

Figure 4.31: Single-Wythe Concrete Masonry Wall Configuration with Foam Core Insulation and Interior Paint (Adapted from NCMA 2013)

Exterior wall system pricing was obtained from Peter Loughney, a certified construction estimator (personal communication, July 22, 2013) of the International Masonry Institute via email contact. The pricing for roof insulation was obtained from the 2011 RSMeans Building Construction Cost Data (RSMeans 2011). The \$4.40/Kg

(\$2/pound) cost of the PCM was based on information provided by Eric Lindquist (personal communication, November 15, 2012) President of Entropy Solutions, Inc. which is the company that manufactures the PureTemp PCM.

Tables 4.5 through 4.10 show the cost estimates for the wall configurations in the small office building. Included in the cost estimate are the costs of additional roof insulation and PCMs where needed to meet the energy cost budget equivalency as required in ASHRAE 90.1 for Atlanta, GA, Albuquerque, NM, and Boulder, CO. A summary the cost estimate results are shown in Table 4.15.

Table 4.5: Cost for Standard Masonry with Interior Insulation in Atlanta, GA

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.60
#7 rebar @ 48" o.c.	0.33
Grout	0.48
Bond beam/cmu+rebar+grout	0.15
Exterior Paint -2 coats, rolled	0.67
1 5/8" galv mtl furr @ 24o.c.	1.46
1.5 " Polyurethane Insulation	1.07
1/2" GWB, taped Fin L4	1.20
Interior paint, 2 cts -rolled	0.62
Total / SF	\$14.58
Grand Total Wall SF	\$34,846.20

Table 4.6: Cost for 15% PCM Masonry with Core Insulation in Atlanta, GA

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.60
#7 rebar @ 48" o.c.	0.33
Grout	0.48
Bond beam/cmu+rebar+grout	0.15
Foamed cells / Drill & Patch	0.50
Exterior Paint -2 coats, rolled	0.67
Interior Paint, 1 prm-1fin-rolled	0.82
15% PCM	9.00
Total / SF	\$20.55
Grand Total Wall SF	\$49,114.50

Table 4.7: Cost for 10% PCM Masonry with Core Insulation and Additional R-2 Roof Insulation in Atlanta, GA

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.60
#7 rebar @ 48" o.c.	0.33
Grout	0.48
Bond beam/cmu+rebar+grout	0.15
Foamed cells / Drill & Patch	0.50
Exterior Paint -2 coats, rolled	0.67
Interior Paint, 1 prm-1fin-rolled	0.82
10% PCM	6.00
Total / SF	\$17.55
Total Wall SF (2390)	\$41,944.50
R-2 Isocyanurate Insulation	0.98
Total / SF	\$0.98
Total Roof SF (5500)	\$5,390.00
Grand Total Wall & Roof	\$47,334.50

Table 4.8: Cost for Standard Masonry with Core Insulation and Additional R-4 Roof Insulation in Atlanta, GA

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.60
#7 rebar @ 48" o.c.	0.33
Grout	0.48
Bond beam/cmu+rebar+grout	0.15
Foamed cells / Drill & Patch	0.50
Exterior Paint -2 coats, rolled	0.67
Interior Paint, 1 prm-1fin-rolled	0.82
Total / SF	\$11.55
Total Wall SF (2390)	\$27,604.50
R-4 Isocyanurate Insulation	1.02
Total / SF	\$1.02
Total Roof SF (5500)	\$5,610.00
Grand Total Wall & Roof	\$33,214.50

Table 4.9: Cost for Standard Masonry with Interior Insulation in Albuquerque, NM

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.80
#7 rebar @ 48" o.c.	0.31
Grout	0.46
Bond beam/cmu+rebar+grout	0.18
Exterior Paint -2 coats, rolled	0.49
1 5/8" galv mtl furr @ 24o.c.	1.23
1.5 " Polyurethane Insulation	1.14
1/2" GWB, taped Fin L4	1.01
Interior paint, 2 cts -rolled	0.45
Total / SF	\$14.07
Grand Total Wall SF	\$33,627.30

Table 4.10: Cost for 10% PCM Masonry with Core Insulation and Additional R-6 Roof Insulation in Albuquerque, NM

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.80
#7 rebar @ 48" o.c.	0.31
Grout	0.46
Bond beam/cmu+rebar+grout	0.18
Foamed cells / Drill & Patch	0.52
Exterior Paint -2 coats, rolled	0.49
Interior Paint, 1 prm-1fin-rolled	0.58
10% PCM	6.00
Total / SF	\$17.34
Total Wall SF (2390)	\$41,442.60
R-6 Isocyanurate Insulation	1.22
Total / SF	\$1.22
Total Roof SF (5500)	\$6,710.00
Grand Total Wall & Roof	\$48,152.60

Table 4.11: Cost for Standard Masonry with Core Insulation and Additional R-6 Roof Insulation in Albuquerque, NM

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	8.80
#7 rebar @ 48" o.c.	0.31
Grout	0.46
Bond beam/cmu+rebar+grout	0.18
Foamed cells / Drill & Patch	0.52
Exterior Paint -2 coats, rolled	0.49
Interior Paint, 1 prm-1fin-rolled	0.58
Total / SF	11.34
Total Wall SF (2390)	\$27,102.60
R-8 Isocyanurate Insulation	1.42
Total / SF	\$1.42
Total Roof SF (5500)	\$7,810.00
Grand Total Wall & Roof	\$34,912.60

Table 4.12: Cost for Standard Masonry with Interior Insulation in Boulder, CO

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	9.00
#7 rebar @ 48" o.c.	0.33
Grout	0.50
Bond beam/cmu+rebar+grout	0.18
Exterior Paint -2 coats, rolled	0.60
1 5/8" Mtl Furr @ 24 o.c.-allow .20/sf to shim	1.82
2.0 " Polyurethane Insulation	1.62
1/2" GWB, taped Fin L4	1.33
Interior paint, 2 cts -rolled	0.54
Total / SF	\$15.92
Grand Total Wall SF	\$38,048.80

Table 4.13: Cost for 10% PCM Masonry with Core Insulation and Additional R-16 Roof Insulation in Boulder, CO

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	9.00
#7 rebar @ 48" o.c.	0.33
Grout	0.50
Bond beam/cmu+rebar+grout	0.18
Foamed cells / Drill & Patch	0.56
Exterior Paint -2 coats, rolled	0.60
Interior Paint, 1 prm-1fin-rolled	0.73
10% PCM	6.00
Total / SF	17.90
Total Wall SF (2390)	\$42,781.00
R-16 Isocyanurate Insulation	2.68
Total / SF	2.68
Total Roof SF (5500)	\$14,740.00
Grand Total Wall & Roof	\$57,521.00

Table 4.14: Cost for Standard Masonry with Core Insulation and Additional R-22 Roof Insulation in Boulder, CO

8" CMU, EXT - reinf alt crs, tool 2 sds, norm wgt	9.00
#7 rebar @ 48" o.c.	0.33
Grout	0.50
Bond beam/cmu+rebar+grout	0.18
Foamed cells / Drill & Patch	0.56
Exterior Paint -2 coats, rolled	0.60
Interior Paint, 1 prm-1fin-rolled	0.73
Total / SF	11.90
Total Wall SF (2390)	\$28,441.00
R-22 Isocyanurate Insulation	2.92
Total / SF	2.92
Total Roof SF (5500)	\$16,060.00
Grand Total Wall & Roof	\$44,501.00

Table 4.15: Summary of Costs for Configurations Meeting ASHRAE 90.1

Configuration	Cost by Climate Zone		
	Atlanta, GA (3A)	Albuquerque, NM (4B)	Boulder, CO (5B)
Std. Masonry w/ Interior Insulation	\$34,846.20	\$33,627.30	\$38,048.80
PCM (15%) Masonry w/ Core Insulation	\$49,114.50	NA	NA
PCM (10%) Masonry w/ Core Insulation & Additional Roof Insulation	\$47,334.50	\$48,152.60	\$57,521.00
Standard Masonry w/ Core Insulation & Additional Roof Insulation	\$33,214.50	\$34,912.60	\$44,501.00

Reviewing the cost summary in Table 4.15, it can be seen that at \$4.40/Kg (\$2/pound) for PCM, PCM exterior wall configurations are currently more expensive than conventional construction configurations. For Atlanta, GA the most economical exterior wall option is to use core insulation with additional roof insulation. The cost effectiveness of the remaining configurations from most to least is as follows; standard masonry exterior walls with interior insulation, followed by 10% PCM masonry exterior wall with core insulation and additional roof insulation, and then 15% PCM masonry with core insulation. For Albuquerque, NM the least expensive wall option was a standard masonry wall with interior insulation, followed by standard masonry with core insulation and additional roof insulation. The most expensive was when a 10% PCM masonry exterior wall with additional roof insulation was used. Boulder, CO provided the same order of results as Albuquerque, NM.

It should be noted that the price of PCM is relatively high at \$4.40/Kg (\$2/pound). With wide scale implementation of PCM in concrete it is likely that the cost will be significantly reduced due to bulk quantities being produced, shipped, and used. In addition, while foam insulation is produced from hydrocarbons, PCM can be produced using plant byproducts. As petroleum prices continue to rise, using PCM produced from plant byproducts may help to offset the price difference.

A comparison was also made to determine at what price PCM can become economically competitive. Using current pricing, comparisons were made for Atlanta, GA (3A) and Albuquerque, NM (4B). These were regions where, based on energy cost

comparisons, PCM could be used in lieu of interior insulation without having to provide additional roof insulation. Both comparisons used 10% PCM exterior masonry walls. The price of a standard concrete masonry wall with 3.81 cm (1.5 inch) interior rigid polyurethane insulation was compared to a standard masonry wall with polyurethane core insulation. The difference in the cost of the two wall configurations represents the required price of PCM needed to provide comparable performance. The price per area needed to break even was divided by the mass of PCM needed per area. This provided a price of PCM by mass that is required to meet the minimum economical requirement as shown in Table 4.16.

Table 4.16: PCM Required Price for Economics

City	Standard CMU with Interior Insulation	Standard CMU with Interior Core Insulation	Interior Insulation vs. Core Insulation Difference	Required PCM Mass/Area	PCM Price Required for Economics
Atlanta, GA	\$156.94/m ² (\$14.58/ft ²)	\$118.95/m ² (\$11.05/ft ²)	\$38.00 (\$3.53/ft ²)	14.66 kg/m ² (3.00 lb/ft ²)	\$2.22/kg (\$1.01/lb)
Albuquerque, NM	\$151.45/m ² (\$14.07/ft ²)	\$122.07/m ² (\$11.34/ft ²)	\$29.39 (\$2.73/ft ²)	14.66 kg/m ² (3.00 lb/ft ²)	\$2.00/ kg (\$0.91/lb)
Average	\$154.20/m ² (\$14.33/ft ²)	\$120.51/m ² (\$11.20/ft ²)	\$33.69 (\$3.13/ft ²)	14.66 kg/m ² (3.00 lb/ft ²)	\$2.11/ kg (\$0.96/lb)

According to the above analysis, PCM price must be reduced significantly in order to be economically viable. Equivalent cost requires that the price of PCM be reduced from the current price of \$4.40/kg (\$2/lb) by approximately 50%, or to \$2.20/kg (\$1/lb). Considering that PCM can be produced from plant byproducts it is possible that waste products can be used to reduce costs. In addition, large scale implementation and commercialization can also help reduce the cost of PCMs.

CHAPTER FIVE: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions

The incorporation of Phase Change Materials into concrete was evaluated and found to be appropriate for use in Concrete Masonry Units during this investigation. Several viable PCM concrete mixes which met the ASTM C90 minimum structural requirements of 13.1 MPa (1900 psi) were developed. Thermal testing was performed on the PCMs as well as the PCM concrete to characterize the performance of these PCM concrete mixes. Finally, the performance of PCM concrete was examined as a building envelope component using holistic energy analyses, indicating that PCM concrete can provide a comparable performance alternative to the prescriptive minimum insulation requirements required by ASHRAE 90.1.

While PCM concrete mixes have been developed in the past, they have typically relied upon micro-encapsulated PCM or immersion of cured concrete specimens. Though micro-encapsulated PCM concrete is viable in concrete, the method is cost prohibitive due to the expense of the micro-encapsulation process. In addition, the encapsulation material consumes a portion of the volume (~20%) which could be devoted to PCM and thus reduces the volume of PCM that can be incorporated by 20%. Furthermore, micro-encapsulation requires that the PCM be mixed as a part of the cement matrix. This in turn

reduces the cement in the mix, thus reducing strength. Therefore, a reduced PCM volume is achievable in the micro-encapsulated PCM mix before becoming deleterious.

Immersion provides good PCM content. However, this process uses surface tension and molecular bonding to provide PCM retention with concrete pore space. Though easily performed, long term stability is questionable due to the likelihood of PCM bleeding.

The PCM vacuum impregnation process developed in this research alleviates the problems associated with micro-encapsulation and immersion. The PCM is directly incorporated into the lightweight concrete aggregate, and since the PCM is within the aggregates, it does not displace the cement matrix. In addition, the PCM which is impregnated into the aggregate is encapsulated by the cement matrix. This improves PCM retention and does not reduce the cement matrix volume. Vacuum impregnation of the PCMs into porous aggregates provided approximately 10% to 13% PCM by mass fraction and was validated using the Dynamic Hot Box Apparatus.

From the EnergyPlus holistic building analyses, it was found that using PCM concrete with 10% to 15%, PCM masonry provided equivalent energy performance as compared to the continuous interior insulation requirements prescribed by ASHRAE 90.1 in Climate Zones 2 through 4. Single-wythe PCM concrete masonry walls with polyurethane core insulation can be used as an acceptable alternative to interior insulated CMU walls. Though currently the cost of PCM makes it more expensive, with wide scale

implementation, the cost of PCM concrete can be reduced to a price at which it is competitive with traditional masonry wall configurations. It was estimated that if PCM price can halved to \$2.20/kg (\$1/lb), then PCM concrete masonry has the potential compete with standard concrete masonry with interior insulation.

Further, there are many potential benefits related to the additional effective thermal mass associated with PCM concrete masonry. These include buffering of interior temperatures associated with heat gains such as electronics, occupants, and solar gains as well as tempering of the interior air mass. Buffering of the heat gains from electronics, occupants, and solar gain can reduce summer overheating. Buffering of the air mass can also alleviate heat losses due to drafts related to periodically opened fenestrations and can help to regulate interior temperatures to improve HVAC performance. This interior environment stabilization can improve HVAC performance by decreasing cycling as HVAC systems initially perform below optimum before reaching steady state. If the HVAC system has fewer cycles with longer run times, performance efficiency can be improved.

In addition, by alleviating the need for interior insulation, furring, and gypsum wallboard, the wall durability is significantly improved, especially in industrial applications. By reducing the wall section to PCM concrete masonry with core insulation along a coat of paint, long term maintenance is reduced.

Further, the phase shift provided by thermal mass can shift peak energy use by several hours. This can delay peak energy use from peak hour to non-peak hours. In areas with demand pricing, this can further reduce energy costs. In addition, the peak shift, for the case of air conditioning, can move peak air conditioning requirements to the night time period. This can improve the HVAC equipment performance by providing a lower ambient air temperature for heat exchange, thus providing higher HVAC efficiency. Finally, the delay of peak energy use provided by the phase shift can help to buffer regional peak energy use. By reducing peak demand, the need for the construction of additional power plants can be lessened, therefore mitigating substantial capital and environmental costs.

5.2 Recommendations

Although this investigation demonstrated performance enhancements with PCM concrete masonry walls, further research is need to realize all of the potential benefits of PCM Concrete Masonry Units. It is expected that examination of ventilation and passive solar strategies should provide significant performance improvements beyond that which was found in this research. Thus, it is recommended that these strategies, including strategic fenestration orientation, overhang shading, night time ventilation, as well as ground coupled masonry core ventilation be further examined.

Ground coupling and solar radiation can be used to capitalize on the effective thermal mass of PCM concrete masonry to store and release thermal energy. In the winter months this can be used to store thermal energy from daytime solar gains for release during the nights. In, addition, strategies can be developed to store solar thermal energy during

summer days to reduce internal loads. Finally, the hollow cores of PCM concrete masonry can be coupled with earth tubes or similar structures so that cool air can be introduced to extract heat from the walls during the summer providing envelope cooling. During the winter, if the ground is warm enough, ground coupling with earth tubes can introduce heat to the PCM masonry walls for radiant heating. An additional option may be to couple the PCM masonry walls with hollow core precast concrete roof panels or other heating techniques so that during sunny winter days, rather than drawing air from the ground, ambient air could be drawn through the concrete roof panels or other structures in order to heat the air before being introduced into the PCM concrete masonry cores for heat exchange.

Further experimental work is needed to quantify the behavior of PCM concrete masonry wall systems. It is recommended that research be performed on PCM concrete masonry wall sections in the Dynamic Hot Box Apparatus to fully quantify the steady-state and transient multi-dimensional heat transfer properties of a PCM CMU wall section with mortar, grout, and cores. This would help to provide the heat storage and transfer characteristics for holistic building energy modeling. This is important in the further development of PCM concrete masonry modeling and will indicate whether simplified models are applicable or if data from the Dynamic Hot Box Apparatus is required for accurate modeling. In addition, it is recommended that a representative PCM concrete structure be constructed or that PCM concrete masonry be retrofitted in an existing structure to examine the performance in the Louisville, KY (Climate Zone 4A) climate or other potential climate zones.

Further work is also recommended to examine whether improvements in the vacuum impregnation process can increase the PCM content of the aggregates and thus the PCM concrete mix energy performance.

Additional research should also be done to quantify the long-term stability as well as the ability of the PCM concrete to retard fire. The PCM concrete should be tested for repeated cycling to determine whether significant loss of PCM occurs. This can be accomplished by placing a PCM concrete sample in the environmental chamber and applying repetitive thermal cycling to the sample. Visual inspection for PCM on the surface will provide information regarding the retention of PCMs. In addition, after periods of cycling, the sample can then be tested for the latent heat using the developed step method. Fire resistance will be a function of PCM retention which can also be determined by applying a heat source for a prescribed amount of time to determine if ignition will occur and if it will remain ignited.

Finally, PCM concrete masonry wall effectiveness may be improved by using strategic holistic building design methods such as building configurations that use PCM concrete masonry in the southern facing wall(s) for maximum solar gain and economics while also locating PCM in the floors exposed to southern fenestration. In addition, using PCM in conjunction with HVAC ductwork to increase HVAC equipment run times has great potential and therefore associated performance improvements should be explored.

REFERENCES

- Alawadhi, E.M. (2008). "Thermal analysis of a building brick containing phase change material." *Energy and Buildings*, 40(3), 351-357.
- ASHRAE (1997) "ASHRAE Handbook of Fundamentals." *American Society of Heating, Refrigeration and Air-Conditioning Engineers*, Atlanta, GA.
- ASHRAE (2010). "ASHRAE 90.1-2010. ASHRAE STANDARD Energy Standard for Building Except Low-Rise Residential Buildings." *American Society of Heating, Refrigeration and Air-Conditioning Engineers*, Atlanta, GA.
- ASTM Standard C39C39M-1a (2012). "Standard Test Method for Compressive Strength of Cylindrical Concrete Samples." *ASTM International*, West Conshohocken, PA C09.61 (04.02).
- ASTM Standard C90-13 (2013). "Standard Specification for Loadbearing Masonry Units." *ASTM International*, West Conshohocken, PA C15.03 (04.05).
- Athientis, A.K., Liu, C., Hawes, D., Banu, D., Feldman, D. (1997). "Investigation of thermal performance of a passive solar test-room with wall latent heat storage." *Building and Environment*, 32(5), 405-410.
- Bannister, T.C. (1967). "The specific heats of five hydrocarbons." *National Aeronautics and Space Administration*, Huntsville, AL.
- BASF, "Phase Change Materials."
<http://www.micronal.de/portal/basf/ien/dt.jsp?setCursor=1_290798> (January 1, 2012).
- BASF, "Micronal PCM®, Intelligent Temperature Management for Buildings."
<http://www.dispersions-pigments.basf.com/portal/load/fid443847/BASF_Micronal_PCM_Brochure%202009_English.pdf> (June 6, 2012).
- Baetens, R. Jelle, B.P., Gustavsen, A. (2010). "Phase change materials for building applications: A state-of-the-art review." *Energy and Buildings* 42 (2010) 1361-1368.

Cabeza, L., Heinz, A. (2005). "Inventory of Phase Change Materials (PCM) A Report of IEA Solar Heating and Cooling programme – Task 32 "Advanced storage concepts for solar and low energy buildings" Report C2 of Subtask C." *International Energy Agency*, Lleida, Spain.

Cabeza, L.F., Castellon, C., Nogues, M., Medrano, M., Leppers, R., Zubillaga, O. (2007). "Use of micro-encapsulated PCM in concrete walls for energy savings." *Energy and Buildings* 39(2), 113-119.

Castellon, C., Nogues, M., Medrano, M., Cabeza, L.F. (2007). "Micro-encapsulated phase change materials (PCM) for building applications." *Department d'Informatica i Eng. Industrial, Universitat de Lleida.*, Lleida, Spain.

Castell, A., Martorell, I., Medrano, M., Perez, G. Cabeza, L.F. (2010). "Experimental study of using PCM in brick constructive solutions for passive cooling." *Energy and Buildings* 42(4), 534-540.

Castell, A., Medrano M., Roca, J., Vila, A., Cabeza, L.F. (2010). "Experimental study of PCM in Mediterranean buildings". *GREA Innovacio Concurrent, Universitat de Lleida.*, Lleida, Spain.

Castellon, C., Medrano, M., Roca, J., Nogues, M., Castell, A., Cabeza, L.F. (2007). "Use of micro-encapsulated phase change materials in building applications." *American Society of Heating, Refrigeration and Air-Conditioning Engineers*, Atlanta, GA.

Castellon, C., Gunther, E., Mehling, H., Heibler, S., Cabeza, L.F. (2008). "Determination of the enthalpy of PCM as a function of temperature using a heat-flux DSC – A study of different measurement procedures and their accuracy." *International Journal of Energy Research* 32(13), 1258-1265.

Castellon, C., Castell, A., Medrano M., Martorell, I., Cabeza, L.F. (2008). Experimental study of PCM inclusion in different building envelopes. *Journal of Solar Engineering*, 131:041006-1-6.

Diaconu, B.M., Cruceru, M. (2010). "Novel concept of composite phase change material wall system for year-round thermal energy savings." *Energy and Buildings*, 42(10), 1759-1772.

Drake, J.B. (1987). "A study of the optimal transition temperature of PCM wallboard for solar energy storage." *Oak Ridge National Laboratory*. TM-10210,1-24.

Duffie, J.A., Beckman, W.A. (1991). "Solar engineering of thermal processes." John Wiley, New York, NY.

EIA, U.S. Energy Information Association (2010). "Total Energy Flow" <<http://www.eia.gov/totalenergy/data/annual/diagram1.cfm>> (March 3, 2013).

EIA, U.S. Energy Information Association (2005). “Average Consumption by Energy End Uses”
<http://www.eia.gov/emeu/recs/recs2005/hc2005_tables/c&e/pdf/tableus14.pdf>
(March 3, 2013).

EIA, U.S. Energy Information Association (2013). “Electricity Data.”
<<http://www.eia.gov/electricity/data.cfm>> (Nov. 2, 2013).

EIA, U.S. Energy Information Association (2013). “Natural Gas Data”
<<http://www.eia.gov/naturalgas/data.cfm>> (November 2, 2013).

EIA, U.S. Energy Information Association (2012) < “U.S. Climate Zone Map”, 1996,
available from <http://www.eia.gov/emeu/recs/recs97/zonemap.pdf>> (June, 11 2013).

EnergyPlus, (2013) “EnergyPlus Engineering Reference”
<<http://apps1.eere.energy.gov/buildings/energyplus/pdfs/engineeringreference.pdf>>
(September 30, 2013).

Entrop, A.G., Brouwers, H.J.H., Reinders, A.H.M.E. (2011). “Experimental research on the use of micro-encapsulated Phase Change Materials to store solar energy in concrete floors and to save energy in Dutch houses.” *Solar Energy*, 85(5) 1007-1020.

EDUCATE, Environmental Design in University Curricula and Architectural Training in Europe (2013), “Thermal Mass Diagram” <https://www.educate-sustainability.eu/kb/sites/www.educate-sustainability.eu.portal/files/images/02.img_assist_custom-435x348.jpg> (Aug.5, 2013).

Energy Modeling of Building Wiki (2013), “ASHRAE Climate Zone Map”
<<http://energymodeling.pbworks.com/w/page/18898438/Energy%20Modeling%20Maps>>
(Oct. 30, 2013).

Farid, M.M., Khudhair, A.M., Razack, S.A.K., Al-Hallaj, S. (2004), “A review on phase change energy storage: materials and applications.” *Energy Conversion and Management*, 45(9-10), 1597-1615.

Gunther, E., Hiebler, S., Mehling, H., Redlich, R. (2009), “Enthalpy of phase change materials as a function of temperature: required accuracy and suitable measurement methods.” *International Journal of Thermophysics*, 30(4), 1257-1269.

Halford, C.K., Boehm, R.F. (2007), “Modeling of phase change material peak load shifting.” *Energy and Buildings*, 39(3), 298-305.

Harrison, K. (2011) “Chemistry, Structures & 3D Molecules @ 3dchem.com.”
<<http://www.3dchem.com/molecules>> (October 25, 2013).

- Hawes, D.W., Feldman, D. (1991), "Absorption of phase change materials in concrete." *Solar Energy Materials and Solar Cells*, 27(2), 91-101.
- Hawes, D.W., Banu, D., Feldman, D. (1991), "Latent heat storage in concrete. II." *Solar Energy Materials*, 21(1), 61-801.
- Hewlett, P.C. (1985), "Lea's Chemistry of Cement and Concrete": *Thomas Telford Ltd.* London, England.
- Hittle, D.C. (2002), "Phase Change Materials in floor tiles for thermal energy storage, Award No. DE-FC26-00NT40999." *Colorado State University Fort Collins*, CO.
- Holm, T.A. (1997), "Recommended Gradation for Structural Lightweight Aggregate used in High Quality Masonry Units." American Concrete Institute, Farmington Hills, MI.
- Holman, J.P. (1981), "Heat Transfer, Fifth", *Mcgraw-Hill, Inc.*, New York, NY.
- Hu, H. Argyropoulos, S.A. (1996), "Mathematical modelling of solidification and melting: a review." *Modelling, Simulation, Material Science, and Engineering*. 4(4), 371-396.
- Hunger, M. Entrop, A.G., Mandilaras, Brouwers, H.H.H, Founti, M. (2009), "The behavior of self-compacting concrete containing micro-encapsulated Phase Change Materials." *Cement and Concrete Composites*. 31, 731-743.
- Incropera, F.P., DeWitt, D.P., Bergman, T.L., Lavine, A.S. (2007), "Introduction to Heat Transfer, Fifth." *John Wiley and Sons*, Notre Dame, IN.
- Karaipekli, A., Sari, S. (2008), "Capric-myristic acid/expanded perlite composite as form-stable phase change material for latent heat thermal energy storage." *Renewable Energy*. 33(12), 2599-2605.
- Karaman, S., Karaipekli, A., Sari, A., Bicer, A. (2011), "Polyethylene glycol (PEG)/diatomite composite as a novel form-stable phase change material for thermal energy storage." *Solar Energy and Solar Cells* 95:1647-1653.
- Karambakkam, B.K., B. Nigusse, J. D. Spitler. (2005), "A One-dimensional Approximation for Transient Multi-dimensional Conduction Heat Transfer in Building Envelopes." *Proc., 7th Symposium on Building Physics in the Nordic Countries, The Icelandic Building Research Institute*, Reykjavik Iceland. Vol. 1, pp. 340-347.
- Khudhair, A.M., Farid, M.M. (2004), "A review on energy conservation in building applications with thermal storage by latent heat using phase change materials." *Energy Conversion and Management* 45(2), 263-275.

- Kim, E.Y., Kim, H.D. (2005), "Preparation and Properties of Micro-encapsulated Octadecane with Waterborne Polyurethane." *Journal of Applied Polymer Science* 96(5), 1596-1604.
- Kosny, J., Kossecka, E., Desjarlais, A., Christian, J. (1998), "Dynamic thermal performance of concrete and masonry walls." *Proc. Thermal Performance of the Exterior Envelopes of Buildings VII*. Atlanta, GA.
- Kosny, J., Petrie, T., Garwin, D., Childs, P., Desjarlais, A., Christian, J. (2001), "Thermal Mass–Energy savings potential in residential buildings." *Oak Ridge National Laboratory*. Oakridge TN.
- Kosny, J. Yarbrough, D. W., Miller, W. A., Wilkes, K. E., Lee, S. L. (2009), "Analysis of the dynamic thermal performance of fibrous insulations containing Phase Change Materials." *Oak Ridge National Laboratory*. Oakridge TN.
- Kosny, J. Kossecka, E. (2002), "Multi-dimensional heat transfer through complex building envelope assemblies in hourly energy simulation programs." *Oak Ridge National Laboratory* 34(5), 445-454.
- Kuznik, F., David, D., Johannes, K., Roux, J.J. (2011) "A review on phase change materials integrated in building walls." *Renewable and Sustainable Energy Reviews* 15(1), 379-391.
- Lea, F.M., Desch, C.H. (1956), "The Chemistry of Cement and Concrete, Second", *Edward Arnold LTD*, London, England.
- Microtek Laboratories Inc. (2010) "MicroPCM Products"
<http://www.microteklabs.com/micropcm_products.html> (June 6, 2012).
- NCMA, National Concrete Masonry Association "NCMA e-Details"
<http://www.ncma.org/edetails/pages/TEK_e-Details.aspx> (November 10, 2013).
- Neeper, D.A. (2000), "Thermal dynamics of wallboard with latent heat storage." *Solar Energy*. 68(5), 393-403.
- Nellis, G., Klein, S. (2001), "Heat Transfer." *Cambridge University Press*, Cambridge
- Noel, J., Roux, J., Schneider, P.S. (2001). "CODYBA, A design tool for buildings performance simulation." *Proc., Seventh International IBPSA Conference*, IBPSA, Rio de Janeiro, Brazil, 67-74.
- NREL, National Renewable Energy Laboratory (2012) "National Solar Radiation Data Base" http://rredc.nrel.gov/solar/old_data/nsrdb/1991-2005/tmy3 (Mar. 3, 2012).
- Ozisik, M. N. (1993). "Heat Conduction, Second Addition." *John Wiley and Sons, Inc.*, New York, NY.

Richardson, M.J., Woods, A.W. (2008). "An analysis of phase change material as thermal mass." *Proc., Royal Society of London*, Royal Society of London, London, England, 464(2092), 1029-1056.

RSMeans, A division of Reed Construction data (2011). "RSMeans Building Construction Cost Data." *Reed Construction Data, Construction Publishers & Consultants*, Norwell, MA.

Saylor, I.O., Sircar, A. K., Kumar, A. (1995). "Advanced phase change materials technology: Evaluation in lightweight solite how-core building blocks." *Intersociety Energy Conversion engineering Conference, 30th IECE Conference*, ASME, New York, NY, 217-224.

Solomon, A. D. (1979). "An Easily Computable Solution to a Two-phase Stefan Problem." *Solar Energy* 23(6), 525-528.

Stoll, F., Drake, M.L., Salyer, I.O. (1996). "Use of Phase Change Materials to prevent overnight freezing of bridge decks." *National Transportation Safety Board*, Washington, DC.

Stovall, T.K., Tomlinson, J.J. (1995), "What are the potential benefits of including latent storage in common wallboard?" *Journal of Solar Energy Engineering*. 117(4), 318-325.

Tabares-Velasco, P. C., Christensen, C., Bianchi, M. (2012). "Verification and validation of EnergyPlus phase change material model for opaque wall assemblies." *Building and Environment*. 54, 186-196.

The Masonry Society. (2010), "*Masonry Designers' Guide Sixth Edition.*" *The National Concrete Masonry Society*, Boulder, CO.

Thermometrics Precision Sensors, "Type K Thermocouple",
<<http://www.thermometricscorp.com/thertypk.html>> (July 19, 2013).

The Weather Channel, "Monthly Average Temperature Graphs",
<<http://www.weather.com/weather/wxclimatology/monthly/graph>> (Oct. 28, 2013).

Van der Graaf, F. (1985), "Research in calibration and application errors of heat flux sensors." *Building Applications of Heat Flux Transducers. ASTM STP*, 885, 79-96.

Voller, V.R., Swaminathan, C.R. (1990). "Fixed grid technique for phase change problems: a review." *International Journal for Numerical Methods in Engineering*, Minneapolis, MN, 30(4), 875-898.

Wilcox, B., Gumerlock, A., Barnaby, C., Mitchell, R., Huizenga, C. (1985). "The effects of thermal mass exterior walls on heating and cooling loads in commercial buildings." *Proc., ASHRAE Building Envelopes Conference*. ASRAE, Atlanta, GA.

Wilkes, K.E. (1989). "Model for Roof Thermal Performance, Report ORNL/CON-274." *Oak Ridge National Laboratory*, Oakridge, TN.

Zalba, B., Marin, J.M., Cabeza, L.F., Mehling, H. (2003). "Review on thermal energy storage with phase change: materials, heat transfer analysis and applications." *Applied Thermal Engineering* 23(3), 251-283.

Zhang, D., Li, Z., Zhou, J., Wu, K. (2003). "Development of thermal energy storage concrete." *Cement and Concrete Research* 23(6), 927-934.

Zhang, C., Chen, Y., Wu, L., Shi, M. (2011). "Thermal response of brick wall filled with phase change materials (PCM) under fluctuating outdoor temperatures." *Energy and Buildings* 43(12), 3514-3520.

Zwanzig, S.D., Lian, Y., Brehob, E.G. (2012) "Numerical simulation of phase change material composite wallboard in a multi-layered building envelope." *Energy Conversion and Management* 69, 27-40.

APPENDIX A: NOMENCLATURE

C_p	=	specific heat capacity ($\text{kJ kg}^{-1} \text{K}^{-1}$)
E	=	energy storage (kJ)
g	=	liquid phase fraction
H	=	enthalpy (kJ kg^{-1})
h	=	heat transfer coefficient (radiation/convection)
k	=	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
L	=	latent heat of fusion (kJ kg^{-1})
m	=	mass (kg)
ρ	=	density (kg m^{-3})
t	=	time (s)
T	=	Temperature ($^{\circ}\text{C}$ or K)
v	=	volume (m^3)
V	=	micro-voltage (μV)
x	=	X spacial coordinate (m)
y	=	Y spacial coordinate (m)
z	=	Z spacial coordinate (m)

APPENDIX B: SIEVE ANALYSIS RESULTS

Figure B.1: Manufactured Limestone Sieve Analysis

Figure B.2: Concrete Sand Sieve Analysis

Figure B.3: Graded Ottawa Sand Sieve Analysis

Figure B.4: Expanded Shale Sieve Analysis

Figure B.5: Expanded Clay Sieve Analysis

Figure B.6: Expanded Clay Sieve Analysis

Figure B.7: Expanded Clay Sieve Analysis

Figure B.8: Perlite Sieve Analysis

Figure B.9: Zonolite Sieve Analysis

Figure B.10: Vermiculite Sieve Analysis

Figure B.11: Vermiculite Sieve Analysis

Figure B.12: Vermiculite Sieve Analysis

Figure B.13: Graphite Sieve Analysis

APPENDIX C: HEAT FLUX SENSOR CALIBRATION

Figure C.1: Heat Flux Sensor Calibration for Sensor Temperature of 0°C

Figure C.2: Heat Flux Sensor Calibration for Sensor Temperature of 10°C

Figure C.3: Heat Flux Sensor Calibration for Sensor Temperature of 20°C

Figure C.4: Heat Flux Sensor Calibration for Sensor Temperature of 30°C

Figure C.5: Heat Flux Sensor Calibration for Sensor Temperature of 40°C

Figure C.6: Heat Flux Sensor Calibration for Sensor Temperature of 50°C

CURRICULUM VITAE

Jeffrey Dee Kiesel

318 Belvar Avenue Louisville, KY 40206 (502) 693-2304
jeffreykiesel@yahoo.com

EDUCATION

Ph.D. in Civil Engineering – <i>with Honors</i> <i>J.B. Speed School of Engineering, University of Louisville</i>	Expected December 2013
M.Eng. in Civil Engineering – <i>with Honors</i> <i>J.B. Speed School of Engineering, University of Louisville</i>	May 11, 2002
B.S. in Civil Engineering <i>J.B. Speed School of Engineering, University of Louisville</i>	May 12, 2001
B.A. in Biology <i>College of Arts & Sciences, University of Louisville</i>	August 15, 1997

PROFESSIONAL LICENSURE

Professional Engineer
Kentucky License No. 24514
Indiana License No. 11200128

Professional Land Surveyor
Kentucky License No. 3713

ENGINEERING EXPERIENCE

University of Louisville	Louisville, KY
<i>Graduate Research Assistant</i>	2010-Present
Research involved the development and testing of concrete that incorporated Phase Change Materials (PCMs). Material development was performed and testing facilities	

were designed and constructed to achieve the goals of the research work. Mechanical testing, thermal testing, and holistic energy analysis was performed.

Kiesel/Meyer Engineers, Planners & Surveyors, Inc.

Louisville, KY

Professional Engineer and Land Surveyor

2001-2010

Engineering and surveying work was performed as a licensed professional in both trades. Work involved high precision standard and ALTA surveys for sites as well mining applications, engineering design of residential, commercial, and institutional sites and facilities as well as large-scale hydrologic and hydraulic analyses. Further, transportation studies were performed and presented to planning commissions, courts and other applicable boards and committees to obtain approval to proceed with the firm's engineering work. Forensic expert witness consulting work was also performed for insurance agencies and legal firms.

Rogers Group, Inc.

Louisville, KY

Mine Surveyor and Junior Engineer

1999-2001

Was in charge of the horizontal and vertical layout of a one mile long slope tunnel that reached a depth of one thousand feet below the surface to provide two production strata one hundred feet apart vertically. During this time, was also in charge of the layout of mechanical equipment as well as maintaining accurate mine maps with all development and structures along with ventilation equipment and air flows. Once production level was reached, responsibilities included layout of the production facilities as well as accurately reaching a fourteen foot diameter bored ventilation / emergency escape shaft.

ACTIVITIES AND HONORS

- Research funding provided by Conn Center for Renewable Energy and Energy Efficiency (2011-2012)
- Research funding provided by National Concrete Masonry Association (2012-2013)
- 3rd in poster competition for 2013 Conn Center for Renewable Energy and Energy Efficiency Workshop
- 4th in poster competition for 2013 J.B. Speed School of Engineering E-Expo
- Chi Epsilon Civil Engineering Honor Society
- Kentucky Society of Professional Engineers
- Kentucky Society of Professional Surveyors