Thermal behaviour of hardened cement paste on heat and mass transfer

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**THERMAL BEHAVIOUR OF HARDENED CEMENT
PASTE ON HEAT AND MASS TRANSFER**

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

2007

Thermal Behaviour of Hardened Cement Paste on Heat and Mass Transfer

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ABSTRACT

Fire is known to cause spalling in concrete structures. Structural integrity of the building will be affected as the reinforcement steels will be weakened when exposed to heat directly in the absence of concrete cover. Fire resistance of concrete structural elements are often predicted based on the assumption that spalling does not occur. This assumption is often not satisfied in real fire test. Researches show that spalling is more susceptible in high strength concrete, silica fume blended cement concrete and concrete of low water/cement ratio. Such quantifications are not always valid. The fundamental cause of spalling is still not addressed. Hence, this research uses the microstructure of hardened cement paste as the foundation for analysing the occurrence of spalling. Material models relating non-evaporable moisture loss and porosity subjected to elevated temperature were developed as they were identified as parameters that influence significantly on gas pressure build up in concrete. The development of material models eliminates uncertainty in material behaviour of various mix proportions when analysing occurrence of spalling. Experimental data on mass loss and volume of pores measurements performed on specimens of different water/cement ratio (including pozzolana) and degree of hydration subjected to different temperatures were used to develop the material models that are applicable to hardened cement paste, cement mortar and concrete. An analytical model on heat and mass transfer based on microstructure model was also developed to solve temperature, mass of vapour and gas pressure distributions within heated hardened cement paste. A key improvement in the proposed model from existing models is the ability to model two plateaus in temperature-time domain corresponding to the evaporation of evaporable (100 °C) and non-evaporable moisture (530 °C) which was observed in experiments. The advantage of having the ability to model the plateaus would enable a more accurate analysis of thermal stresses and structural responses of hardened cement paste and concrete. Results of the simulation were validated with experimental data on temperature distribution in hardened cement paste of different moisture content and rate of heating. Results of the parametric analysis show that the proposed model is able to address the problem of spalling better than using indirect parameters such as compressive strength, water/cement ratio, blended cement paste.

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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION	1
1.1 Background	1
1.2 Objective and Scope of Research.....	4
1.3 Organisation of Report.....	5
CHAPTER 2: LITERATURE REVIEW	7
2.1 Overview	7
2.2 Definition of Terms.....	7
2.3 Constituents of Mortar and Concrete	8
2.4 Microstructure of Normal Cement Paste	9
2.4.1 Chemical Composition of OPC	9
2.4.2 Phase Composition of OPC	10
2.4.3 Models to Predict Hydration Products	11
2.4.3.1 Powers's Model (1958).....	11
2.4.3.2 Jennings and Tennis's Equations (1994)	13
2.4.4 Degree of Hydration	14
2.4.5 Pore Structure	15
2.5 Microstructure of Blended Cement Paste	17
2.5.1 Chemical Composition of Pozzolanas	17
2.5.2 Hydration Products	18
2.6 Properties of Concrete at Elevated Temperature	20
2.6.1 Microstructure Behaviour of Hardened Cement Paste	20
2.6.1.1 Loss of Non-Evaporable Moisture.....	20
2.6.1.2 Porosity	21
2.7 Spalling of Concrete.....	22
2.7.1 Spalling Mechanism	22
2.7.2 Experimental Investigations	24
2.7.3 Modelling of Heat and Mass Transfer in Concrete at Elevated Temperature	27
2.7.3.1 Assumptions.....	27
2.7.3.2 Model by Bazant and Thonguthai (1979).....	29
2.7.3.3 Model by Ichikawa and England (2001).....	32
2.7.3.4 Model by Tenchev <i>et al.</i> (2001).....	33

2.8	Reported Cases of Spalling	35
2.9	Methods to Reduce Spalling	36
2.10	Summary.....	37
CHAPTER 3: EXPERIMENTAL INVESTIGATIONS		39
3.1	Overview	39
3.2	Experimental Methodology.....	39
3.2.1	Mix Proportions	39
3.2.2	Heating Program	40
3.2.3	Degree of Hydration	43
3.2.4	Mass Loss Test.....	44
3.2.5	Pore Structure Test.....	46
3.3	Sample Preparation	47
3.4	Test Results	49
3.4.1	Degree of Hydration	49
3.4.2	Compressive Strength	51
3.4.3	Tensile Splitting Strength	52
3.5	Summary	53
CHAPTER 4: ANALYSIS OF TEST RESULTS		54
4.1	Overview	54
4.2	Test Results	54
4.2.1	TGA	54
4.2.2	MIP	58
4.2.2.1	Pore Structure	58
4.2.2.2	Density Measurements.....	62
4.2.3	Temperature Measurements.....	64
4.3	Derived Properties.....	69
4.3.1	Shrinkage	69
4.3.2	Permeability	73
4.4	Summary	75
CHAPTER 5: DECOMPOSITION PROFILE OF HYDRATION PRODUCTS.....		77
5.1	Introduction.....	77
5.2	Review of Previous Works	78
5.2.1	Decomposition of Hydration Products	78
5.2.2	Non-Evaporable Moisture Loss	82

5.3	Analytical Procedure to Derive Decomposition Profile From TGA/DTG ...	84
5.3.1	Influence of Temperature Range at which CH Decompose	90
5.3.2	Influence of Mix Proportions.....	92
5.3.2.1	W/C Ratio & Degree of Hydration	93
5.3.2.2	Volume Ratio of Amorphous Hydrates to CH.....	94
5.3.3	Total Mass Loss at Thermal Equilibrium	95
5.3.4	Effects of Decomposition on Physical Structure of Amorphous Hydrates	96
5.3.4.1	Physical and Chemical Properties of C-S-H Gel	97
5.3.4.2	Decompose Depth.....	98
5.4	Predicting Non-Evaporable Moisture Loss for Different Mix Proportion....	99
5.5	Summary	105
CHAPTER 6: RESIDUAL POROSITY OF HARDENED CEMENT PASTE		106
6.1	Introduction.....	106
6.2	Development of A Model for Residual Porosity	107
6.2.1	Proposed Model for Hardened Cement Paste	107
6.2.2	Derivation of n_0 and V_{hyd}	109
6.2.3	Breakdown of Gel and Capillary Pores	117
6.2.4	Proposed Model for Cement Mortar and Concrete.....	119
6.2.5	Influence of ITZ on Residual Porosity	123
6.3	Analytical Derivation of Porosity at Heated State	125
6.4	Conclusion	127
CHAPTER 7: MODELLING OF HEAT AND MASS TRANSFER IN CEMENT-BASED MATERIALS.....		128
7.1	Introduction.....	128
7.2	Proposed Model and Formulation.....	130
7.3	Physical Structure of Concrete.....	131
7.4	Formulation of Equations for Heat and Mass Transfer.....	133
7.4.1	Governing Equations	133
7.4.1.1	Energy	133
7.4.1.2	Free Water.....	134
7.4.1.3	Vapour	135

7.4.1.4	Dry Air	137
7.4.2	Coupling of Governing Equations	137
7.4.3	Boundary Conditions	139
7.4.3.1	Energy	139
7.4.3.2	Vapour	140
7.4.3.3	Air	141
7.4.3.4	Assembling Boundary Terms	141
7.4.4	Finite Element Formulation	143
7.4.5	Finite Difference Method	145
7.4.6	Shape Function	146
7.5	Thermal Properties of Hardened Cement Paste and Concrete	148
7.5.1	Non-Evaporable Moisture Loss	148
7.5.2	Porosity at Elevated Temperature	149
7.5.3	Thermal Conductivity	150
7.5.4	Specific Heat	151
7.5.5	Free Water Content	152
7.5.6	Intrinsic Permeability	153
7.6	Spalling Criterion	154
7.6.1	Tensile Stress	155
7.6.2	Tensile Strength	155
7.7	Summary	156
CHAPTER 8: NUMERICAL ANALYSIS OF EXPERIMENTAL DATA		158
8.1	Overview	158
8.2	Implementation in Matlab	158
8.3	Results of Numerical Simulations	161
8.4	Validation of Computer Model	165
8.4.1	Comparing Temperature Profile	165
8.4.2	Comparison Between Models	169
8.4.3	Verify Spalling Criterion	170
8.5	Discussion	171
8.5.1	Effects of W/C on Temperature and Gas Pressure	171
8.5.2	Effects of Pozzolana on Temperature and Gas Pressure	173
8.5.3	Effect of Degree of Hydration on Temperature and Gas Pressure	175

8.5.4	Effect of Different Types of Cement on Temperature and Gas Pressure	178
8.5.5	Effect of Using Specific Heat of Dry and Moist Hardened Cement Paste	181
8.5.6	Effect of Non-Evaporable Moisture Loss on Heat and Mass Transfer	182
8.6	Summary	184
CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS		185
9.1	Summary and Conclusions.....	185
9.2	Recommendations for Future Research	187
REFERENCES		
APPENDIX A		
APPENDIX B		
APPENDIX C		

LIST OF FIGURES

Figure 2.1: Schematic of Various Types of Cement-Based Materials.....	9
Figure 2.2: Simplified Model of Paste Structure (Powers, 1958).....	12
Figure 2.3: Porosity at Various Curing Duration (Ji, 2003)	16
Figure 2.4: Schematic Illustration of the 3 Zones (Anderberg, 1997).....	23
Figure 2.5: Experimental Setup by Harada and Terai (1997).....	25
Figure 2.6: Experimental Setup by Kalifa et al. (2000).....	25
Figure 2.7: Summary of Factors Affecting Spalling.....	27
Figure 2.8: Temperature – Pressure Profile for Unsealed Wall (Simulated) (Bazant and Kaplan, 1996)	31
Figure 2.9: Moving Interface of Moisture in Concrete (Ichikawa and England, 2001)	33
Figure 2.10: Distribution Profiles of Volumic Fractions (Left) and Masses (Right) (Tenchev <i>et al.</i> , 2001)	35
Figure 3.1: Nabertherm Electric Furnace (Left) and Digital Controller (Right)	41
Figure 3.2: Difference between Targeted and Gas Temperature	42
Figure 3.3: Temperature Profile within Specimen.....	43
Figure 3.4: Apparatus for TGA.....	45
Figure 3.5: Mercury Intrusion Porosimetry and Vacuum Desiccator.....	46
Figure 3.6: 50 mm Cubes Specimens	49
Figure 3.7: Compressive Strength Testing Machine.....	51
Figure 4.1: Percentage of Mass Remaining in HCP28	55
Figure 4.2: Percentage of Mass Remaining in HCP35	55
Figure 4.3: Percentage of Mass Remaining in HCP40	56
Figure 4.4: Percentage of Mass Remaining in HCP45	56
Figure 4.5: Percentage of Mass Remaining in BCP40	57
Figure 4.6: Pore Structure for HCP28.....	59
Figure 4.7: Pore Structure for HCP35.....	59
Figure 4.8: Pore Structure for HCP40.....	59
Figure 4.9: Pore Structure for HCP45.....	60
Figure 4.10: Pore Structure for BCP40.....	60
Figure 4.11: Behaviour of Bulk Density.....	63
Figure 4.12: Behaviour of Skeleton Density.....	64

Figure 4.13: Temperature Profile for SP2.....	66
Figure 4.14: Temperature Profile for SP3.....	66
Figure 4.15: Temperature Profile for SP4.....	67
Figure 4.16: Temperature Profile for SP5.....	67
Figure 4.17: Reduction in Volume at Various Temperatures	71
Figure 4.18: Reduction in Length at Various Temperatures.....	72
Figure 4.19: Measurement of the Length of Specimen.....	72
Figure 4.20: Comparing Calculated Permeability with Experimental Measured Permeability Using Total Porosity (Breyse and Gerard, 1997).....	75
Figure 5.1: Percentage Remaining of C-S-H gel at Various Heating Duration (Peng <i>et al.</i> , 2001)	79
Figure 5.2: Degree of Decomposition of C-S-H Gel and CH (Harmathy, 1970)	80
Figure 5.3: Comparison of Experimental Results.....	81
Figure 5.4: Coefficient $\bar{T}$ at Elevated Temperature (Hilsdorf, 1967).....	83
Figure 5.5: Typical DTG for HCP28	86
Figure 5.6: Typical DTG for HCP35	86
Figure 5.7: Typical DTG for HCP40	87
Figure 5.8: Typical DTG for HCP45	87
Figure 5.9: Typical DTG for BCP40	88
Figure 5.10: Typical TGA Result Showing Effects of CH for HCP28	89
Figure 5.11: Derived Fraction Decomposed of Various Phases for HCP28.....	90
Figure 5.12: DTG of Pure CH.....	91
Figure 5.13: Decomposition Profile for Various Mix Proportion.....	93
Figure 5.14: Simplified Amorphous Hydrate Structure.....	97
Figure 5.15: Decompose Depth at Various Elevated Temperature	98
Figure 5.16: Simplified C-S-H Gel Structure (Odler, 1998)	99
Figure 5.17: Flow Chart for Determining Non-Evaporable Moisture Loss.....	100
Figure 5.18: Non-Evaporable Moisture Loss for HCP28	102
Figure 5.19: Non-Evaporable Moisture Loss for HCP35	103
Figure 5.20: Non-Evaporable Moisture Loss for HCP40	103
Figure 5.21: Non-Evaporable Moisture Loss for HCP45	104
Figure 5.22: Non-Evaporable Moisture Loss for BCP40	104
Figure 6.1: Effects of V_{hyd} on Δn_T (Equation 6.3).....	110

Figure 6.2: Effects on W/c and α on n_0	112
Figure 6.3: Effects on W/c and α on V_{hyd}	112
Figure 6.4: Experimental and Predicted Porosity for HCP28	113
Figure 6.5: Experimental and Predicted Porosity for HCP35	114
Figure 6.6: Experimental and Predicted Porosity for HCP40	114
Figure 6.7: Experimental and Predicted Porosity for HCP45	115
Figure 6.8: Experimental and Predicted Porosity for BCP40	117
Figure 6.9: Experimental and Predicted Residual Gel Pores	118
Figure 6.10: Experimental and Predicted Residual Capillary Pores	119
Figure 6.11: Location of Specimen Used in MIP	120
Figure 6.12: Comparison between Porosity and Predicted Porosity	122
Figure 6.13: Distributions of Pores in Aggregate-Paste Interface (Scrivener and Nemati, 1996)	124
Figure 6.14: Comparison of Heated and Residual Porosity for HCP35	126
Figure 7.1: General Workflow of the Model	131
Figure 7.2: Breakdown of Skeleton Volume in Concrete	132
Figure 7.3: Breakdown of Pore Volume in Concrete	133
Figure 7.4: Thermal Conductivity of Various Types of Concrete	150
Figure 7.5: Specific Heat of Hardened Cement Paste and Concrete	152
Figure 7.6: Behaviour of Intrinsic Permeability	154
Figure 7.7: Residual Split-Tensile Strength of Concrete (Carette <i>et al.</i> , 1982)	156
Figure 8.1: Screen Shot of Simulation in Progress	159
Figure 8.2: Flow Chart of Program	160
Figure 8.3: Simulation Results for SP1	162
Figure 8.4: Simulation Results for SP2	162
Figure 8.5: Simulation Results for SP3	163
Figure 8.6: Simulation Results for SP4	163
Figure 8.7: Simulation Results for SP5	164
Figure 8.8: Comparison of Temperature Distributions for SP1	166
Figure 8.9: Comparison of Temperature Distributions for SP2	166
Figure 8.10: Comparison of Temperature Distributions for SP3	167
Figure 8.11: Comparison of Temperature Distributions for SP4	167
Figure 8.12: Comparison of Temperature Distributions for SP5	168

Figure 8.13: Comparison between Experimental Data, Ichikawa and England's (2001) (—) model and Proposed Model (- - -)	170
Figure 8.14: Temperature Profile for Various Mix proportions	172
Figure 8.15: Gas Pressure Profile for Various Mix proportions (30 min)	173
Figure 8.16: Temperature Profile of HCP40 and BCP40	174
Figure 8.17: Gas Pressure Profile of HCP40 and BCP40	175
Figure 8.18: Non-Evaporable Moisture Profile for HCP40 at Various Degree of Hydration.....	176
Figure 8.19: Porosity Profile for HCP40 at Various Degree of Hydration.....	177
Figure 8.20: Gas Pressure Profile for HCP40 at Various Degree of Hydration	177
Figure 8.21: Temperature Distribution of Various Types of Cement.....	179
Figure 8.22: Maximum Gas Pressure Envelop of Various Types of Cement.....	180
Figure 8.23: Temperature Profile of SP2	182
Figure 8.24: Comparison of Simulation Results for SP2.....	183

LIST OF TABLES

Table 2.1: Oxide and Corresponding Letter	7
Table 2.2: Abbreviation of Compounds.....	8
Table 2.3: Typical Range of Chemical Composition of OPC	9
Table 2.4: Powers's Model	11
Table 2.5: Physical Properties of Cementitious Materials.....	14
Table 2.6: Chemical Compositions and Physical Properties of OPC & Pozzolanas ...	18
Table 2.7: $Ca(OH)_2$ Content of Normal and FA Blended Cement Paste (Xu <i>et al.</i> , 2001)	19
Table 2.8: Decomposition of Hydration Products at Elevated Temperature	20
Table 2.9: ANOVA Significance for Explosive Spalling (Sullivan, 2001).....	26
Table 2.10: Temperature at which Spalling Occurs.....	36
Table 3.1: Mix Proportions for Cement Paste	39
Table 3.2: Comparison between Measured and Predicted Gel Pores	47
Table 3.3: Chemical Compositions of OPC and SF	48
Table 3.4: Phase Composition of OPC	48
Table 3.5: LOI for OPC	50
Table 3.6: α of Various Specimen	50
Table 3.7: Volumetric Ratio of Hydration Products for Various Specimens	50
Table 3.8: Compressive Strength of Specimens	52
Table 4.1: Percentage Mass Loss between 400 °C and 500 °C	57
Table 4.2: Breakdown of Capillary and Gel Pores	61
Table 4.3: Comparison of Peak Values in $\frac{dV}{d \log D}$	62
Table 4.4: Initial and Heating Condition	65
Table 4.5: Calculation of Shrinkage	70
Table 4.6: Calculation of K and a	74
Table 5.1: Phase Composition of Various Cement Paste Computed Using CemMicro (Ji, 2003)	81
Table 5.2: Observed Temperature Range at which CH Decompose	91
Table 5.3: Predicted Volumetric Ratio of Various Phases using CemMicro	94
Table 5.4: Total Mass Remaining (%) At Elevated Temperature for HCP35	96

Table 5.5: Calculation of k_m	101
Table 6.1: Chemical and Physical Properties of OPC and Pozzolana	117
Table 7.1: Various Types of Skeleton System.....	132
Table 8.1: Mix proportion of Concrete Used in Experiment (Ichikawa and England, 2001)	170
Table 8.2: Microstructure at Different Degree of Hydration.....	176
Table 8.3: Compound Composition of Different Types of OPC (Neville, 1996).....	178
Table 8.4: Microstructure of Different Cement	179
Table 8.5: Peak Gas Pressure for Different Cement.....	180

LIST OF SYMBOLS

A	Cross-Sectional Area
C	Specific Heat of Concrete
C_a	Specific Heat of Absorbed Water
C_A	Specific Heat of Air
C_L	Specific Heat of Liquid
C_S	Specific Heat of Solid Skeleton
C_V	Specific Heat of Vapour
C_w	Specific Heat of Capillary Water
D	Diffusion Coefficient of Concrete
D_{AV}	Diffusion Coefficient of Air or Vapour in a Gaseous Mixture
$D_{AV,\infty}$	Diffusion Coefficient of Air or Vapour in Surrounding Gaseous Mix,
D_G	Diffusion Coefficient if a Component in a Binary Mixture
$\dot{E}$	Evaporation Rate of Free Water
F	Force
$H(X)$	Heaviside Function
J	Moisture Flux
K	Intrinsic Permeability
K_c	Ratio of Hydration Products in Cement Mortar or Concrete
K_G	Relative Permeability of Gaseous Phase Through Dry Hardened Cement Paste and Concrete
$\tilde{M}_A$	Mass of Air in Unit Volume of Binary Gas Mixture
$M_{an,T}$	Percentage of Mass Remaining in Analytical TGA Result
$M_{ex,T}$	Percentage of Mass Remaining in Experimental TGA Result
$M_{cem,T}$	Mass of Cement Powder Subjected to Elevated Temperature
$M_{bind,T}$	Mass of Hardened Cement Paste Subjected to Elevated Temperature
$\tilde{M}_G$	Mass of Gas in Unit Volume of Binary Gas Mixture

M_L	Mass Concentration of Liquid
0M_L	Initial Mass Concentration of Liquid
$\tilde{M}_V$	Mass of Vapour in Unit Volume of Binary Gas Mixture
$\tilde{M}_{V,\infty}$	Mass of Vapour in Unit Volume of Surrounding Gas
P	Pressure
P_G	Pressure in Binary Gas Mixture
$P_{G,\alpha}$	Pressure in Surrounding Binary Gas Mixture
P_L	Pressure in Liquid
P_{sat}	Saturation Pressure
P_V	Pressure in Vapour
R_A	Gas Constant for Air
R_V	Gas Constant for Vapour
T	Temperature
0T	Initial Temperature
T_∞	Surrounding or Fire Temperature
T_0	Room Temperature
V_A	Volumetric Ratio of Aggregate in Mix Proportion
V_a	Volumetric Ratio of AFm Hydrate
V_{air}	Volumetric Ratio of Air in Gaseous Mixture
V_{agg}	Volumetric Ratio of Aggregate in Solid Skeleton System
$V_{B,A}$	Volumetric Ratio of Cement Mortar in Concrete
V_{bind}	Volumetric Ratio of Hardened Cement Paste in Solid Skeleton System
V_C	Volumetric Ratio of Ordinary Portland Cement in Mix Proportion
V_c	Volumetric Ratio of C-S-H Hydrate less Gel Pores
$V_{c,nor}$	Volumetric Ratio of C-S-H Hydrate Including Gel Pores Form under Normal Cement Hydration

$V_{c,poz}$	Volumetric Ratio of C-S-H Hydrate Including Gel Pores Form under Pozzolanic Reaction
V_G	Volumetric Ratio of Gas
V_{hyd}	Volumetric Ratio of Hydration Products Less Gel Pores for Hardened Cement Paste
$V_{hyd,B}$	Volumetric Ratio of Hydration Products Less Gel Pores for Cement Mortar
V_L	Volumetric Ratio of Liquid
V_P	Volumetric Ratio of Pozzolana in Mix Proportion
V_p	Volumetric Ratio of Calcium Hydroxide
V_{pore}	Volumetric Ratio of Pore in Hardened Cement Paste
V_S	Volumetric Ratio of Sand in Mix Proportion
V_{sand}	Volumetric Ratio of Sand in Solid Skeleton System
V_{skel}	Volumetric Ratio of Solid Skeleton in Hardened Cement Paste
V_u	Volumetric Ratio of Unreacted Cement Powder
V_{vap}	Volumetric Ratio of Vapour in Gaseous Mixture
V_W	Volumetric Ratio of Water in Mix Proportion
W_n	Moisture Content
W_e	Mass of Non-Evaporable Moisture
a	Permeability
d	Pore Diameter
d_{cr}	Threshold Diameter
e	Emissivity of Boundary Surface
g	Acceleration Due to Gravity
h_{qr}	Combined Convective and Radiation Heat Transfer Coefficient
h_q	Convective Heat Transfer Coefficient
h_r	Radiation Heat Transfer Coefficient
k	Thermal Conductivity

k_a	Volumetric Ratio of Moisture in AFm Hydrate
k_c	Volumetric Ratio of Moisture in C-S-H Hydrate
k_p	Volumetric Ratio of Moisture Calcium Hydroxide
m_{gw-rel}	Mass of Released Gel Water
m_{nw-rel}	Mass of Released Chemically Bound Water
n	Direction Normal to Mass Convection
n_0	Initial Porosity for Hardened Cement Paste
$n_{0,B}$	Initial Porosity for Cement Mortar
$n_{0,gel}$	Initial Gel Pores
n_{cap}	Capillary Porosity
n_T	Porosity Subjected to Elevated Temperature for Hardened Cement Paste
$n_{T,B}$	Porosity Subjected to Elevated Temperature for Cement Mortar
$n_{T,C}$	Porosity Subjected to Elevated Temperature for Concrete
$n_{T,cap}$	Capillary Pores Subjected to Elevated Temperature
$n_{T,gel}$	Gel Pores Subjected to Elevated Temperature
$n_{T,moist}$	Calculated Porosity Subjected to Elevated Temperature for Hardened Cement Paste using TGA Results
q	Heat Flux
t	Time
w	Specific Water Content
w_d	Mass of Non-Evaporable Moisture
$w_{d,T}$	Mass of Non-Evaporable Moisture At Elevated Temperature
α	Degree of Hydration
α_A	Thermal Diffusivity of Air
β	Mass Convection Coefficient
ε_g	Volume of gaseous mixture in Unit Volume of Concrete
ε_l	Volume of free water in Unit Volume of Concrete

ε_s	Volume of Solid Skeleton in Unit Volume of Concrete
λ_d	Specific Heat of Dehydration of Chemically Bound Water
λ_e	Latent Heat of Evaporation of Free Water
ρ_A	Mass Concentration of Dry Air
$\rho_{a,w}$	Density of Moisture in AFm Hydrate
$\rho_{c,w}$	Density of Moisture in C-S-H Hydrate
ρ_{cem}	Mass of Anhydrous Cement per Unit Volume of Concrete
ρ_{con}	Density of Concrete
ρ_{fw}	Density of Free Water
ρ_G	Specific Weight of Gas Mixture
ρ_L	Density of Water
$\rho_{p,w}$	Density of Moisture in Calcium Hydroxide
ρ_V	Mass Concentration of Dry Air
ρC	Overall Specific Heat Capacity
$(\rho C)_A$	Specific Heat Capacity of Air
σ	Stefan-Boltzman constant
σ_c	Compressive Strength
σ_T	Tensile Splitting Strength
$\sigma_{T,T}$	Elevated Temperature Tensile Splitting Strength
σ_T'	Tensile Stress
γ	Surface Tension of Mercury
φ	Contact Angle of Mercury
v	Migration Velocity
v_G	Migration Velocity of Gaseous Mixture
v_L	Migration Velocity of Free Water
μ_L	Dynamic Viscosity of Water

Chapter 1: Introduction

1.1 Background

Concrete is a widely used construction material. It can be found in most of the residential, industrial and military structures. The excellent structural performance of concrete makes it a suitable material to be used in slabs, beams and columns in a building. However, structural performance of concrete deteriorates in the presence of elevated temperature. Elevated temperature can exist in various forms from extreme heat in a nuclear reactor to industrial fire.

Rapid heating of concrete can lead to spalling. Spalling of concrete is a phenomenon whereby pieces of concrete break off from the surface of concrete element. There are many concerns with the integrity of reinforced concrete elements with regards to the occurrence of spalling. A weak plane of bond typically occurs at the interface of the reinforcement steel and concrete cover. The purpose of the concrete cover is to act as a thermal insulator for the reinforcement steel. When spalling occurs, layers of concrete are removed from the surface of the concrete element and the reinforcement steel will be exposing to direct heat. The heated bars will experience a rapid reduction in its load bearing capacity which may cause the concrete element to fail (Ali *et al.*, 2001; Bailey, 2002; Chan *et al.*, 1999; Dotreppe *et al.*, 1996; Kalifa *et al.*, 2000; Khoury, 2002).

Many researchers (Anderberg, 1997; Bazant and Thonguthai, 1979; Consolazio *et al.*, 1998; Harada and Terai, 1997) concluded that the occurrence of spalling is largely due to presence of moisture in concrete and high rate of heating. The effect of moisture and rate of heating on spalling is two fold. Firstly, the high moisture content delays the rate of heat transfer resulting in high thermal stresses within the affected concrete element. High rate of heating can also increase the temperature gradient and subsequently thermal stresses. Secondly, moisture in hardened concrete evaporates and become steam to fill the pores in hardened concrete. High rate of heating can increase the rate of moisture release within the heated concrete. Pressure starts to build up when the steam

generation is greater than steam migration. When pressure exceeds the tensile strength of concrete, spalling occurs.

Researches were conducted to quantify spalling. Some researchers (Chan *et al.*, 1999; Khoury, 1992; Sullivan, 2001) made use of compressive strength of concrete to quantify spalling. They concluded that spalling is more prominent in High Strength Concrete (HSC) than Normal Strength Concrete (NSC). This approach of quantifying spalling is accepted by practicing engineers as they prefer to use compressive strength of concrete to address problems. There are two problems when associating compressive strength with spalling. Firstly, compressive strength of concrete is a mechanical property derived from the microstructure of hardened concrete. Having similar compressive strength does not necessarily relate to similar microstructure. The microstructure can be very different with the inclusion of other minerals such as pozzolanas into the mix proportion. Spalling should be referenced from the microstructure of concrete rather from the mechanical properties of concrete. Hence, relating spalling with compressive strength of concrete is inadequate and can be misleading.

The second problem is related to the definition of HSC and NSC. The definition of HSC given by ACI Committee 363 in 1992 is concrete having a design compressive strength greater or equal to 41 MPa. Hence, it can be deduced that NSC refers to concrete having a design compressive less than 41 MPa. As time progresses, such definition of HSC and NSC will be invalid as the compressive strength of concrete is increasing. Other researches also have different interpretation of HSC and NSC. This makes the comparison of experimental results difficult as the definition of HSC varies between countries and time line.

There are also some difficulties in predicting the isotherm in heated concrete. The use of Fourier's Law of heat conduction is inadequate as the microstructure of concrete changes when heated. Moisture that is released during heating is found to delay the heat transfer process (Huang *et al.*, 1996), resulting in high thermal gradient within heated concrete. Therefore, mass transfer of moisture within the heated concrete should also be considered when predicting the temperature gradient within heated concrete.

Furthermore, the presence of moisture increases the pore pressure in heated concrete. The magnitude of pore pressure would be dependent on the volume of pores and rate of moisture migration. The behaviour of pore widening should also be investigated. An understanding on the behaviour of moisture release and pore widening is necessary to facilitate the modelling of isotherm and pore pressure within heated concrete. However, experimental results of the dehydration function of chemically bound moisture and pore widening for various types of concrete, in particular blended cement concrete are scarce. Hence, the proposed approach to predict moisture release and pore widening should be established from the microstructure instead of compressive strength of concrete.

Efforts were also made to reduce the occurrence of spalling. Design guides gave recommendation on the reduction on the risk of spalling. For instance, design guides (BS 8110: Part 2: Section 4.1.6, 1985; FIP/CEB Report, 1978) mentioned that concrete with moisture content less than 2% will have a significant reduction in the risk of explosive spalling. Such guide lines are not applicable to concrete placed in humid area such as in Singapore. Moisture content of test specimens used in this research was as high as 8.6%, indicating high possibility of spalling which is impractical. Furthermore, the use of one parameter to govern the occurrence of spalling is too simplified. Other approaches should be developed to suit local conditions and various mix proportions. The latest draft of Eurocode also mentioned the use of polypropylene fibres (minimum of 2.0 kg/m^3) to reduce the occurrence of spalling. However, placing of polypropylene fibres into concrete will only benefit new concrete structures. Proposed approach should also be applicable to existing concrete structures.

To summarise, the present modelling technique used in the heat and mass transfer in concrete is inadequate. The generalisation of HSC being more prone to spalling should be better understood. Researches should be conducted on determining the dehydration profile of chemically bound moisture and pore widening within heated concrete. Current guide lines given in design codes are not applicable to concrete structure placed in tropical areas. Prediction of spalling in concrete should be verified using hardened cement paste before applying it to concrete. This is because the effects of sand and

aggregate are removed from hardened cement paste, resulting in a fairly homogeneous material. The following section will define the scope of the investigation.

1.2 Objective and Scope of Research

The objective of this research is to investigate the effects of microstructural change in hardened cement paste due to elevated temperature on heat and mass transfer and tendency of spalling. Prediction of the temperature profile will be compared with experimental data. The methodology to extend the proposed models from hardened cement paste to concrete will also be provided. The scopes of the research are as follows:

1. To study the effects of temperature on microstructure of hardened cement paste which includes moisture release, porosity and pore size distributions
2. To determine the microstructure of hardened cement paste of different mix proportions using hydration model for modelling of non-evaporable moisture loss and behaviour of porosity subjected to elevated temperature
3. To develop a model to analyse spalling using microstructure approach
4. To predict the tendency of spalling by integrating proposed non-evaporable moisture release and porosity into heat and mass transfer simulation
5. To develop a computer program to perform the heat and mass transfer simulation and to verify the results of simulation with experimental temperature profile
6. To perform a parametric analysis using the resultant microstructure to validate current methods of quantifying spalling

Material behaviour and properties are examined at various temperatures. Five types of hardened cement paste cast from different water/cement ratio were tested for moisture loss, porosity and unheated compressive strength. Temperature profiles within 150 x 150 x 150 mm cubes and 150 mm diameter cylinders during heating were collected and used to verify the proposed heat and mass transfer simulation.

1.3 Organisation of Report

This thesis consists of nine chapters and three appendices.

Chapter 2 presents a literature review on the microstructure of hardened cement paste followed by mechanical properties and behaviour of concrete at elevated temperature. Mechanism of spalling and parameters affecting spalling are also discussed in this chapter.

Chapter 3 describes the experimental program including methodology, casting and testing of various types of specimens. Thermogravimetric Analysis (TGA) and Mercury Intrusion Porosimetry (MIP) are used to evaluate the microstructure of hardened cement paste.

Chapter 4 presents the test results obtained from experiments. Temperature measurements on specimens with different moisture content are also investigated.

Chapter 5 describes a model to predict non-linear non-evaporable moisture loss in hardened cement paste when subjected to elevated temperature. Experimental results from TGA are used for this procedure. Comparisons between predicted and experimental results are also conducted.

Chapter 6 introduces a model to predict porosity of hardened cement paste at elevated temperature. The model is able to predict porosity of different mix proportion including blended cement paste. Results from MIP are used to develop the model.

Chapter 7 presents a non-linear transient model to predict temperature and gas pressure distribution in heated hardened cement paste. Non-evaporable moisture loss and behaviour of porosity at elevated temperature which is specific to different mix proportion are used in the model.

Chapter 8 validates the proposed heat and mass transfer model proposed in Chapter 7 using experimental temperature profile. A model develop in Matlab is used to solve the

proposed model. Sensitivity analyses are also conducted to determine the effects of different water/cement ratio, inclusion of pozzolana, degree of hydration and types of cement on temperature and gas pressure. The improvement of using non-linear non-evaporable moisture loss on heat and mass transfer is also discussed.

Chapter 9 summarises the main findings of this research. Recommendations for future work are also included.

Appendix A shows the mix proportion and reported porosity after subjecting to elevated temperature. The data are used to verify the proposed model to predict porosity subjected to elevated temperature.

Appendix B presents the formulation and equations used to determine the microstructure of hardened cement paste that is used in the proposed models.

Appendix C provides the finite element formulation for the heat and mass transfer equations used in Chapter 7. The mathematical procedure to simplify the governing equations for heat and mass transfer into a suitable form for finite element analysis is also provided.

Chapter 2: Literature Review

2.1 Overview

The approach of this research is to relate microstructure of hardened cement paste with heat and mass transfer and spalling instead of using mechanical properties such as compressive strength. Hence, the literature review will summarise works relating to microstructure of hardened cement paste, mechanical properties subjected to elevated temperature, mechanisms of spalling, experimental investigations and numerical models for heat transfer and pore pressure development.

2.2 Definition of Terms

In the following sections, the details on the chemical composition, phase composition and development of the hydration products will be presented. This is an important topic as it provides a mean of determining the preheated chemical composition in hydrated cement paste. Before proceeding to the following sections, there is a need to clarify the terms which will be presented later. In the field of cement research, cement chemists prefer to use shortened notation to describe individual oxide and water in hydrated cement by a single letter. Table 2.1 shows various oxides and the corresponding letter.

Table 2.1: Oxide and Corresponding Letter

	Oxide	Letter
Calcium Oxide	CaO	C
Silicon Dioxide	SiO ₂	S
Aluminium Oxide	Al ₂ O ₃	A
Ferric Oxide	Fe ₂ O ₃	F
Magnesium Oxide	MgO	M
Sodium Oxide	Na ₂ O	N
Water	H ₂ O	H

Table 2.2 shows the resulting abbreviation of the major compounds of Ordinary Portland Cement (OPC) when the shortened notation is used (Neville, 1996). The abbreviation is used to represent a group of silicates and not a particular type of silicate.

This is because pure compounds in cement are rare and they often contain small quantity of other oxide in the mix.

Table 2.2: Abbreviation of Compounds

Name of Compounds	Oxide Composition	Abbreviation
Tricalcium Silicate	$3\text{CaO}.\text{SiO}_2$	C_3S
Dicalcium Silicate	$2\text{CaO}.\text{SiO}_2$	C_2S
Tricalcium Aluminate	$3\text{CaO}.\text{Al}_2\text{O}_3$	C_3A
Tetracalcium Aluminoferrite	$4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$	C_4AF

Another term that needs to be differentiated would be normal or blended hardened cement paste. The constituents of blended cement paste include OPC, water and an addition of at least one or more mineral while normal cement paste consist of OPC and water only. Pozzolanas are usually mixed with OPC and water to produce concrete with enhanced properties such as high strength and high durability. Massazza (1998) defined pozzolana as an inorganic material, either natural or artificial, which harden in water when mixed with calcium hydroxide or with materials that can release calcium hydroxide such as OPC. Hence, pozzolanic reaction refers to the chemical reaction between pozzolana and calcium hydroxide. Some pozzolanas that are commonly used in mix proportion are Fly Ash (FA), Ground Granulated Blastfurnace Slag (GGBS) and Silica Fume (SF).

2.3 Constituents of Mortar and Concrete

There are generally three types of materials that can be produced using OPC namely 1) hardened cement paste, 2) cement mortar and 3) concrete. The difference between them lies in the constituents that are added during mixing. Figure 2.1 shows the schematic of the various types of cement-based materials. The inclusion of sand and aggregates does not affect the normal cement and pozzolanic reactions. However, water content of sand and aggregates must be determined and considered as part of total water added during mixing.

Figure 2.1: Schematic of Various Types of Cement-Based Materials

Water/cement ratio (w/c) is often used to describe the mass ratio of water and cement per unit volume of hardened cement paste used in mixing. If sand or aggregates are included, hardened cement paste will act as cement binder to hold the additional inclusions together to form concrete.

2.4 Microstructure of Normal Cement Paste

2.4.1 Chemical Composition of OPC

Cement is unlike any other material such as metal. Metal is usually made up of a single mineral and some impurities. Impurities can be removed and metal of high purity of up to 99.999% can be obtained. Since metal is made up of a single mineral, mechanical properties and behaviour are generally assumed to be isotropic in nature. The chemical composition of cement is closer to a composite material such as alloy. Alloys are obtained by mixing various minerals of different portions in liquid state. They inherit characteristic which comes from the minerals that are added to the mix.

Table 2.3: Typical Range of Chemical Composition of OPC

Oxide	Content (% wt)
<i>CaO</i>	60 – 67
<i>SiO₂</i>	17 – 25
<i>Al₂O₃</i>	3 – 8
<i>Fe₂O₃</i>	0.5 – 6.0
<i>MgO</i>	0.5 – 4.0
<i>Na₂O</i>	0.3 – 1.2
<i>SO₃</i>	2.0 – 3.5

Hardened cement paste on the other hand is slightly different from metallic alloy. Ingredients such as clay and chalk of various portions are grinded and mixed at high temperature. Clinkers are formed in high temperature through total or partial fusion. As a result, the chemical compositions of the clinkers are different and non-homogeneous. Cement is obtained by grinding the clinkers into a fine powder. Typical chemical composition of cement (Neville, 1996) is shown in Table 2.3. The percentage of mass of the individual oxides can be obtained using titrimetric methods or X-Ray Fluorescence (XRF) spectroscopy analysis.

Both cement and alloy at this stage are finished product of mixing. However cement has to undergo a chemical reaction stage before it can be used as a construction material. In recent years, the use of blended cement is gaining popularity. Additional mineral additives such as SF (high in SiO_2) are added to OPC. The chemical composition is modified and affects the volume of the various hydration products in hardened cement paste. This will be discussed in the later section.

2.4.2 Phase Composition of OPC

A 'phase' is used to describe any compounds within a system that is physically homogeneous and bounded by a surface so that it is possible to separate it from other parts of the system (Macphee and Lachowski, 1998). Four types of compounds have been identified in OPC as listed in Table 2.2. Phase composition of OPC is used to calculate the volumetric ratio of hydration products. The probable quantity of four main compounds can be calculated using Bogue's Equations as given in Equations (2.1) to (2.4) (Lawrence, 1998). The terms in brackets refer to the percentage of total weight of the respective oxide in cement powder. Minor oxide compounds are ignored.

$$C_3S = 4.071(CaO) - 7.600(SiO_2) - 6.718(Al_2O_3) - 1.430(Fe_2O_3) - 2.852(SO_3) \quad (2.1)$$

$$C_2S = 2.867(SiO_2) - 0.7544(C_3S) \quad (2.2)$$

$$C_3A = 2.650(Al_2O_3) - 1.692(Fe_2O_3) \quad (2.3)$$

$$C_4AF = 3.043(Fe_2O_3) \quad (2.4)$$

However, this set of equations do not produce very accurate results especially for alite (an impure form of C_3S) and belite (an impure form of C_2S) (Lawrence, 1998). Experimental investigation using X-Ray Diffraction method (XRD) shows that the percentage of alite is greater than the calculated C_3S obtained from the Bogue's Equations while belite is less than the calculated C_2S . The discrepancy lies in the assumption that all the chemical compounds in the heated clinker are completely crystalline and no glass or amorphous compound are formed during cooling. This is not true in modern cement manufacturing as the clinkers are cooled rapidly. But nevertheless, Bogue's Equations are still widely used.

2.4.3 Models to Predict Hydration Products

2.4.3.1 Powers's Model (1958)

Powers is a pioneer in the research of the microstructure development of cement paste. He investigated the quantity of evaporable and non-evaporable water in hydration products of completely hydrated cement, water absorption characteristics and specific volume measurement before arriving to the classical model on the fractional volume of cement paste. His research work on the microstructure model was developed based on w/c and the degree of hydration (α).

Table 2.4: Powers's Model

Fractional Volume	Formula
Cement Gel	$\frac{0.68\alpha}{(w/c) + 0.32}$
Gel Pores	$\frac{0.19\alpha}{(w/c) + 0.32}$
Capillary Pores	$\frac{(w/c) - 0.36\alpha}{(w/c) + 0.32}$
Unhydrated Cement	$\frac{0.32(1 - \alpha)}{(w/c) + 0.32}$
Total Pores	$\frac{(w/c) - 0.17\alpha}{(w/c) + 0.32}$
Empty Capillary Pores	$\frac{0.0575\alpha}{(w/c) + 0.32}$

He assumed that the microstructure comprises mainly of 3 components: 1) unreacted OPC, 2) calcium silicate hydrate (C-S-H) gels and 3) capillary pores. The fractional volume of the major hydration products and pores in the microstructure of hardened cement paste can be obtained from the sets of equations given in Table 2.4. The pores in the system can be further refined into capillary and gel pores. Capillary pores are pores created by previously water filled space after expansion of hydration products. They have a nominal diameter of 1300 nm but the majority has a diameter of 100 nm. Gel pores are pores within C-S-H gel and have a porosity of 28%. Other assumptions made in the model include mass of non-evaporable water is 23% of mass of anhydrous cement, specific gravity of anhydrous cement is 3.15 and the increase in volume of hydrated cement is 0.746 (1-0.254) of mass of anhydrous cement. The nominal diameter is 2 nm to 3 nm which is 1 order of magnitude more than the water molecule. The different types of pores can be represented in Figure 2.2 (Neville, 1996). The C-S-H gel particles are represented as dark spots while the gel pores are the interstitial spaces. Capillary pores are represented with spaces marked 'C'.

Figure 2.2: Simplified Model of Paste Structure (Powers, 1958)

Its simplicity in calculation made it popular for the past 50 years. The model is not without limitations. Firstly, it ignores the variation in chemical and phase composition of the cement mix. With the introduction of additional minerals into the cement, the chemical and phase composition would be modified. The blended cement mix would differ a little if not greatly from the OPC Powers had investigated. Lastly, it does not distinguish the individual volume of the hydration products mainly C-S-H gel and calcium hydroxide. Without an understanding of the individual volume of the hydration

products, it would be difficult to quantify the roles of individual hydration products when they are subjected to elevated temperature.

2.4.3.2 Jennings and Tennis's Equations (1994)

The $CaO - Al_2O_3 - Fe_2O_3 - SiO_2$ system is of most relevance to cement as it constitutes 90-95% of the composition in Portland cement (Table 2.3). Therefore, the chemical reaction of the major compound of cement mainly C_3S , C_2S , C_3A and C_4AF will govern the rate of hydration and quantity of hydration products. The hydration products formed during hydration of OPC are chemically similar with the hydration products formed during the reaction of individual compounds with water (Odler, 1998). It must be noted that due to the complexity of the reaction, the process of hydration of each compound will influence and interact with other reactions.

$$1 \quad 1.34 \quad 1.521 \quad 0.61$$

$$1 \quad 1.49 \quad 2.077 \quad 0.191$$

$$1 \quad 2.42 \quad 1.05 \quad 4.40$$

$$1 \quad 5.07 \quad 2.27 \quad 7.656 \quad 0.364$$

Jennings and Tennis (1994) expressed the chemical reaction of OPC with water using Equations (2.5) to (2.8). The three main hydration products are AFm hydrate, C-S-H hydrate and calcium hydroxide. This set of equations is widely used in cement hydration model (Bentz *et al.*, 1996; Ji, 2003). The numbers indicated below the compounds refers to the volume stoichiometry (approximate) derived from saturated samples using Table 2.5. The chemical reactions of the compounds are exothermic which means that thermal energy is released during the chemical reactions.

Table 2.5: Physical Properties of Cementitious Materials

Compound Name	Compound Formula	Density (kg/m ³)	Molar Volume (10 ⁻⁵ m ³ /mol)
Alite	C_3S	3150	7.24
Belite	C_2S	3280	5.24
Aluminate	C_3A	3030	8.29
Ferrite	C_4AF	3730	13.03
Water	H_2O	1000	1.80
Gypsum	$\bar{C}\bar{S}H_2$	2320	7.41
Calcium Hydroxide	CH	2242	3.31
AFm, saturated	$C_4\bar{A}\bar{S}H_{14}$	1900	34.6
AFm, D-dried	$C_4\bar{A}\bar{S}H_8$	2400	22.9
C-S-H, saturated	$C_{3.4}S_2H_8$	1760	25.9
C-S-H, D-dried	$C_{3.4}S_2H_3$	2860	12.8

Equations (2.5) to (2.8) will be used in this research to determine the volumetric ratio of the hydration products. Jennings and Tennis's equations overcome one of the limitations in Powers's model which is ability to provide information on the volume of AFm, C-S-H gel and calcium hydroxide which is lumped in Powers's model. This refinement is necessary if any model is going to incorporate the effects of pozzolana.

2.4.4 Degree of Hydration

Degree of hydration (α) is defined as the ratio of amount of cement reacted to the total amount of cement used in mixing. It is a parameter commonly used to determine the volume of hydration products formed using either Powers's model or Jennings and Tennis's equations. Hydration products are not formed instantly when water is added to OPC. Instead, the volume of hydration products formed is rapid initially and the rate slowly decays to zero. The rate of hydration is dependent on chemical composition, particle size distribution, water available for curing and curing temperature (Ji, 2003; Kim *et al.*, 1998; Koenders and Breugel, 1997; Neville, 1996).

α can be determined through the use of either qualitative or quantitative analysis of experimental results. A qualitative approach is to correlate α with the ratio of the compressive strength of hardened cement paste with the compressive strength of

hardened cement paste that can attain over a long period of time (Bagel, 1998). α is directly proportional to the volume of hydration products form during cement reaction. The hydration products (in particular the C-S-H gel) contribute to the strength of the cement. Hence, assessing the gain in compressive strength will give an indication on α . Another technique of determining α qualitatively is to measure the amount of heat released during the hydration process. This is possible as the chemical reactions are exothermic in nature and large energy dissipation would indicate completion of cement reaction.

A commonly used method of determining α quantitatively is to measure the mass of non-evaporable moisture remaining in the hydrated cement particle. Non-evaporable moisture is taken as the mass loss in hardened cement paste between 105 °C and 1050 °C (Lam *et al.*, 2000; Pinto *et al.*, 2000). Researchers (Ji, 2003; Weber and Reinhardt, 1997) commonly assume that hydration is completed after a year being mixed. This is because complete hydration of cement could take years. Hence, non-evaporable moisture at a year is then used as a benchmark to determine α in other specimens of similar cement mix. α is calculated by taking the ratio of the mass of non-evaporable moisture to the mass of non-evaporable moisture after a year of curing. It is important to note that complete hydration may not occur for cement paste of a low w/c. Powers and Brownyard (1946) demonstrated that a minimum w/c of 0.38 is required to ensure complete hydration in cement paste. Capillary pores within the cement paste will be reduced to zero and there are no unhydrated cement particles. This condition can only be achieved if there is sufficient water for hydration to occur.

2.4.5 Pore Structure

Pores are voids within hardened cement paste. They are the space where water is previously filled during mixing with OPC less volume of expansion in cement particle. Porosity is commonly used to indicate the percentage of pores within the material. They are often determined from experiments and are related with the compressive strength of concrete (Ji, 2003; Lam *et al.*, 2000; Neville, 1996; Poon *et al.*, 2001; Taylor, 1990) and permeability (Breyssse and Gerard, 1997; Ollivier *et al.*, 1996). The relationship between

capillary porosity, curing duration and w/c is presented in Figure 2.3a (Ji, 2003). Capillary pores generally decreases as hydration progress. However, gel pores are observed to increase as hydration progresses as they are formed together with C-S-H gel (Figure 2.3b). The sum of the two types of pores corresponds to porosity of hardened cement paste.

Figure 2.3: Porosity at Various Curing Duration (Ji, 2003)

Porosity is commonly measured using Mercury Intrusion Porosimetry (MIP). The principle behind the test is to measure the volume of mercury injected into the specimens. Equation (2.9) is the well-known Washburn equation that is used to relate the pressure (P) with pore diameter (d). γ and ϕ are surface tension taken as 485 dyne/cm at 20 °C and contact angle taken as 130° respectively.

$$d = -\left(\frac{1}{P}\right)4\gamma \cos \phi \quad (2.9)$$

The key limitation of the Washburn equation is the assumption that all pores are cylindrical in geometry. It has been observed that this assumption is not true in other investigations (Cook and Hover, 1999; Diamond, 2000). Some other known limitations include ink-bottle effect and incomplete measurement of gel pores. Ink-bottle effect misallocates the pore size within hardened cement paste. This results in difficulties in comparing pore size distributions amongst other specimens. Incomplete measurement of

gel pores is expected as it can be deduced from Equation (2.9) that the test apparatus is required to generate an infinite pressure in order to cover the entire range of pore diameters which is unattainable with existing technique (Cook and Hover, 1999; Ji, 2003; Moro and Bohni, 2002).

2.5 Microstructure of Blended Cement Paste

2.5.1 Chemical Composition of Pozzolanas

The cost of cement making (including grinding of clinker) is a very expensive process. Environmental awareness promotes the use of industrial by-products in the manufacturing of concrete to reduce the amount of waste which requires disposal. The most common by-products used in the manufacturing of blended cement concrete are FA, GGBS and SF. These materials possess some or no cementitious properties when mixed with water. Instead, they react with calcium hydroxide produced during the hydration of OPC and water to produce additional C-S-H gels (Bentz and Remond, 1997; Xu *et al.*, 2001).

FA is generally produced when the exhaust gases of coal-fired power plant precipitate either electrostatically or mechanically to form spherical particles. FA is classified into a few categories with different chemical composition. There are 2 broad groups in the classification used in ASTM C 618-94a. Class F and Class C FA refers to ash derives from bituminous coal (high in silicon oxide) and ash derives from sub-bituminous coal and lignite (high in lime) respectively. GGBS is a by-product in the manufacture of pig iron. The chemical composition can be reasonably consistent or varied to a great extent due to the different process used to cool the slag. SF exists in the form of extremely fine spherical particles as the result of the oxidation of SiO gas to produce SiO_2 . SiO is released during the manufacturing of silicon or silicon alloy. The chemical composition of silica fume tends to be relatively stable as it is the by-product of a highly-purified material. Due to the extreme fineness of SF particles, they are often condensed into pellets for ease of handling.

Table 2.6: Chemical Compositions and Physical Properties of OPC & Pozzolanas

	OPC	FA	GGBS	SF
SiO ₂	20.7	44.9	34.4	94.0
CaO	64.4	5.7	44.8	0.3
Al ₂ O ₃	5.4	35.4	9.0	0.3
Fe ₂ O ₃	2.3	4.9	2.58	0.8
MgO	0.9	1.2	4.43	0.4
Na ₂ O	0.13	1.0	0.62	1.0
K ₂ O	0.4	1.0	0.5	-
SO ₃	2.4	0.7	2.26	0.2
L.O.I.	0.97	5.6	1.32	2.8
Specific Gravity	3.1	2.1	2.79	2.2
Specific Surface Area (m ² /kg)	355	528	599	20,000
Average Particle Size (μm)	14	5.41	3.59	0.1
Glass Phase (%)	-	55	90	96
Diffusion Rate (μm ² /hr)	-	0.0100	0.0150	0.0457

Table 2.6 shows the comparison of the chemical compositions and physical properties between OPC and the various pozzolana reported by various researchers (Ji, 2003; Li and Zhao, 2003; Neville, 1996; Taylor, 1990). A noticeable difference between the 3 pozzolanas is the percentage of SiO_2 , CaO and Al_2O_3 . The chemical composition of FA is dependent on the place of origin and could either be high in silicon oxide or lime. GGBS have approximately the same constituents with cement except for some difference in the amount of constituents. Since SF is obtained through the oxidation of SiO gas, the major constituent in SF should be silicon oxide.

2.5.2 Hydration Products

Pozzolana does not react immediately with water. Instead, they react with calcium hydroxide ($Ca(OH)_2$) produced in the hydration process to produce another variant of C-S-H gel which is of a lower C/S ratio when compared with the C-S-H gel produced from the hydration of cement which is of a higher C/S ratio. Since the C-S-H gel produced by cement and pozzolana are different, the total quantity of the C-S-H gel will have to be determined separately. Bentz and Remond (1997) published chemical

reactions and volume stoichiometry for pozzolana and are presented below as Equation (2.10) and (2.11).

AS and C_2ASH_8 is known as aluminosilicate and stratlingite respectively. Besides the usual C-S-H gel that is produced, an additional product known as C_2ASH_8 is formed when high lime fly ash is formed. However, if gypsum is added to the cement mix, C_2ASH_8 gradually decreases and disappears after 60 days.

An observation was made with regards to the quantity of $Ca(OH)_2$ by mass in blended cement paste. Table 2.7 shows the $Ca(OH)_2$ content of normal and FA blended cement paste over a period of time (Xu *et al.*, 2001). OPC will continue to hydrate to produce $Ca(OH)_2$ as time progress. On the other hand, the amount of $Ca(OH)_2$ decrease in the long run due to the pozzolanic reaction of FA with $Ca(OH)_2$. This is due to the continuation of chemical reaction between $Ca(OH)_2$ and unreacted FA residing within the cement matrix. The rate of decrease in $Ca(OH)_2$ gives an indication on the rate of hydration of pozzolana.

Table 2.7: $Ca(OH)_2$ Content of Normal and FA Blended Cement Paste (Xu *et al.*, 2001)

w/b	Fly Ash Replacement (%)	$Ca(OH)_2$ Content (%)		
		7 days	28 days	90 days
0.3	0	11.8	12.55	12.83
	25	9.08	8.84	6.98
	55	5.50	4.05	3.03
0.5	0	15.32	14.79	15.78
	55	6.83	4.79	3.30

2.6 Properties of Concrete at Elevated Temperature

Much emphasis was placed on determining the mechanical properties of concrete at elevated temperature as it governs the structural behaviour under fire. Works were conducted on the microstructure of concrete but rarely incorporated in structure analysis.

2.6.1 Microstructure Behaviour of Hardened Cement Paste

Hardened cement paste starts to degrade when exposed to elevated temperature. The decomposition of hydration products in hardened cement paste when exposed to elevated temperature can be summarised as shown in Table 2.8 (Bazant and Kaplan, 1996; dos Santos *et al.*, 2002; Lin *et al.*, 1996; Peng *et al.*, 2001; Saad *et al.*, 1996). Microstructural change in heated hardened cement paste is accompanied with mass loss and increase in porosity (Harmathy and Allen, 1973; Hilsdorf, 1967; Khoury, 1992). The range of temperature for the decomposition of C-S-H gel and $Ca(OH)_2$ is large. This is probably due to the different chemical composition within cement powder, mix proportions, percentage replacement of pozzolana and rate of heating in the specimens.

Table 2.8: Decomposition of Hydration Products at Elevated Temperature

Temperature (°C)	Event
100 – 105	water evaporation occurs, no reduction in strength
400 - 600	decomposition of $Ca(OH)_2$, releasing lime and water vapour
400 – 850	decomposition of silicate hydrates into $\beta - C_2S$ and C_3S
720	decomposition of $CaCO_3$

2.6.1.1 Loss of Non-Evaporable Moisture

Non-evaporable moisture refers to moisture loss upon heated at temperature greater than 105 °C. This information is often used to determine the degree of hydration within hardened cement paste. Pinto *et al.* (2000) reported that the volume of non-evaporable water in the cement matrix increases with the curing age. This is due to the continuation of the hydration process of the unreacted cement particles. England and Khoylou (1995)

found that heating the concrete to constant mass at 105 °C, as much as 60% of the mixing water is loss while the remaining 40% of the mixing water remained as non-evaporable water. Similar observation was also made by Li *et al.* (1996). Non-evaporable moisture loss is reported to be non-linear (Bazant and Kaplan, 1996; Harmathy, 1993). It can be observed from both cement hydration and pozzolanic reaction given in Equations (2.5) to (2.8) and (2.10) to (2.11) that water molecules are part of the hydrate. Hence, different quantities of hydrates and calcium hydroxide will have an effect on the total non-evaporable moisture loss within hardened cement paste.

A possible error that maybe included in mass measurement at elevated temperature is the decomposition of CaCO_3 into CaO and CO_2 at approximately 720 °C. A rapid reduction in mass was observed in Thermo Gravimetric Analysis (TGA) (Harmathy, 1993). The reduction in mass due to release of CO_2 into the atmosphere does not correspond to non-evaporable moisture loss and total mass loss should be corrected to account for this error.

2.6.1.2 Porosity

Works on the behaviour of porosity at elevated temperature are scarce. The porosity measured is residual in nature which means that porosity was measured after the heated cement paste had cooled to room temperature. Researches (Bazant and Thonguthai, 1979) suggest that porosity increase is attributed to the loss of non-evaporable moisture in hydration products. Generally, residual porosity increases after subjected to elevated temperature. A comprehensive study on the effect of various pozzolanas on residual porosity of HSC and NSC subjected to elevated temperature was performed by Poon *et al.* (2001). Various blended cement concrete specimens of size 100 mm (W) x 100 mm (H) x 100 mm (H) were heated to the targeted temperature (20 °C, 600 °C and 800 °C) at a rate of 2.5 °C/min. Unheated porosity of blended cement concrete is always less than that in normal concrete due to the dense microstructure within the cement matrix. At 600 °C, the percentage gain in porosity in ascending order is FA, SF then GGBS. However at 800 °C, the order changed to FA, GGBS and SF. Specimen with 10% SF replacement showed the greatest increase in residual porosity (570%) when compared

with the unheated specimen. This suggests that SF blended cement concrete suffered the most damage when exposed to elevated temperature while FA and GGBS blended cement concrete were found to be able to retain their properties at elevated temperature. This is due to the low unheated porosity measured in SF blended cement concrete as compared with FA and GGBS blended cement concrete.

A summary of mix proportion and residual porosity is given in Appendix A. Comparison between experimental data proves difficult due to the different mix proportion and heating rates used in the investigation. It is also unsure whether steady state condition (no temperature gradient) was satisfied before measuring pore volume. Such limitations should be addressed in models to predict residual porosity.

2.7 Spalling of Concrete

2.7.1 Spalling Mechanism

Currently, there are two mechanisms with regards to the occurrence of spalling. One group of researchers believes that spalling is caused by the pore pressure build up in the cement matrix while the other believes that spalling is caused due to thermal and mechanical stresses. Much debate has been going on till now and the criterion of spalling is still in the hypothesis stage.

Anderberg (1997) gave an account on spalling caused by vapour pressure. The mechanism is believed to be the same for both HPC and NSC. He defined 3 zones as illustrated in Figure 2.4 for a 1-D heating scenario: 1) dry zone, 2) vapour zone and 3) partially saturated zone. The water at the heated face starts to vaporise when temperature reaches 100 °C. A dry zone is created at the boundary of the heated face and the thickness of this layer increases rapidly in NSC than HPC. The temperature gradient rises sharply in this zone as water, being high in specific heat capacity, is vaporised and no longer exist to absorb the heat energy. Gas diffusivity is also believed to increase rapidly with temperature.

Figure 2.4: Schematic Illustration of the 3 Zones (Anderberg, 1997)

A vapour zone immediately follows behind the dry zone. It is a zone where vapour and free water coexist together. Moisture content within the vapour zone rises and obstructs the vapour to migrate into the direction of the unheated face. This phenomenon is known as “moisture clog”. Vapour pressure starts to build up within the concrete even though the vapour continues to migrate in both directions (towards the heated and unheated face). Condensation is observed in the unheated face.

A possible criterion for spalling could exist when the tensile stress due to vapour pressure exceeds the tensile strength of the concrete (Anderberg, 1997; Bazant and Thonguthai, 1979; Ichikawa and England, 2001). Anderberg (1997) also observed that spalling is progressive. Spalling will continue to occur until the tensile stress due to vapour pressure is less than the tensile strength of concrete.

Arita *et al.* (2002) believes that spalling is caused by thermal stress. He documented the observations made in his experiments. Initially, the sound of crack propagation can be heard during the first 3 to 10 minutes. Small pieces of concrete gets dislodge from the surface. Explosive spalling occurs at around 11 minute which corresponds to approximately 700 °C. A hypothesis on the mechanism of spalling due to thermal stress is made by Arita *et al.* (2002) from the observations made in his experiment. Two factors are identified that lead to spalling: 1) high density of concrete and 2) large water

content in concrete. High density concrete has a high initial vapour pressure existing within the pores. The large water content in concrete tends to delay the temperature rise within the concrete resulting in high thermal gradient across the section. This will lead to an increase in thermal stress as thermal expansion in the heated region of the concrete is restrained from expanding. When the thermal stress exceeds a threshold, a crack-split-buckling effect will cause spalling.

From both spalling mechanisms mentioned in the above, water (either evaporable or non-evaporable) does have a role to play in spalling. An investigation on the quantity of water and the rate of dehydration can provide a better insight on the cause of spalling. However, such an investigation requires the determination and understanding of the microstructure and behaviour of cement paste subjected to elevated temperature.

2.7.2 Experimental Investigations

Not many papers published experimental setup and procedures with regards to pore pressure measurement (Consolazio *et al.*, 1998; England and Khoylou, 1995; Harada and Terai, 1997; Kalifa *et al.*, 2001). Most of the experiments were designed for 1-D heating. Each procedure is unique thus making quantitative comparison of the results difficult. Harada and Terai (1997) conducted experiments to determine the temperature and pressure profile in a 40mm thick slab. The slab is orientated vertically like a wall with an electric furnace supplying the heat conforming to ISO 834 fire curve (Figure 2.5). Steam was observed to be released from both sides of the slab and condensation occurs on the unheated face. This observation was in accordance with Anderberg's (1997) description of the spalling mechanism. Only one pressure gauge is installed in the slab making it cost effective but unable to provide the pore pressure development across the slab thickness. The slab is relatively thin (40mm) and the moisture vapour is able to be released with ease. Hence, the peak pore pressure reading of approximately 2.3 MPa is considered small. Harada (Arita *et al.*, 2002) concluded that the contribution of thermal stress to spalling is more significant than pore pressure build up within heated concrete sections.

Figure 2.5: Experimental Setup by Harada and Terai (1997)

Kalifa *et al.* (2000) conducted experiments using silica fume blended cement concrete slab of size 300 mm (L) x 300 mm (W) x 120 mm (H). Five pore pressure and temperature measuring probes were cast in the slab at depths from 10 mm to 50 mm at 10 mm intervals. A radiant panel capable of supplying up to 800 °C is placed 30 mm above from the slab as shown in Figure 2.6.

Figure 2.6: Experimental Setup by Kalifa et al. (2000)

The specimen was placed on a balance so that mass loss during heating was monitored throughout the experiment. The strength of this experiment over Harada and Terai's (1997) experiment is the ability to plot the pore pressure profile in the slab resulting from the use of five pore pressure measure probes instead of one. The slab was heated

immediately from room temperature to either 450 °C, 600 °C or 800 °C. The maximum pore pressure measurement in Grade 100 and Grade 30 concrete was 38 bar (3.8 MPa) and 18 bar (1.8 MPa) respectively.

An interesting observation was made from the above mentioned experiments. No occurrences of spalling take place when pore pressure measurements are taken. The probes inserted into the concrete slab probably act as pressure release outlets which reduces the peak pressure in the slab.

Another area where researchers paid attention was on the factors that cause spalling. Sullivan (2001) conducted a probabilistic analysis of variance on plain and reinforced concrete beam of size 50 mm (W) x 75 mm (D) x 850 mm (L) and 60 mm (W) x 85 mm (D) x 850 mm (L) respectively. The temperature in the furnace was ramped up from room temperature to 700 °C. Once the furnace attained the temperature, it is maintained for another 15 minutes before the power is switched off. He observed that explosive spalling took place between 27 and 50 minutes at 400 °C to 600 °C.

Table 2.9: ANOVA Significance for Explosive Spalling (Sullivan, 2001)

Factor	Significance (%)	
	Plain Concrete	RC
Curing	-	>90
Heating	>95	>>99
Loading	<95	-
W/C Ratio	-	>95
Aggregate	-	>>95

The results of his investigations are shown in Table 2.9. The use of statistical approach is able to show the qualitative relationship of the factors that causes spalling. Practicing engineers tends to be interested with such qualitative conclusions. However, such approach is unable to determine the true nature of spalling and an effective solution for spalling cannot be prescribed. Nevertheless, the results of this approach are able to show the future direction of research work relating with spalling. A standard testing procedure for concrete spalling can be made from his observations.

The mechanism of spalling can be classified into 2 main areas (thermal stress and pore pressure) based on the research by Anderberg (1997) and Arita *et al.* (2002). The factors that influence spalling due to pore pressure can further be broken down into two sections as shown in Figure 2.7 namely environmental and material dependent factors.

Figure 2.7: Summary of Factors Affecting Spalling

2.7.3 Modelling of Heat and Mass Transfer in Concrete at Elevated Temperature

2.7.3.1 Assumptions

Due to the technical difficulties in measuring the pore pressure in the cement matrix, there are very little experimental data with regards to the pore pressure development. However, many had developed mathematical models (Bazant and Thonguthai, 1979; Gong and Majumdar, 1995; Harada and Terai, 1997; Ichikawa and England, 2001; Khoury *et al.*, 2002; Majumdar *et al.*, 1995; Tenchev *et al.*, 2001) to simulate and predict isotherm and the pore pressure within the specimen. Most of the models are solved using the finite element method.

Common assumptions made in the models:

1. Conservation of energy and mass is maintained during heating.
2. Concrete is defined as a multiphase material. It consists of aggregate, cement, chemically bound water and gel water. When exposed to temperature, the chemically bound water and gel water are released into the capillary pores by dehydration.
3. Materials are homogeneous and isotropic. Physical properties are expressed as an effective property. Some researchers assumed constant physical properties and free from thermal effects.
4. Temperature and pressure are coupled together. Pressure is highly dependent on temperature (Ideal gas law) and by coupling them in the model, it will provide better predictions.
5. Ideal gas law is been applied to vapour. While this is not entirely true, it provides a means of determining pressure. Dalton's law is used to determine the pore pressure.
6. Mass flow rate of moisture in concrete is governed by both pressure (Darcy's law) and diffusion induced flow (Fick's law).

In addition to the above mentioned assumptions, the models proposed by researchers require the use of the International Association for the Properties of Water and Steam (IAPWS) Industrial Formulation for the Thermodynamic Properties of Water and Steam as part of the formulation. The current formulation in use is IAPWS-IF97 which supersedes ASME Steam Table.

It was mentioned in Chapter 1 that there are problems with the use of thermal properties (in particular the dehydration function) in heat and mass transfer models. Typically, researchers will measure the initial conditions of various parameters (e.g. porosity and water content) of concrete prior to the start of the experiment. These initial parameters will be used in heat and mass transfer models. The behaviour of unheated and heated cement paste was obtained from Powers and Brownyard (1946) and Harmathy and Allen (1973) respectively. The behaviour of cement paste by Powers and Brownyard (1946) and Harmathy and Allen (1973) were derived from cement paste having a

water/cement ratio of 0.4-0.5 and 0.5 respectively. The cement used in the experiments may have different chemical composition due to the different source and time of acquisition of cement. Different types of cement and mix ratio should influence the behaviour of cement paste especially non-evaporable moisture loss and porosity at heated state. Applying the above mentioned behaviour to experiments without justifications may introduce errors in the simulated isotherm and pressure contour for the specimen. A possible way of reducing such errors will be to determine the required properties and parameters on the cement paste used for the heat and mass transfer model. The chemical composition and mix proportion must be clearly stated for the cement paste being investigated.

2.7.3.2 Model by Bazant and Thonguthai (1979)

Perhaps one of the earliest heat and mass transfer models was proposed by Bazant and Thonguthai (1979). It was initially developed to evaluate the safety of nuclear vessels under accidents. The 2-equations model was developed using the conservation of mass and energy in the system. This model sets the framework for the development of future models. Equation (2.12) and (2.13) show the principal equations while Equations (2.14) and (2.15) shows the equations of various parameters.

$$\frac{\partial w}{\partial t} = -\text{div}(J) + \frac{\partial w_d}{\partial t} \quad (2.12)$$

where J , t , w and w_d refers to moisture flux vector, time, specific water content of concrete and water liberated by dehydration respectively. Equation (2.12) is derived from conservation of mass.

$$\rho C \frac{\partial T}{\partial t} - C_a \frac{\partial w}{\partial t} - C_w(J) \cdot \text{grad}(T) = -\text{div}(q) \quad (2.13)$$

where C , C_a , C_w , q , T and ρ refers to isobaric heat capacities of concrete, isobaric heat capacities of absorbed water, isobaric heat capacities of capillary water, heat flux

vector, temperature and mass density respectively. Equation (2.13) is derived from conservation of energy. J and q can be obtained using Equation (2.14) and (2.15).

$$J = -\frac{a}{g} \text{grad}(P) \quad (2.14)$$

$$q = -k \cdot \text{grad}(T) \quad (2.15)$$

where a , g , k and P represents permeability, gravity acceleration, heat conductivity and pressure respectively. Equation (2.14) is the same with Darcy's law and Equation (2.15) is the same with heat conduction.

The parameters in the model are often expressed in terms of the relative vapour pressure which is defined as the ratio of existing vapour pressure over the saturated vapour pressure determined from the ASME steam table. The model considered the effect of absorption of free water into the hydrated cement due to moisture migration. Water content in the hydrated cement will rise and affect the thermal equilibrium of the system. Distinction between saturated and non-saturated samples is required as free water will cease to exist at temperature greater than 347.15 °C which is a critical point of water. Comparison of the simulation results with the experimental results obtained by Zhukov and Shevchenko (1974) and Chapman and England (1977) showed the accuracy of the model.

The simulated results by Bazant and Thonguthai (1979) were in accordance with a hypothesis first published by Harmathy in 1965 known as the 'moisture clog'. Through experiments, Harmathy observed the formation of an oversaturated zone within heated specimen and this zone impedes moisture escape from the specimen. No detail was given on the build up of pore pressure. Bazant and Thonguthai (1979) observed a very steep downward slope of the pressure (Figure 2.8) curve within the specimen and deduced that the pressure experienced difficulties in migrating towards the unheated face of the specimen. As heating continues, the moisture being unable to migrate into the specimen creates a region of oversaturated zone. Hence, the mathematical formulation is able to show the phenomenon of "moisture clog" theoretically.

Figure 2.8: Temperature – Pressure Profile for Unsealed Wall (Simulated) (Bazant and Kaplan, 1996)

Another phenomenon called “hot spot” is introduced in the model. It refers to an extreme case of non-uniform and rapid heating along the surface of the wall such as a point source of heat applied on the surface of the wall. The 2-D model shows a pressure peak increase of 50% compared to the 1-D model. This is probably due to the increase in permeability within the small heated region and the release of vapour pressure is slow due to the narrow passage of migration. Furthermore, the trend in pressure change is more erratic and produces an oscillating time curve. This is due to the limitation of the computational algorithms and further works is needed in this area.

It should be noted that the parameters used in the model were derived from the experimental results obtained by Powers and Brownyard (1946). The cement paste used in the experiments was OPC. These parameters may require modification if the model is to be use with blended cement paste.

2.7.3.3 Model by Ichikawa and England (2001)

Ichikawa and England (2001) simulated the heat and mass flow in concrete using two equations given below as Equation (2.16) and (2.17) derived from the conservation of energy and mass. These equations are quite similar with the one proposed by Bazant and Thonguthai (1979). The predicted results from the model are in accordance with Chapman's experiment.

$$\rho_{con} C \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \quad (2.16)$$

where ρ_{con} , C , k and T are density, specific heat, thermal conductivity and temperature of concrete respectively.

$$\frac{\partial W_n}{\partial t} = \frac{\partial}{\partial x} \left(a \frac{\rho_{fw}}{\mu_L} \frac{\partial P}{\partial x} \right) + \frac{\partial}{\partial x} \left(D \frac{\partial W_n}{\partial x} \right) + \frac{\partial}{\partial t} (m_{gw-rel} + m_{mw-rel}) \quad (2.17)$$

where W_n , a , D , P , ρ_{fw} , μ_L , m_{gw-rel} and m_{mw-rel} represents the moisture content, permeability, diffusion coefficient of concrete, pressure, density, dynamic viscosity of free water, mass of released gel water and mass of released chemically bound water respectively. The terms in the right hand side of Equation (2.17) represents pressure induced flow, diffusion base flow and release of gel and chemically bound water in the order left to right.

The strength of this model is the ability to show the moving interface of moisture in concrete calculated from density of free water, density of dry saturated water vapour and density of saturated liquid water. This helps in the visualisation of the migration of moisture and the thickness of each zone. The moving interface which identifies the various zones in the concrete is similar with the spalling mechanism proposed by Anderberg (1997). Figure 2.9 shows the moisture interface across the depth of the concrete with respect to time. Free water can exist in a single phase as compressed

liquid water in a saturated zone or exist in two phases as liquid water and water vapour in a wet zone.

Figure 2.9: Moving Interface of Moisture in Concrete (Ichikawa and England, 2001)

In addition, the model is compact and simplified. It considers the movement of the water and the injection of additional water from the C-S-H gel. This two equations model is computationally efficient as the physical properties are assumed constant.

2.7.3.4 Model by Tenchev *et al.* (2001)

A more complicated model proposed by Tenchev *et al.* (2001) involves the determination of the mass flow rate of free water, dry air and vapour. A total of four equations were derived from the conservation of energy, mass of free water, mass of dry air and mass of vapour are shown as Equations (2.18) to (2.21) respectively.

$$(\rho C) \frac{\partial T}{\partial t} = \nabla(k \nabla T) - (\rho C v) \nabla T - \lambda_e \dot{E} - \lambda_d \frac{\partial}{\partial t}(w_d) \quad (2.18)$$

where ρC , k , v , λ_e , λ_d , $\dot{E}$ and w_d refer to overall specific heat, thermal conductivity, migration velocity, latent heat of evaporation of free water, specific heat

of dehydration of non-evaporable moisture, evaporation rate of free water and mass of non-evaporable moisture respectively.

$$\frac{\partial}{\partial t}(M_L) = -\nabla[M_L v_L] - \dot{E} + \frac{\partial}{\partial t}(w_d) \quad (2.19)$$

$$\frac{\partial}{\partial t}(\rho_A \varepsilon_g) = -\nabla \left[(\rho_A \varepsilon_g) v_G - D_G (\rho_G \varepsilon_g) \nabla \left(\frac{\rho_A}{\rho_G} \right) \right] \quad (2.20)$$

$$\frac{\partial}{\partial t}(\rho_V \varepsilon_g) = -\nabla \left[(\rho_V \varepsilon_g) v_G - D_G (\rho_G \varepsilon_g) \nabla \left(\frac{\rho_V}{\rho_G} \right) \right] + \dot{E} \quad (2.21)$$

where M_L , ρ_A , ρ_V , $\rho_G = \rho_A + \rho_V$, D_g , v_L and v_G refer to mass concentration of liquid, dry air, mass concentration of water vapour, specific weight of gaseous mixture, diffusion coefficient of a component in a binary mixture, migration velocity of free water and migration velocity of gaseous mixture respectively.

A strength of this model over Ichikawa and England's (2001) model is the breaking down of the components of the concrete into solid skeleton (ε_s), free water (ε_l) and gaseous mixture (ε_g). The response of volume and mass changes to elevated temperature is illustrated in Figure 2.10. This model is able to clarify some doubts in the behaviour of evaporation and migration of free water and the influence on the spatial distributions of temperature and pore pressure.

It can also be deduced from Figure 2.10 that evaporation is a major contributor in the early stages of heating while dehydration of chemically bound water is not as severe. The temperature at which evaporation takes place is 200 °C instead of 100 °C due to the high pressure in the pore. The peak of the water vapour pressure is also the evaporation front. The simulation results are in accordance with Anderberg's (1997) spalling mechanism. A sensitivity study on the influence of moisture migration is conducted. This is achieved by artificially modifying the relative permeability of the liquid phase. Simulation results shows that a low permeability indeed slows down the heat transfer process as the moisture in the region are still absorbing the heat.

Figure 2.10: Distribution Profiles of Volumic Fractions (Left) and Masses (Right)
(Tenchev *et al.*, 2001)

This model is more complex and requires high computational effort. It provides more details when compared with other models. However, Tenchev's model is unable to model saturated concrete. Saturated concrete will not have any gaseous phase and the conductance matrix will be rank deficient, which also means determinant is equal to zero. Such equations cannot be solved and improvement to his model is required.

2.8 Reported Cases of Spalling

Table 2.10 summaries the range of heating duration and temperature that spalling could occur. Most of the reported values are obtained by subjecting specimens to high heating rate. The difference in test parameters such as material, heating rate and size of specimen makes it difficult for any quantitative comparisons to be made. There is also a lack of standard protocol on defining the spalling temperature (exterior or interior). If

the temperature is obtained from the interior of the specimen, the corresponding location of the thermocouple should be stated.

Table 2.10: Temperature at which Spalling Occurs

Investigator	Specimen Shape	Dimension (mm)	Heating Duration (min)	Temperature (°C)
Ali <i>et al.</i> (2001)	Column	127 (L) x 127 (W) x 1800 (H)	5 - 22	530 - 700
Arita <i>et al.</i> (2002)	Cylinder	25 (D) x 100 (H)	11	700
Chan <i>et al.</i> (2000)	Cube	100 (W) x 100 (D) x 100 (L)	-	480 - 500
Hertz (1992)	Cylinder	100 (D) x 200 (H)	-	400*
Phan <i>et al.</i> (2001)	Cylinder	102 (D) x 204 (H)	130 - 140	500
Poon <i>et al.</i> (2001)	Cube	100 (W) x 100 (D) x 100 (L)	150 - 230	400 - 600
Sanjayan and Stocks (1993)	Beam	Varies	18	715
Sullivan (2001)	Beam	Varies	27 - 50	400 - 600

*: Location of temperature reading unknown

2.9 Methods to Reduce Spalling

Various methods were proposed to reduce the occurrence such as limit the maximum percentage of cement been replaced by SF at 15% (Khoury, 1992) or to include polypropylene fibres into the concrete mix. The use of polypropylene fibres probably received the most attention as experimental investigations (Kalifa *et al.*, 2001; Kodur *et al.*, 2003) show the effectiveness of polypropylene fibres. When polypropylene fibres melt at 170 °C, it is partially absorbed by the cement matrix and leaves behind a path of outward migration of gas which results in the reduction of pore pressure (Kalifa *et al.*, 2001). Migration of gas can only occur outward is because the temperature in the inner depths of concrete are cooler than the exposed surface and the temperature is not sufficiently high enough to melt the polypropylene fibres. No pathway is formed on the cooler face to facilitate migration of gas inwards and hence, migration of gas can only occur outwards.

Kalifa *et al.* (2001) investigated the effect of various dosages of polypropylene fibres on temperature and pressure development in concrete. An increase in the fibre dosage was found to lower the maximum pressure, temperature at maximum pressure and pressure gradient. A fibre dosage of 0.9 kg/m^3 appeared to prevent spalling. Sullivan (2001) observed that a fibre dosage of 1 to 3 kg/m^3 is capable of preventing spalling even though the specimen is 100% moist. The latest draft of Eurocode mentioned the use of polypropylene fibres (minimum of 2.0 kg/m^3) to reduce the occurrence of spalling.

There is also a lack of investigation on the heated and residual compressive strength of concrete with polypropylene fibres. Luo *et al.* (2000) commented that the use of 1.82 kg/m^3 of fibre did not cause significant reduction in residual strength when compared with the case when it was not added. The gel/space ratio decrease due to the increase in voids in the cement matrix when the fibre melts. This should lead to a reduction in the compressive strength of concrete and may affect the integrity of the building during fire. A point to note is that throughout the investigation by Kalifa *et al.* (2000), there was no occurrence of spalling.

2.10 Summary

This chapter presented the oxide composition of OPC, compound composition of OPC and various microstructure models. The strength and weakness of both Powers's model and Jennings and Tennis's Equations were discussed. The chapter further mentioned the various types of pozzolana and its hydration products. The change in microstructure which includes non-evaporable moisture loss and porosity at elevated temperature are also mentioned. Further works relating to the decomposition of the chemical composition will be extended from this chapter. It was observed that the link between microstructure and behaviour of materials are not well established and researchers are unsure of the behaviour of non-evaporable moisture loss and porosity to be incorporated into the heat and mass transfer models

Despite the different experiment procedures among researchers, some generalised conclusion can be drawn:

1. Higher exposed temperature increases the non-evaporable moisture loss and porosity.
2. High moisture content, high heating rate, high percentage of pozzolana replacement, low w/c and low permeability increases the possibility of spalling.
3. Polypropylene fibres are effective against spalling.

This research will introduce the use of microstructural parameters such as non-evaporable moisture and porosity into the numerical prediction of isotherm and pore pressure. The review of the works done by other researchers in this chapter will help in establishing experimental methodology required to complete the investigation of the microstructure and behaviour of hardened cement paste subjected to elevated temperature.

Chapter 3: Experimental Investigations

3.1 Overview

This chapter describes the details of the experiments for degree of hydration, heating procedure, non-evaporable moisture loss, pore structure and thermal measurements. The objectives of the experimental investigations were to determine the behaviour of non-evaporable moisture loss and pore widening in hardened cement paste subjected to elevated temperature. Thermal measurements will be used to verify the proposed heat and mass transfer model. Hardened cement paste was used throughout the experimental investigations in order to achieve the state of homogeneity within the specimen.

3.2 Experimental Methodology

3.2.1 Mix Proportions

Hardened cement paste of water/cement ratios (w/c) ranging from 0.28 to 0.45 were prepared. Details on the mix proportions of cement paste are given in Table 3.1. These values were selected based on the findings of various researchers (Ali *et al.*, 2001; Arita *et al.*, 2002; Phan *et al.*, 2001; Sullivan, 2001) investigating factors affecting spalling. An additional type of blended cement paste with 10% Silica Fume (SF) replacement was also investigated as it was concluded from experimental results that concrete of w/c less than 0.35 and a cement replacement of 10% by mass with SF is highly susceptible to spalling.

Table 3.1: Mix Proportions for Cement Paste

	HCP28	HCP35	HCP40	HCP45	BCP40
w/c	0.28	0.35	0.40	0.45	0.40
Water (kg)	0.28	0.35	0.40	0.45	0.40
Cement (kg)	1.00	1.00	1.00	1.00	0.90
Silica Fume (kg)	-	-	-	-	0.10
% Replacement	-	-	-	-	10

The focus of the research is to relate microstructure change in hardened cement paste to cement mortar and concrete. Sand and aggregate being chemically stable at elevated temperature up to 500 °C (Harmathy and Allen, 1973) is excluded from this investigation. Therefore, investigating hardened cement paste of w/c 0.28, 0.35, 0.4 and 0.45 provide an insight on the microstructure change of various types of hardened cement paste present in concrete due to elevated temperature.

3.2.2 Heating Program

The specimens must be uniformly heated before further testing can be conducted. Heat is transferred from the hotter to cooler region. The process takes time before the specimen reaches thermal equilibrium. The time between the end of ramp heating and thermal equilibrium is termed as holding period. During this period, programmed temperature at the end of ramp heating is maintained. The duration of the holding period is dependent on the rate of heating, thermal conductivity, specific heat capacity and size of specimen. Specimens with thermal gradient during testing would make quantification of thermal effects on material behaviour difficult. Hence, thermal equilibrium was considered throughout the research.

The heating program used by researchers varies greatly. The condition of thermal equilibrium is often not reported. No existing standards or recommendations were made regarding the heating program except the ISO 834 and parametric fire curve which described transient heating condition. The expression for ISO 834 fire curve is given in Equation (3.1).

$$T = T_0 + 345 \log_{10} \left(\frac{8t}{60} + 1 \right) \quad (3.1)$$

where T , T_0 and t refer to temperature (°C), initial room temperature (°C) and time (s) respectively. Most researchers used the ISO 834 fire curve for the heating program. This allows the comparison of experimental results between researchers. However, due to the excessive high heating rate in the beginning of the heating phase, most electric furnaces are unable to supply the heat in such a short time. Another problem arises even though

the ISO 834 fire curve was used in the experiment. The digital controller for the electric furnace could be set to follow the ISO 834 fire curve. However, due to the limitation of the heating elements and volume of space enclosed by an electric furnace, the gas temperature in the furnace may be far from the specified temperature calculated using Equation (3.1). An electric furnace heating test was conducted to determine the accuracy of the actual and programmed heating rate. Figure 3.1 shows the electric furnace and digital controller used in the investigation.

Figure 3.1: Nabertherm Electric Furnace (Left) and Digital Controller (Right)

The temperature step in the controller was set to follow the ISO 834 fire curve at 5 minute interval. Temperature readings were taken at 1 minute interval using a data logger. A scenario described in Figure 3.2 was obtained from the furnace test. Both time and temperature lag were observed. This is undesirable as researchers tend to compare experimental results using the same heating rate. They may not have considered the difference in the actual heating rate provided by the gas and the ISO 834 fire curve. Therefore, a practical heating rate should be used in the research of spalling to minimise the difference between the targeted and measured temperature. The rate of heating experienced in the gas is approximately 30 °C/min. This rate also represents the maximum heating rate achievable by the electric furnace. The gas and targeted temperature calculated using Equation (3.1) coincides after 30 minutes of heating.

Figure 3.2: Difference between Targeted and Gas Temperature

Therefore, a heating rate of 10 °C/min was adopted in this research as researchers (Anderberg, 1997; Chan *et al.*, 2000; Hertz, 1992) commonly observed that spalling occurred at that heating rate. Specifying a higher heating rate than 10 °C/min is necessary to induce but not ensure spalling. If the heating rate is specified too high, a large difference in gas temperature and targeted temperature would occur. A heating rate of 10 °C/min would satisfy the above mentioned criterion and not exceeding the capacity of the electric furnace. The temperature which the microstructure were investigated are 20 °C, 105 °C, 200 °C, 400 °C, 500 °C, 600 °C and 800 °C. The peak temperature of 800 °C was chosen as it was observed by researchers that the occurrence of spalling occurred before 800 °C and the decomposition of C-S-H gel and CH would be complete at approximately 800 °C (Harmathy, 1970; Peng *et al.*, 2001).

A 150 mm cube (HCP35) was used to evaluate the holding period required. Type K thermocouples with a welded tip of 0.2 mm were installed from the surface to centre of the cube at depth of 25 mm, 50 mm and 75 mm. The specimen was subjected to uniform heating at all surfaces. The rate of heating and maximum elevated temperature exposed

was 10 °C/min and 800 °C respectively. Temperature readings were taken at 1 minute interval. Ramp heating ended after 72 minutes from start of heating. It can be observed from Figure 3.3 that a holding period of 8 hours is required for 150 mm cube to achieve thermal equilibrium. Previous experience with heating 100 mm diameter concrete cylinder require 2 hour holding period to achieve thermal equilibrium. Vodak *et al.* (2004) used a holding period of two hours for a 5 mm cube fragment to attain thermal equilibrium before measuring the pores at residual state. Hence, a holding period of two hours is sufficient to achieve thermal equilibrium and is used throughout the experiment.

Figure 3.3: Temperature Profile within Specimen

3.2.3 Degree of Hydration

Degree of hydration (α) was been evaluated to calculate the volumetric ratio of hydration products using volume stoichiometry relationship that were incorporated into the proposed models. Powers and Brownyard (1946) demonstrated that hardened cement paste with w/c of 0.38 will have no capillary pores and consist entirely of

hydration products. Such condition can only be achieved given sufficient water for hydration and long period of curing. It was also observed that hydration products obtained from unit mass of cement produced 0.227 kg of non-evaporable moisture and 0.211 kg of gel water (saturated state) after underwent complete hydration. The mass of non-evaporable moisture (0.227 kg) is independent of w/c as long as cement is completely hydrated. Equations (3.2) to (3.4) were used to calculate α . The concept in calculating α is to compare difference in mass reading obtained from experiments with the expected non-evaporable moisture loss based on Powers and Brownyard's findings.

$$LOI = 100 \times \left(\frac{M_{cem,105} - M_{cem,1050}}{M_{cem,1050}} \right) \quad (3.2)$$

$$\frac{W_n}{C} = \frac{M_{bind,105} - M_{bind,1050}}{M_{bind,1050}} - \frac{LOI}{100} \quad (3.3)$$

$$\alpha = \frac{W_n}{0.23C} \quad (3.4)$$

where M , LOI and $\frac{W_n}{C}$ refer to mass (kg), loss of ignition (%) and non-evaporable moisture content (kg/kg) respectively. *cem* and *bind* in the first subscript of M denote OPC and hardened cement paste respectively while the second subscript state the temperature exposed.

3.2.4 Mass Loss Test

Mass loss in hardened cement paste occurs when subjected to elevated temperature. There are typically two ways of measuring mass loss in specimens. A commonly used approach involves weighing the specimens before and after heating. Specimens are usually placed in ceramic crucible during heating. Problem arises when measuring the mass at elevated temperature. Heat will be transferred from the heated crucible to electronic weighing scale. This may cause damage to the equipment. Mass reading was observed to be continuously fluctuating during trial with an insulating material (wood, ceramic bowl and concrete). The use of insulation material may increase the mass loss in heated specimen as evaporable moisture on the insulating material starts to vaporise

when comes in contact with the heated crucible almost instantly. Mass gain on the heated specimen due to surface absorption of moisture can also occur almost instantly, thus corrections to readings cannot be determined. Charing was also observed on wood and it can lead to higher mass loss during measurement. If the mass were taken after the specimen had cooled, there is a possibility that moisture will be absorbed onto the surface of the specimen thus increasing the total mass of the specimen.

Thermo Gravimetric Analysis (TGA) was selected for mass loss test in order to reduce the possible source of error due to surface absorbed moisture. TGA was measured using Perkin Elmer TGA-7 (Figure 3.4) which is a specialise apparatus capable of measuring mass with an accuracy of 1×10^{-6} mg at elevated temperature. The results from TGA are also repeatable making it a suitable equipment to be used for this research. Very small amount of specimen is required. Ground specimens (particle size $< 150 \mu\text{m}$) weighing 12 mg were used in TGA to ensure thermal equilibrium is achieved during transient heating.

Figure 3.4: Apparatus for TGA

3.2.5 Pore Structure Test

Pore structure in hardened cement paste includes porosity, pore size and pore size distribution. They were investigated using Mercury Intrusion Porosimetry (MIP). Mercury is a non wetting material and cannot be absorbed into the specimen. Hence, the volume of mercury intruded into the specimen corresponds to volume of pores. Fragments of 5 mm cube weighing approximately 1.5 g were tested before and after heating. Unheated specimens were soaked in acetone and then vacuum dried in a desiccator to prevent further hydration of the specimen which reduces volume of pores. Heated specimens were removed from the electric furnace at heated state and immediately placed in the vacuum desiccator to cool down and prevent rehydration of the specimen. MIP was conducted 24 hours after removing from electric furnace. Figure 3.5 shows the apparatus (Micromeritics Autopore III and vacuum desiccator) used for the pore structure test. The glass penetrometer used in MIP must be dry to minimize errors in calculating the volume of mercury filling the penetrometer.

Figure 3.5: Mercury Intrusion Porosimetry and Vacuum Desiccator

Pressure is applied into the glass penetrometer in multiple steps to overcome surface tension forces and allow mercury to fill the voids in the specimen. Washburn's equation provided in Equation (2.9) was used to calculate the corresponding pore diameter. The

main limitation of this equipment is the maximum pressure that can be generated is 60,000 pounds per square inch absolute which corresponds to pore diameter 3 nm. Therefore, only part of the gel pores is detected using this technique. Isolated pores are also undetectable using this method. This will tend to underestimate the quantity of gel pores measured from MIP.

It can be deduced that this effect is most significant at unheated state and slowly approaches to zero once all hydrates within the specimens have been decomposed. The difference between predicted (Jennings and Tennis's Equations) and measured gel pores (MIP) due to isolated pores and gel pores less than 3 nm ranges from 5.1 % to 9.6 % of total volume of specimen as shown in Table 3.2. It is important to note that predicted gel pores are by no means the actual gel pores within the specimen due to the complexity of hydration process and simplification of the volume stoichiometry relationship used to calculate gel pores. In this case, it serves as a common platform for comparison. Despite the difference in gel pores, no correction factor will be introduced into the material model for porosity subjected to elevated temperature as quantification of the combine effect is not possible in this research. In addition, the uncorrected material model can also serve as a technique to predict the maximum temperature experienced by a specimen when exposed to fire.

Table 3.2: Comparison between Measured and Predicted Gel Pores

Specimen ID	Measured Gel Pores (%)	Predicted Gel Pores (%)	Difference (%)
HCP28	7.289	13.382	6.093
HCP35	4.511	14.094	9.583
HCP40	5.601	13.097	7.496
HCP45	7.812	12.932	5.120

3.3 Sample Preparation

Ordinary Portland Cement (OPC) and commercial condensed Silica Fume (SF) of various proportions were used to produce test specimens used in this research. Table 3.3 list the chemical compositions of OPC and SF obtained from X-Ray Fluorescence (XRF). Bogue's Equations were then used to calculate the approximate phase composition in OPC (Table 3.4) and subsequently used to calculate the volume of

hydration products in the test specimens. Bogue's Equations were not extended to SF as they do not possess cementitious properties and does not take part in hydration of cement directly.

Table 3.3: Chemical Compositions of OPC and SF

Chemical Compositions	OPC	SF
CaO	64.34	0.24
SiO ₂	20.25	99.12
Al ₂ O ₃	3.84	0.31
Fe ₂ O ₃	3.33	0.63
SO ₃	3.03	0.30
MgO	2.13	0.74
K ₂ O	0.33	0.92
Na ₂ O	0.21	0.27

Table 3.4: Phase Composition of OPC

Phase	% Mass
C ₃ S	68.83
C ₂ S	6.13
C ₃ A	4.55
C ₄ AF	10.13

A predetermined quantity of water was then added to OPC to produce a slurry paste. BCP40 specimens were produced by mixing SF with water for 5 minutes in order to breakdown the condense pellets into a slurry mix before added to OPC. An improvised paste mixer was used to blend the cement paste. The slurry paste was mixed for three minutes before pouring it into a steel mould in two stages. In the first stage, the steel moulds were half-filled with fresh cement paste. The steel moulds were then vibrated for a minute to remove the air bubbles trapped in the fresh cement paste.

In the second stage, the steel moulds were completely filled with fresh cement paste and were vibrated for a further minute before being left to cure. The specimens were sealed with plastic sheet to prevent the loss of water through evaporation. The moulds were removed after 24 hours from casting and the specimens were stored in water of an average temperature of 20 °C. The specimens were water cured in separate water tanks to prevent pozzolanic reaction between SF present in BCP40 and calcium hydroxide

released from other types of specimens. Outbreak of fire generally occurs during the service period of concrete structures. Hence, hardened cement paste will have the degree of hydration close to one (depending on w/c and duration of curing). The curing period should be as long as possible and the supply of water to hardened cement paste must always be available to ensure continuous hydration. Therefore, specimens were water cured for 90 days and air dried for another 30 days before testing.

Figure 3.6: 50 mm Cubes Specimens

Figure 3.6 shows the specimens of various w/c used in this research. A total of three types of specimens were used in this research. 50 mm cube specimens were either ground using mortar and pestle or broken into 5 mm fragments for evaluation of microstructural behaviour of hardened cement paste subjected to elevated temperature. Specimen having 150 (D) x 150 (H) mm cylinder and 150 mm cube were used to measure the temperature contour within heated specimen.

3.4 Test Results

3.4.1 Degree of Hydration

An electronic balance with a precision of 0.0001 g was used for all mass measurement. Ground specimens weighing between 12 g to 15 g were contained using ceramic crucible. Mass readings were taken after heating the specimen to 105 °C for 24 hours and 1050 °C for 3 hours. Equations (3.3) to (3.5) were used to calculate α . However,

this set of equations is not applicable to blended cement paste due to the presence of pozzolanic reaction which alters the volumetric ratio of hydration products and non-evaporable moisture content in the specimen.

Table 3.5: LOI for OPC

Specimen ID	$M_{C,105}$ (g)	$M_{C,1050}$ (g)	LOI (%)
OPC	14.1300	13.9854	1.0407

Table 3.6: α of Various Specimen

Specimen ID	$M_{P,20}$ (g)	$M_{P,105}$ (g)	$M_{P,1050}$ (g)	$\frac{W_n}{C}$	α
HCP28	14.8800	13.6879	11.5551	0.1742	0.757
HCP35	13.6070	12.5463	10.3232	0.2049	0.891
HCP40	12.3444	10.9439	9.0064	0.2047	0.890
HCP45	14.5512	12.8767	10.4978	0.2162	0.940
BCP40	12.8112	11.3496	9.3469	-	-

The results of the calculation are tabulated in Table 3.5 and Table 3.6. It was observed from Table 3.6 that specimens of low w/c experienced a lower α for the same curing program due to insufficient space to accommodate the expansion of OPC (Lam *et al.*, 2000). α obtained from this investigation were used to determine the volume of hydration products within various specimens using volume stoichiometry relationships as provided in Appendix B. The volumetric ratio of hydration products used in subsequent models is listed in Table 3.7.

Table 3.7: Volumetric Ratio of Hydration Products for Various Specimens

Specimen ID	α	V_a	V_c	V_p	V_{hyd}
HCP28	0.757	0.229	0.344	0.176	0.749
HCP35	0.891	0.241	0.362	0.186	0.789
HCP40	0.890	0.224	0.337	0.172	0.734
HCP45	0.940	0.221	0.333	0.170	0.724
BCP40	0.890	0.198	0.454*	0.083	0.735

*: $V_{c,nor} = 0.297$ and $V_{c,poz} = 0.156$

V_a , V_c , V_p and V_{hyd} refer to volumetric ratio of AFm hydrates, C-S-H gel less gel pores, calcium hydroxide and sum of hydration products in hardened cement paste

respectively. Calcium hydroxide in BCP40 is the lowest due to the occurrence of pozzolanic reaction to form additional C-S-H gels. HCP35 has the highest V_{hyd} , followed by HCP28, BCP40, HCP40 and HCP45.

3.4.2 Compressive Strength

While mechanical properties are not within the scope of this research, compressive strength of hardened cement paste were measured to provide additional information on the specimens used in this research. The cross sectional areas were measured before subjecting the specimens to compression test. Compressive load were applied to the specimens using a compressive strength testing machine (Figure 3.7) at a rate of 38 kN/min, which conform to BS EN 12390-3:2001 Section 6.2 for a 50 mm cube specimen.

Figure 3.7: Compressive Strength Testing Machine

The compressive strength of the specimen (σ_c) was calculated by taking the load (F) over cross sectional area (A) as given in Equation (3.5).

$$\sigma_c = \frac{F}{A} \quad (3.5)$$

Table 3.8: Compressive Strength of Specimens

Specimen ID	Average Compressive Strength (MPa)
HCP28	61.09
HCP35	111.50
HCP40	91.72
HCP45	67.38
BCP40	92.04

Compressive strength of the specimens was measured after the curing procedure. Table 3.8 summaries the results of the experiment. Generally, the compressive strength is lower for higher w/c. However, the maximum compressive strength attained by HCP28 is the lowest amongst all specimens. This could be due to poor compaction of the specimen.

No significant increase in compressive strength was observed in BCP40 from HCP40 despite presence of SF. A possible reason for the similar compressive strength can be due to the ineffectiveness in breaking down the agglomeration of silica fume particles (Ji and Cahyadi, 2003) into the extremely fine particle of size 0.2 μm .

3.4.3 Tensile Splitting Strength

Cylinder split tensile strength of HCP35 were measured using the same compressive strength testing machine shown in Figure 3.7 except that the steel platen were removed and replaced with a cylinder splitting jig. Tensile splitting test was conducted after the curing procedure. Cylinder length and diameter were measure before testing to determine the cross sectional area of the specimen. Compressive load were applied at the rate of 84.8 kN/min, which conform to BS EN 12390-6:2001 Section 6.3 for a 150 mm (diameter) x 300 mm (length) cylinder specimen. The split tensile strength of the specimen (σ_T) was calculated by taking the load (F) over cross sectional area (A) as given in Equation (3.6). The average tensile splitting strength of two specimens (HCP35) was calculated to be 1.548 MPa.

$$\sigma_T = \frac{F}{A} \quad (3.6)$$

3.5 Summary

The experimental methodology is been discussed in this chapter. TGA and MIP were selected to investigate the mass loss and microstructure of various types of hardened cement paste. The condition of thermal equilibrium was maintained throughout the experiments. Heat transfer within heated hardened cement paste was also investigated to verify the proposed heat and mass transfer model. Degree of hydration of specimens of low w/c was found to be the low. Addition of silica fume into the specimen does not have effect on strength development when compared with another specimen having the same water/binder ratio without silica fume replacement. This is probably due to the ineffectiveness in breaking down the agglomeration of silica fume particles into the fine particle size.

Chapter 4: Analysis of Test Results

4.1 Overview

This chapter presents findings from mass loss and microstructure investigation of heated specimens. Material properties that can be derived from experimental data obtained in this research are also discussed. Mass loss and pore structure measurements can be used to evaluate shrinkage of heated specimen. Permeability of unheated specimens and behaviour of permeability subjected to elevated temperature can also be derived using established material transport properties. Observations on the temperature profiles in heated hardened cement paste subjected to different heating rate and moisture content are also reported.

4.2 Test Results

4.2.1 TGA

Ground specimens were used for TGA. The rate of heating and flow rate of nitrogen was 10 °C/min and 20.0 ml/min respectively. Mass readings were continuously taken from 20 °C to 900 °C at 0.333 second interval. The end temperature of 900 °C for TGA was selected based on the maximum safety limit of the machine. Heating took place in a nitrogen gas environment to prevent oxidation of compounds which will affect mass reading. Any change in mass will be attributed to the dehydration of hydration products. DTG was calculated from total mass remaining using the method of linear least squares fitting. Figure 4.1 to Figure 4.5 shows the raw results from TGA for various types of specimens.

Generally, the total percentage of mass remaining after heated to 900 °C ranged between 71 % and 78 %. All specimens experience a rapid decline in percentage of mass between 400 °C and 500 °C. Decomposition of hydration products ceased at approximately 900 °C as there were no further change in percentage of mass remaining.

Figure 4.1: Percentage of Mass Remaining in HCP28

Figure 4.2: Percentage of Mass Remaining in HCP35

Figure 4.3: Percentage of Mass Remaining in HCP40

Figure 4.4: Percentage of Mass Remaining in HCP45

Figure 4.5: Percentage of Mass Remaining in BCP40

Table 4.1: Percentage Mass Loss between 400 °C and 500 °C

Specimen ID	1 st Sample	2 nd Sample	Average
HCP28	4.339	4.348	4.344
HCP35	4.779	4.817	4.798
HCP40	4.801	4.870	4.835
HCP45	5.063	5.063	5.063
BCP40	4.054	4.016	4.035

The percentage of mass loss for various specimens between 400 °C and 500 °C are tabulated in Table 4.1. The difference in mass reading is due to the simultaneous decomposition of both calcium hydroxide and C-S-H gel. Normal cement pastes having a higher w/c and high degree of hydration experience a larger percentage decrease. Blended cement paste experienced the least decrease in percentage of mass due to the occurrence of pozzolanic reaction which consumes calcium hydroxide released during normal cement hydration to produce additional C-S-H gel within the specimen. Therefore, techniques used to derive the decomposition profile of hydration products must be able to account for the percentage difference in volume of C-S-H gel and

calcium hydroxide within the sample due to pozzolanic reaction in order to extend the proposed mass loss model to blended cement paste.

4.2.2 MIP

4.2.2.1 Pore Structure

Porosity of specimens was measured before and after heating. Temperature, density of mercury, contact angle and surface tension used in MIP were 20 °C, 13.5462 g/mL, 130° and 485 dynes/cm respectively. No surface cracking was observed on the heated fragments before and after testing. The cumulative porosity and log differential pore size distribution curves for the various specimens measured using MIP are shown from Figure 4.6 to Figure 4.10.

The breakdown of average capillary (pore diameter greater and equal to 10 nm) and gel (pore diameter less than 10 nm) pores is presented in Table 4.2. It was observed that while total and capillary pores increase at higher elevated temperature, gel pore decreases. This is because the existence of gel pores is dependent on the presence of C-S-H gel. When exposed to elevated temperature, C-S-H gel decompose into $\beta - C_2S$ and C_3S (Bazant and Kaplan, 1996) and shrink in volume. Gel pores which previously existed in C-S-H gel become part of capillary pores. The percentage of gel pores in heated specimens started to increase at approximately 200 °C. This is because isolated pores and gel pores less than 3 nm which were undetected previously joined the network of pores. Isolated pores are surrounded by hydration products which makes them undetectable using MIP. When hydration products are decomposed, it creates a pathway for mercury to penetrate into the isolated pores. It can be observed from Figure 4.6 to Figure 4.10 that the diameter with a peak in log differential pore size shift towards right which indicated that the pores were widened to a greater extent when exposed to high elevated temperature. Therefore, gel pores with diameter less than 3 nm will experience an increase in pore diameter which makes them detectable using MIP.

Figure 4.6: Pore Structure for HCP28

Figure 4.7: Pore Structure for HCP35

Figure 4.8: Pore Structure for HCP40

Figure 4.9: Pore Structure for HCP45

Figure 4.10: Pore Structure for BCP40

$\frac{dV}{d \log D}$ represents the change in volume of pores with respect to a change in the

logarithmic diameter. The location of the peak $\frac{dV}{d \log D}$ is known as threshold diameter.

Both $\frac{dV}{d \log D}$ and threshold diameter was observed to increase by one order of magnitude at higher exposed temperature (Table 4.3). Generally, specimens of low w/c experienced the largest increase in threshold diameter. This is due to the decomposition of hydration products which creates new pathways and enlarges existing pathways for mercury to intrude.

Table 4.2: Breakdown of Capillary and Gel Pores

Temperature (°C)	Type	HCP28	HCP35	HCP40	HCP45	BCP40
20	Total	10.253	13.519	15.833	19.281	15.895
	Cap	2.963	9.008	10.232	11.468	10.081
	Gel	7.289	4.511	5.601	7.812	5.813
105	Total	15.905	16.134	18.688	21.777	16.995
	Cap	13.475	12.580	14.639	18.269	12.331
	Gel	2.430	3.553	4.049	3.509	4.664
200	Total	18.489	17.854	22.629	26.150	18.108
	Cap	14.951	14.941	17.195	19.708	13.272
	Gel	3.538	2.913	5.434	6.442	4.836
400	Total	21.956	23.095	26.798	29.267	21.822
	Cap	18.819	18.352	21.186	23.145	17.125
	Gel	3.138	4.743	5.611	6.121	4.698
500	Total	28.452	28.517	31.772	35.364	28.278
	Cap	24.812	24.836	26.585	30.228	23.237
	Gel	3.640	3.682	5.187	5.136	5.041
600	Total	31.348	34.546	36.722	37.255	32.360
	Cap	28.483	30.920	32.977	33.264	28.461
	Gel	2.865	3.626	3.745	3.991	3.899
800	Total	41.943	41.865	44.252	47.380	40.062
	Cap	41.562	41.469	43.583	46.872	39.407
	Gel	0.380	0.396	0.669	0.508	0.655

Both HCP40 and BCP40 have similar compressive strength and unheated porosity. Despite having similar unheated porosity, total porosity for HCP40 and BCP40 starts to deviate when subjected to elevated temperature as low as 105 °C. Total porosity of BCP40 subjected to elevated temperature is generally lower than HCP40. This is because C-S-H gel produced from normal cement hydration and pozzolanic reaction are different. The volume of gel pores residing in normal and blended C-S-H gel are 28% and 19% respectively (Copeland and Hayes, 1953; Ji, 2003) which indicate that decomposition of blended C-S-H gel would contribute less to total porosity when exposed to elevated temperature. This observation is consistent with observations made from spalling research that concrete with SF have a higher tendency to spall. Pore volume represents the space where the vapour is located during heating. A small pore volume would lead to a higher pressure build up when compared with a large pore volume for the same amount of vapour. Hence, blended cement concrete would experience a high tendency of spalling during heating.

Table 4.3: Comparison of Peak Values in $\frac{dV}{d \log D}$

Temperature (°C)	Type	HCP28	HCP35	HCP40	HCP45	BCP40
20	Diameter (nm)	11.0	17.6	35.4	35.5	35.6
	Peak (mL/g)	0.111	0.092	0.082	0.209	0.177
	Norm Peak	1.000	1.000	1.000	1.000	1.000
105	Diameter (nm)	44.7	36.1	56.3	91	44.8
	Peak (mL/g)	0.184	0.228	0.145	0.242	0.149
	Norm Peak	1.658	2.478	1.768	1.158	0.842
200	Diameter (nm)	44.7	56.7	57.5	112.5	56.5
	Peak (mL/g)	0.215	0.225	0.177	0.209	0.156
	Norm Peak	1.937	2.446	2.159	1.000	0.881
400	Diameter (nm)	56.8	56.7	72.4	140.5	71.1
	Peak (mL/g)	0.239	0.208	0.215	0.230	0.168
	Norm Peak	2.153	2.261	2.622	1.100	0.949
500	Diameter (nm)	72.3	72.6	80.1	127.5	88.7
	Peak (mL/g)	0.197	0.274	0.200	0.191	0.120
	Norm Peak	1.775	2.978	2.439	0.914	0.678
600	Diameter (nm)	71.8	75.5	92.5	91.3	89.9
	Peak (mL/g)	0.240	0.328	0.278	0.159	0.256
	Norm Peak	2.162	3.565	3.390	0.761	1.446
800	Diameter (nm)	120.1	131.0	152.1	150.1	144
	Peak (mL/g)	0.587	0.466	0.422	0.457	0.353
	Norm Peak	5.290	5.065	5.146	2.187	1.994

4.2.2.2 Density Measurements

The primary function of MIP is to measure the volume of pores intruded into a specimen. Different intruded volume at different pressure indicates the pore size distribution. Porosity is then calculated by taking the ratio of the volume of pores with the bulk volume of the specimen. Mass of specimen is required as an input for MIP to calculate the volume of mercury intruded into the glass penetrometer of a known volume. Hence, bulk and skeleton density of the specimen can be calculated since the mass and volume of the specimen are known.

The thermal behaviour of bulk and skeleton density of various specimens are shown in Figure 4.11 and Figure 4.12 respectively. Bulk density decreases when heated. The decrease in bulk density is most significant when the specimens were heated to 105 °C.

The evaporation of surface bounded moisture is responsible for the change in bulk density since mass of specimen decrease without significant change in microstructure. Bulk density remained relatively constant thereafter. This is because hardened cement paste experienced both shrinkage and loss of mass when heated due to the loss of non-evaporable water. Since non-evaporable water has a density of 1000 kg/m^3 (Bazant and Kaplan, 1996), the percentage change in mass will lead to an equal percentage change in volume.

Figure 4.11: Behaviour of Bulk Density

Specimens with high w/c have low bulk density. The high water content during mixing with OPC creates large volume of voids within the specimen. This led to a lighter specimen per unit volume and is responsible for the low bulk density. It is also observed that the bulk density for BCP40 is slightly lower than HCP40 despite having similar compressive strength. The replacement by pozzolana, which has a lower density than OPC, lowers the overall mass of the specimen and subsequently lowers the bulk density of the specimen.

Figure 4.12: Behaviour of Skeleton Density

Skeleton density behaves differently from bulk density. Skeleton density experiences a slight decrease at 105 °C. The decrease in skeleton density at 105 °C is due to the evaporation of surface moisture residing within the pores of the specimen. Decomposition of hydration products occurring after 105 °C is responsible for the increase in skeleton density. A rapid rate of change in skeleton density was observed at 400 °C probably due to the penetration of mercury into previously isolated gel pores and start of decomposition of calcium hydroxide. Skeleton density of all normal cement paste subjected to 800 °C converges to a point (3.12 - 3.19 kg/m³) which is close to the density of OPC.

4.2.3 Temperature Measurements

Besides the temperature profile obtained during the electric furnace test, temperature profiles of other specimens with different moisture content and heating rates were also measured. Moisture content of two similar cylindrical specimens (HCP35) cured and air dried in the same condition with 50 mm cubes was determined following BS EN 772-

10:1999. The unheated mass was measured before and after heating at 105 °C for 24 hour. Moisture content was calculated using Equation (4.1).

$$W_n = \frac{M_{bind,20} - M_{bind,105}}{M_{bind,105}} \times 100 \quad (4.1)$$

where W_n , $M_{bind,20}$ and $M_{bind,105}$ refer to moisture content (%), unheated mass (kg) and heated mass (kg) respectively. The average moisture content for two air dried specimens was calculated to be 8.6%. Table 4.4 shows the different test conditions of the specimens used in the heating test. Saturated specimens were prepared by soaking the air dried specimens back into the curing tank for approximately 7 days. Total mass of free water was calculated by summing the difference in mass before and after soaking and mass of evaporable moisture calculated from moisture content. Cracking sounds were observed at approximately 10 minutes from start of heating and continued for an hour for all specimens. However, there was no occurrence of explosive spalling. Temperature readings were continuously captured using a data logger at one minute interval. The temperature profiles for SP2 to SP4 are shown from Figure 4.13 to Figure 4.16. SP1 refer to the specimen used in the furnace test and hence, the temperature profile is provided in Figure 3.3.

Table 4.4: Initial and Heating Condition

Specimen ID	Type	Condition	Mass of Free Water (kg/m ³)	Rate (°C/min)	Max Temperature (°C)
SP1	Cube	Air Dried	175	10	800
SP2	Cube	Saturated	304	30	800
SP3	Cylindrical	Saturated	304	30	900
SP4	Cylindrical	Saturated	304	20	900
SP5	Cube	Air Dried	175	30	800

Figure 4.13: Temperature Profile for SP2 **Figure 4.14: Temperature Profile for SP3**

Figure 4.15: Temperature Profile for SP4

Figure 4.16: Temperature Profile for SP5

Two plateaus in the temperature profiles for all specimens were observed at approximately 100 °C and 530 °C regardless of moisture content and rate of heating. The temperatures correspond to the evaporation of free water and moisture released from the decomposition of calcium hydroxide respectively. During evaporation of moisture, energy transfer into the system does not increase the temperature over a period of time. The consistent occurrence of plateau at 530 °C indicates non-evaporable moisture release is a material property and is independent to moisture content and rate of heating. The plateaus were most distinct for the temperature reading located at the centre of the specimen as both heat and moisture were transported into the centre of the specimen when subjected to all round heating.

The duration of the plateau (100 °C) was observed to be dependent on the quantity of free water present within the pores of the specimen and is most critical for saturated specimens. It lasted approximately 30 minutes for the centre temperature reading before experiencing an increase in temperature. The duration of the plateau for air dried specimen was approximately 20 minutes. The duration of the second plateau for the centre temperature reading lasted approximately 20 minutes and is depending on the rate of heating. All specimens, having the same microstructure, released equal quantity of non-evaporable moisture. The duration of the plateau for heat rate of 10, 20 and 30 °C/min were observed to be approximately 10 (SP1), 15 (SP4) and 20 (SP2, SP3) minutes respectively. A high rate of heating would lead to a high rate of non-evaporation moisture release. Since non-evaporable moisture was restricted from escaping from the specimen, time was spent to vaporise the large quantity of non-evaporable moisture.

Cement-based materials are generally known for its poor thermal conductivity. This will lead to large thermal gradient during heating. Maximum thermal gradient between the surface exposed to heating and centre thermocouple reading was observed to occur during the first plateau (100 °C).

4.3 Derived Properties

4.3.1 Shrinkage

Hardened cement paste shrink after subjected to elevated temperature. Shrinkage is often expressed as a reduction in length or volume. Instead of measuring shrinkage in length experimentally, it can be derived analytically by using mass loss and residual skeleton density measurement obtained from TGA and MIP respectively. By assuming unit volume of hardened cement paste before heating, the shrinkage in volume can be calculated using Equation (4.2) and (4.3). Residual mass is obtained by taking the mass of unit volume of unheated hardened cement paste multiply with fraction of mass remaining subjected to elevated temperature obtained from TGA.

$$\text{Shrinkage} = \text{Unheated Volume} - \text{Residual Volume} \quad (4.2)$$

$$\text{Residual Volume} = \frac{\text{Residual Mass}}{\text{Residual Skeleton Density}} \quad (4.3)$$

$$\text{Shrinkage (length)} = \text{Unheated Length} - \text{Residual Volume}^{\frac{1}{3}} \quad (4.4)$$

Equation (4.4) is then used to calculate shrinkage in length. The formulation (Equation 4.4) assumes the geometry of the specimen before and after heating remains as a cube. Specimens are isotropic and experience equal reduction in length in all dimensions. Since unheated cubic specimen is assumed to be unit volume, the unheated length of the specimen works out to be 1 m. Table 4.5 shows the details on calculating shrinkage for various specimens. The percentage reduction in volume and length is shown in Figure 4.17 and Figure 4.18 respectively.

Table 4.5: Calculation of Shrinkage

Specimen ID	Temp (°C)	Residual Skeleton Density (kg/m ³)	Mass Remain (%)	Residual Mass (kg)	Residual Vol (m ³)	Shrink. Vol (m ³)	Shrink. Length (x10 ⁻³ m)
HCP28	20	2403.4	100.000	2403.4	1.00000	0.00000	0.00
	105	2328.1	91.989	2210.9	0.94967	0.05033	17.07
	200	2358.7	87.663	2106.9	0.89324	0.10676	36.93
	400	2370.8	83.534	2007.7	0.84684	0.15316	53.91
	500	2564.0	79.191	1903.3	0.74232	0.25768	94.55
	600	2724.2	78.514	1887.0	0.69270	0.30730	115.19
	800	3200.9	77.806	1870.0	0.58422	0.41578	164.03
HCP35	20	2289.3	100.000	2289.3	1.00000	0.00000	0.00
	105	2274.2	92.169	2110.0	0.92783	0.07217	24.66
	200	2226.3	86.900	1989.4	0.89357	0.10643	36.82
	400	2349.8	82.044	1878.2	0.79931	0.20069	71.95
	500	2527.1	77.246	1768.4	0.69977	0.30023	112.19
	600	2786.9	76.507	1751.5	0.62847	0.37153	143.43
	800	3135.6	75.952	1738.8	0.55453	0.44547	178.43
HCP40	20	2218.5	100.000	2218.5	1.00000	0.00000	0.00
	105	2236.8	88.635	1966.4	0.87907	0.12093	42.05
	200	2222.9	83.978	1863.1	0.83811	0.16189	57.17
	400	2325.0	79.134	1755.6	0.75508	0.24492	89.39
	500	2506.4	74.299	1648.3	0.65765	0.34235	130.38
	600	2724.1	73.683	1634.6	0.60008	0.39992	156.53
	800	3119.8	73.112	1622.0	0.51990	0.48010	195.91
HCP45	20	2241.6	100.000	2241.6	1.00000	0.00000	0.00
	105	2113.2	88.211	1977.3	0.93571	0.06429	21.91
	200	2274.3	83.231	1865.7	0.82035	0.17965	63.88
	400	2385.1	78.273	1754.6	0.73563	0.26437	97.28
	500	2422.5	73.210	1641.1	0.67744	0.32256	121.74
	600	2574.2	72.566	1626.6	0.63189	0.36811	141.88
	800	3193.8	71.919	1612.1	0.50476	0.49524	203.79
BCP40	20	2122.2	100.000	2122.2	1.00000	0.00000	0.00
	105	2059.6	88.607	1880.4	0.91302	0.08698	29.88
	200	2046.7	83.137	1764.4	0.86208	0.13792	48.27
	400	2115.0	78.422	1664.3	0.78692	0.21308	76.77
	500	2332.6	74.385	1578.6	0.67678	0.32322	122.02
	600	2494.4	73.765	1565.5	0.62759	0.37241	143.83
	800	2866.0	73.118	1551.7	0.54143	0.45857	184.96

Figure 4.17: Reduction in Volume at Various Temperatures

All specimens exhibit shrinkage when exposed to elevated temperature. Specimens with high w/c experience a larger reduction in volume and length. At 105 °C, the specimens generally experience shrinkage of 5 % to 12 % in volume or 1.7 % to 4.2 % in length. The change in volume and length is most rapid between 20 °C to 105 °C and 400 °C to 500 °C. This is because specimens experience a rapid decrease in mass due to loss of evaporable moisture and decomposition of calcium hydroxide respectively. Volume shrinkage in normal cement paste (HCP40) is observed to be slightly higher (2.6 %) than blended cement paste (BCP40) at various elevated temperatures despite having the same w/b (Figure 4.17). This is due to the presence of gel pores within different types of C-S-H gels that influence shrinkage. When C-S-H gel decomposes, the sum of volume of chemically bound water removed and gel pores within C-S-H gel will be total shrinkage volume. Since gel pores in C-S-H gel formed by pozzolanic reaction is 19 % compared to 28 % in C-S-H gel formed by normal cement hydration, shrinkage will be lower in blended cement paste than normal cement paste. This difference in percentage of gel pores residing within C-S-H gel will be considered when developing a model to predict porosity of heated hardened cement paste in the later chapter.

Figure 4.18: Reduction in Length at Various Temperatures

Figure 4.19: Measurement of the Length of Specimen

The methodology in calculating shrinkage using skeleton volume is different from experiments which measure the change in overall length of the specimen (Harmathy and Allen, 1973). A key difference between the two methods is the treatment of cracks which lays transverse to the dimension being investigated. The existences of crack lines are most severe at higher exposed temperature (Lin *et al.*, 1996; Poon *et al.*, 2001).

Crack lines are normally included in external length measurement as shown in Figure 4.19. Since hardened cement paste shrink when heated, the inclusion of crack width in length measurement would underestimate shrinkage. Shrinkage calculated from skeleton density will be higher than shrinkage obtained from externally measured dimensions. This is because shrinkage calculated from skeleton density obtained from MIP exclude crack lines since mercury fill in the gaps of the cracks. This signifies that shrinkage calculated from skeleton density gives a better representation of shrinkage within hardened cement paste rather than using externally measured dimensions.

4.3.2 Permeability

Permeability is responsible for the rate of moisture transfer in heated hardened cement paste. Permeability of various fluids in a porous material is different. Hence, instead of using permeability as a single parameter to define transport mechanism, it is broken into intrinsic permeability and relative permeability of various phases through dry hardened cement paste. The objective of this section is to calculate unheated intrinsic permeability of the specimen. Intrinsic permeability is a parameter to define permeability which is independent of the fluid been transported. The advantage of this formulation is the effects of temperature on permeability can be incorporated resulting from the thermal behaviour of dynamic viscosity of the fluid in the porous material. The relationship between permeability, a (m/s), and intrinsic permeability, K (m²) is given in Equation (4.5) (Harmathy, 1993).

$$\rho_L \frac{K}{\mu_L} = \frac{a}{g} \quad (4.5)$$

where ρ_L , μ_L and g refer to density of water (20 °C), dynamic viscosity of water (20 °C) and acceleration due to gravity (9.81 m/s²) respectively. Permeability was observed to be dependent on the threshold diameter of the porous material. Katz and Thompson (1986) proposed to calculate intrinsic permeability of a saturated porous material at 20 °C using Equation (4.6). The term $\frac{D}{D_0}$ which represents the relative diffusivity is calculated using Equation (4.7) by Bentz *et al.* (1996).

$$K = \frac{1}{226} d_{cr}^2 \left(\frac{D}{D_0} \right) \quad (4.6)$$

$$\frac{D}{D_0} = 0.001 + 0.07 n_{cap}^2 + H(n_{cap} - 0.18) \times 1.8 (n_{cap} - 0.18)^2 \quad (4.7)$$

where d_{cr} , n_{cap} and $H(X)$ refer to threshold diameter (m), capillary porosity ($\geq 10 \mu\text{m}$ diameter) and Heaviside function. The value of $H(X)$ is taken to be 1 for $n_{cap} \geq 0.18$ and 0 for $n_{cap} < 0.18$. The results of the computation are tabulated in Table 4.6. Total porosity and n_{cap} are experimental obtained values for unheated specimens (20 °C) listed in Table 4.2. ρ_L and μ_L are 1000 kg/m³ and 0.001 kg/(m.s) respectively.

Table 4.6: Calculation of K and a

Specimen ID	Total Porosity (%)*	n_{cap} (%)*	D/D_0 (x10 ⁻³)	d_{cr} (x10 ⁻⁹ m)	K (x10 ⁻²⁰ m ²)	a (x10 ⁻¹³ m/s)
HCP28	10.253	2.963	1.061	11.000	0.057	0.056
HCP35	13.519	9.008	1.568	17.600	0.215	0.211
HCP40	15.833	10.232	1.733	35.400	0.961	0.943
HCP45	19.281	11.468	1.921	35.500	1.071	1.051
BCP40	15.895	10.081	1.711	35.600	0.960	0.941

*: Total porosity (%) and n_{cap} (%) are taken at unheated state (20 °C) from Table 4.2

Permeability calculated using Equation (4.5) and (4.6) were compared with permeability obtained from experiments conducted by Breysse and Gerard (1997) and is shown in Figure 4.20. X-axis represents total porosity while y-axis represents permeability. Both calculated and experimental results of permeability are in accordance.

Figure 4.20: Comparing Calculated Permeability with Experimental Measured Permeability Using Total Porosity (Breyse and Gerard, 1997)

4.4 Summary

Various experiments were conducted to determine the behaviour of microstructure of various types of hardened cement paste subjected to elevated temperature. Experimental results were used to verify the proposed material models and heat and mass transfer model. Ground hardened cement paste experienced a mass loss ranging from 22 % to 29 % when heated up to 900 °C. Specimens with high w/c and degree of hydration experience the largest mass loss. Blended cement paste (BCP40) was observed to have a lower mass loss when compared with normal cement paste of the same w/b (HCP40) due to the difference in volume of calcium hydroxide and C-S-H gel within the specimens. A rapid decrease in mass was detected between 400 °C and 500 °C for all specimens due to the decomposition of calcium hydroxide. Decomposition of hydration products was observed to cease at approximately 900 °C.

Results from MIP show that specimen having high w/c experience the largest increase in porosity after subjecting to elevated temperature. Despite having the same compressive strength for both HCP40 and BCP40, the behaviour of pore structure subjected to elevated temperature was observed to be different. Porosity measurements

of blended cement paste (BCP40) subjected to elevated temperature is about 10% lower than normal cement paste (HCP40). The difference in the porosity behaviour between BCP40 and HCP40 is due to the difference in C-S-H gel formed by normal cement hydration and pozzolanic reaction. This factor will be considered when modelling the behaviour of porosity subjected to elevated temperature for blended cement paste.

Generally, bulk density experience a rapid decrease when heated to 105 °C and remains fairly constant up to 800 °C. Specimens with high w/c will have low bulk density due to the high water content used in mixing. Skeleton density experiences a slight decrease when heated to 105 °C. Once heated beyond 105 °C, skeleton density starts to increase and converges to a point which is close to the density of OPC. Shrinkage in hardened cement paste calculated using skeleton density will be higher than measuring the external dimensions of the specimen due to the difference in treatment of cracks within the specimen.

Two plateaus were observed during heating of hardened cement paste at approximately 100 °C and 530 °C. They correspond to the evaporation of free water and moisture released from the decomposition of calcium hydroxide respectively. The occurrence of the first plateau at the centre of the specimen will also indicate maximum thermal gradient within the specimen when heated at a rate higher than 10 °C/min. No occurrence of spalling was detected during the experiments. Observations made in the heat transfer test were used to verify heat and mass transfer model proposed in the subsequent chapter.

Chapter 5: Decomposition Profile of Hydration Products

5.1 Introduction

Once hardened cement paste is heated beyond 105 °C, it will experience microstructural changes which include dehydration of hydrates and conversion of various compounds. The most prominent microstructural change in heated hardened cement paste at temperatures greater than 105 °C is the decomposition of calcium hydroxide (CH) into calcium oxide and moisture within hardened cement paste generally occurring between 380 °C to 600 °C (Bazant and Kaplan, 1996; Harmathy, 1970; Taylor, 1990). The remaining amorphous hydration products such as calcium silicate hydrate gel (C-S-H gel) decompose into β -dicalcium silicate (β -C₂S) and moisture over a temperature range of 105 °C to 900 °C (Bazant and Kaplan, 1996; Janotka and Bagel, 2002).

Decomposition of hydration products is accompanied by moisture release. The release of chemically bound moisture during transient heating limits the applicability of Fourier's law of heat conduction in heat transfer analysis. Experimental investigations conducted during the course of this research shows that the presence of moisture delays heat transfers. This will lead to an under estimation of thermal gradient which will affect thermal stress analysis. Decomposition of hydration products also has an effect on explosive spalling analysis. Spalling is a phenomenon whereby pieces of concrete break off from the surface of concrete element. A high rate of decomposition of amorphous hydrates would release large quantity of vaporised moisture into the pores of the hardened cement paste within a short time. Low permeability limits the rate of flow of moisture, leading to an increase in pore pressure and formation of moisture clog. High tensile stress will be generated around the pore wall and explosive failure occurs when the tensile stress is greater than tensile strength of concrete.

It is possible to study the decomposition profile of the hydration products by analysing the total mass loss of heated cement paste. Mass loss occurs when moisture molecule escapes into the atmosphere. Moisture loss within heated cement paste is not due solely to the decomposition of hydration products. The two types of moisture loss are

evaporable and non-evaporable moisture loss. They are demarcated by mass loss at temperature below 105 °C for the former and temperature greater or equal than 105 °C for the latter. Evaporable moisture does not have any chemical bond with hardened cement paste. Non-evaporable moisture is moisture that is released during the decomposition of hydration products.

This chapter investigate one of the two microstructural changes in hardened cement paste. The objective of this chapter is to determine the decomposition profile of hydration products and to relate decomposition profile with non-evaporable moisture loss for various types of mix proportion. Some limitations in experimental procedures in previous researches are addressed in this research. A method is proposed to predict non-evaporable moisture loss which considers the effects of different mix proportion using Ordinary Portland Cement (OPC), including blended cement paste and degree of hydration. No differentiation between concrete and hardened cement paste is required since the research work emphasize on the hydration products. Hardened cement paste of various mix proportions were used to determine the decomposition profile for the hydration products.

5.2 Review of Previous Works

5.2.1 Decomposition of Hydration Products

The evaluation of the decomposition profile of the hydration products is an important part in understanding the microstructural change and non-evaporable moisture loss in heated hardened cement paste. Little information is available on the decomposition profile of hydration products. Various techniques can be used to determine the decomposition profile. Peng *et al.* (2001) used quantitative X-Ray Diffraction (XRD) to determine the decomposition profile for C-S-H gel when subjected to elevated temperature. Hardened cement paste of water/cement ratio (w/c) 0.38 was heated to various targeted temperature ranging from 20 °C to 800 °C before allowing it to cool to room temperature. Specimens were then ground before determining the chemical compositions at residual state using XRD.

Figure 5.1: Percentage Remaining of C-S-H gel at Various Heating Duration (Peng *et al.*, 2001)

Figure 5.1 shows the percentage of C-S-H gel remaining in hardened cement paste generally declines when heated. Specimens heated at 800 °C experienced the highest rate of decomposition and all of the C-S-H gel has decomposed after heating for 100 minute. It can also be observed from the percentage of C-S-H gel remaining in the specimen at duration greater than 400 minutes is dependent on the temperature increment. Peng *et al.* (2001) concluded that decomposition of C-S-H gel start at approximately 560 °C based on his experimental findings. Hence, no information on the decomposition profile of C-S-H gel for elevated temperature below 600 °C was provided. CH, being the other major phase in hardened cement paste, was not investigated and the decomposition profile of C-S-H gel alone cannot be used to describe the behaviour of hardened cement paste at elevated temperature.

A different phenomenon was observed between the works by Harmathy (1970) and Peng *et al.* (2001). Harmathy (1970) investigated the decomposition profile of both CH and C-S-H gel in hardened cement paste ($w/c=0.5$). Decomposition profile was derived using results obtained from Thermo Gravimetric Analysis (TGA) and Differential Thermo Gravimetric (DTG). Figure 5.2 shows the degree of conversion of C-S-H gel and CH at various temperatures. C-S-H gel was observed to decompose across the range of temperatures instead of decomposing after 560 °C (Peng *et al.*, 2001). A change in the rate of decomposition of C-S-H gel occurred at approximately 700 °C. It could be due to the decomposition of calcium carbonate into carbon dioxide and calcium oxide

which affected the mass reading. Decomposition of C-S-H gel was completed at 900 °C. Crystalline CH was observed to decompose between 380 °C and 600 °C (Harmathy, 1970) instead 450 °C and 550 °C (Bazant and Kaplan, 1996).

Figure 5.2: Degree of Decomposition of C-S-H Gel and CH (Harmathy, 1970)

Figure 5.3 shows the comparison between Peng's *et al.* (2001) and Harmathy's (1970) experimental results. The curve for Peng's *et al.* (2001) in Figure 5.3 was calculated by taking the difference between 100 (%) and the final value of the percentage of C-S-H remaining at the respective temperatures. The rate of decomposition, which corresponds to the gradient of the curves in Figure 5.3, was observed to be higher for Peng's *et al.* (2001) than Harmathy's (1970).

The cause for the difference could be due to the difference in w/c for both specimens prior to heating since both used different w/c in their investigations. A comparison on the hydration products which include volumetric ratios of C-S-H gel and CH for both mixes prior to heating using CemMicro (Ji, 2003) is given in Table 5.1. Ordinary Portland Cement (OPC) used in the calculation was assumed to be the same for both tests. While this is not true in any case, it provides a common platform for comparison. Harmathy's (1970) specimen generally has approximately 7% more hydration products compared with Peng's *et al.* (2001) specimen. A high volume of hydration products would lead to larger mass loss. However, difference in w/c should not affect the

decomposition profile for various phases significantly as shown in Figure 5.3. Decomposition profile is obtained by normalising mass loss at various elevated temperature with total mass loss. It is phase specific and should not dependent on volume of phase. The rate of decomposition for the various hydration products will be investigated as part of the research.

Figure 5.3: Comparison of Experimental Results

Table 5.1: Phase Composition of Various Cement Paste Computed Using CemMicro (Ji, 2003)

Water/Cement Ratio	0.38	0.5*
Duration of Hydration	90 days	4 years
Degree of Hydration	0.798	1.0
Volume of C-S-H	0.432	0.461 (6.7%)
Volume of CH	0.159	0.170 (6.9%)
Volume of Other Products	0.207	0.221 (6.8%)
Volume of Gel Pores	0.121	0.129 (6.6%)

*Values in brackets are percentage increase of each phase for w/c=0.50 with respect to w/c=0.38

Differences in experimental methodologies, such as equipment, heating program and size of specimen subjected to heating could be responsible for the difference in decomposition profile. In Peng's *et al.* (2001) research, the decomposition profile was obtained by considering peak intensities which show up within the diffraction angle

(2 θ) range of 20° to 40°. Amorphous phase such as C-S-H gel does not have distinctive peaks in XRD results and exist over a large diffraction angle range. Hence, large quantity of C-S-H gel may be undetected. The amount of C-S-H gel in the specimens can be measured more accurately by increasing the scan duration of XRD and consider a wider range of diffraction angle. The use of TGA in Harmathy's (1970) investigation makes it possible to measure the mass loss of the decomposition of amorphous hydrates within the specimen which is not measurable using XRD. However, the contributions of each phase on total mass loss are lumped. When a phase decomposes, the total mass loss will experience a rapid increase. Hence, DTG can be used to identify the quantity of mass loss for each phase. Conducting the test in an inert environment can filter effects of oxidation of various compounds in hardened cement paste during heating. Works are required to determine the applicability of the decomposition profile for other mix proportion.

Heating program and size of specimen subjected to heating are equally important in the derivation of decomposition profile of hydration products. Large specimens will experience thermal gradient in transient heating. The thermal gradient will cause hydrates along the direction of heat transfer to experience different percentage of C-S-H gel been decomposed. Once the transient heated specimen is ground, it is impossible to distinguish the volume of the ground specimen that had been heated to the targeted temperature. The results obtained from XRD or any other form of investigation will not provide much information about the microstructural behaviour at the targeted temperature. Measurements of phase composition should be taken only when the specimen have reached thermal equilibrium between the exposed surface and centre core. Ground specimens should be used during heating to ensure thermal equilibrium could be reached in a shorter duration. If large specimens are used, the duration of heating should also be increased. These limitations in experimental methodologies should be addressed when deriving the decomposition profile of hydration products.

5.2.2 Non-Evaporable Moisture Loss

Various researchers had investigated the effect of temperature on non-evaporable moisture loss for hardened cement paste and concrete. The objectives of the researches

were to identify the total mass loss in the specimen to quantify degree of hydration (Bazant and Kaplan, 1996; Lam *et al.*, 2000; Pinto *et al.*, 2000) or to determine the maximum temperature experienced by the specimen (Harmathy, 1968). However, limited studies have been published on non-evaporable moisture loss in blended cement paste (Li *et al.*, 1996). A model to predict non-evaporable moisture loss for various mix proportions at elevated temperature is also non-existent. Thus, researchers are often unsure of the non-evaporable moisture loss profile that should be implemented in the simulation of heat and mass transfer for various types of heated concrete.

Non-evaporable moisture loss is observed to be non-linear (Harmathy and Allen, 1973; Hilsdorf, 1967). Hilsdorf (1967) proposed to calculate non-evaporable moisture remaining in concrete (W_e) using Equation (5.1). α and ρ_{cem} refer to degree of hydration and mass of anhydrous cement per unit volume of concrete (kg/m^3) respectively. The coefficient $\bar{T}$ is to be determined using Figure 5.4.

$$W_e = 0.24\alpha\rho_{cem}\bar{T} \quad (5.1)$$

Figure 5.4: Coefficient $\bar{T}$ at Elevated Temperature (Hilsdorf, 1967)

Tenchev *et al.* (2001) used a bilinear line given in Equation (5.2) to model the behaviour of non-evaporable moisture loss per unit volume of concrete (w_d) as a

function of temperature (T) and mass of anhydrous cement (ρ_{cem}) in heat and mass simulation.

$$w_d = \begin{cases} 0 & , T < 100^\circ\text{C} \\ 0.04\left(\frac{T}{100} - 1\right)\rho_{cem} & , 100^\circ\text{C} \leq T \leq 700^\circ\text{C} \\ 0.24\rho_{cem} & , T > 700^\circ\text{C} \end{cases} \quad (5.2)$$

The bilinear line by Tenchev *et al.* (2001) is unable to represent the sudden release of moisture resulting from the decomposition of CH. Both equations attempt to model the behaviour of non-evaporable moisture loss for different types of concrete using mass of anhydrous cement per unit volume of concrete. Such formulation is limited to normal cement concrete. The mass of non-evaporable moisture for blended cement concrete cannot be predicted accurately due to pozzolanic reaction. The occurrence of pozzolanic reaction will lead to the formation of additional C-S-H gel and consumption of CH, which affects the non-evaporable moisture content in a specimen. Hence, an improved formulation to predict the mass of non-evaporable moisture loss which separates the effects of C-S-H gel and CH for both normal and blended cement concrete is required.

5.3 Analytical Procedure to Derive Decomposition Profile From TGA/DTG

In this study, results from TGA/DTG are used in the derivation of the decomposition profile of hydration products. TGA is used to determine the percentage of total mass loss in specimen at elevated temperature while DTG is the time derivative of TGA. Decomposition of amorphous and crystalline phase is assumed to occur simultaneously between 400 °C and 550 °C. The principal behind the procedure is to remove the effects of decomposition of CH in the time derivative of the percentage of total mass loss rather than at the percentage of total mass loss. This is to ensure continuity in the rate of decomposition of amorphous phase between 400 °C and 550 °C and will mathematically ensure continuity in the percentage of mass loss of amorphous phase. This approach is appropriate as compounds experience a continuous rate of decomposition except at the peak value.

Identify effects of CH in DTG

DTG was calculated from total mass remaining using the method of linear least squares fitting. A peak in DTG signifies a rapid drop in total mass remaining in the heated specimen. There are generally three major peaks in the plot of DTG as shown from Figure 5.6 to Figure 5.9. The peaks occurring at 60 °C, 100 °C and 450 °C corresponds to the decomposition of ettringite, release of evaporable moisture and decomposition of CH respectively. Decomposition of hydration products ceased at temperatures greater than 900 °C as DTG approached zero. A quadratic polynomial curve was used to interpolate the DTG results of heated cement paste between 400 °C and 550 °C which corresponds to the decomposition of CH. The quadratic polynomial curve to predict derivative weight (y) is represented by following equation:

$$y = aT^2 + bT + c, 400\text{ °C} \leq T \leq 550\text{ °C} \quad (5.3)$$

where a ($\times 10^{-6}$), b ($\times 10^{-3}$) and c ($\times 10^{-0}$) are coefficients to be determined from the DTG results. The extrapolation of the quadratic polynomial curve beyond 400 °C and 550 °C should match the DTG results to ensure continuity. This curve demarcates the effects of decomposition due to the amorphous phase from CH for a given specimen. The coefficients for the polynomial used in the interpolation of DTG are listed together with the plot of DTG for various mix proportion (Figure 5.5 to Figure 5.9).

Figure 5.5: Typical DTG for HCP28

Figure 5.6: Typical DTG for HCP35

Figure 5.7: Typical DTG for HCP40

Figure 5.8: Typical DTG for HCP45

Figure 5.9: Typical DTG for BCP40

Calculate Analytical TGA results without CH

The quadratic polynomial curve used to interpolate the DTG between the temperature 400 °C and 550 °C will affect the TGA results for the specimen. The analytical TGA result, which excludes the percentage of mass loss due to the decomposition of CH, was back calculated using Goal Seek in Microsoft Excel. The process is automated using Macro for data points with temperature greater than 400 °C which corresponds to the start of the decomposition of CH. A typical TGA result showing the percentage of mass remaining and the breakdown of percentage of total mass loss due to amorphous phase and CH is given in Figure 5.10. Both profiles have the same percentage of mass remaining and rate of decomposition for temperature less than 400 °C. Deviation of the two profiles occurs after 400 °C due to the decomposition of CH. The rate of decomposition for amorphous hydrates for both profiles (experimental and analytical) at temperatures greater than 550 °C remains unchanged. The difference in percentage of total mass remaining at various elevated temperature between the analytical and experimental TGA results corresponds to the percentage of mass of CH decomposed

while the percentage of mass of amorphous hydrate decomposed is taken to be the difference between 100 (%) and analytical TGA.

Figure 5.10: Typical TGA Result Showing Effects of CH for HCP28

Calculate decomposition profile of various phases

The fraction of amorphous phase ($f_h(T)$) and CH ($f_p(T)$) decomposed at elevated temperature is determined using Equation (5.4) and (5.5) respectively.

$$f_h(T) = \frac{100 - M_{an,T}}{100 - M_{an,900}} \quad (5.4)$$

$$f_p(T) = \frac{M_{an,T} - M_{ex,T}}{M_{an,900} - M_{ex,900}} \quad (5.5)$$

The term M refers to the percentage of total mass remaining. The first subscript ‘an’ and ‘ex’ refer to analytical and experimental TGA results, respectively, and the second subscript indicates the temperature (°C). The temperature of 900 °C is selected as it is

the last data point measured from TGA and DTG is close to zero, which indicates the end of decomposition of the hydration products. The fraction decomposed is then referenced from 105 °C to remove the effects of evaporable moisture loss on total mass loss in the specimen (Figure 5.11).

Figure 5.11: Derived Fraction Decomposed of Various Phases for HCP28

It can be observed from Figure 5.11 that the crystalline CH decomposed rapidly and completely within the temperature range of 400 °C to 550 °C whereas amorphous hydrates experienced a gradual decrease in the rate of decomposition between 105 °C and 900 °C. The observations made in the present study are consistent with Harmathy's observations (1970).

5.3.1 Influence of Temperature Range at which CH Decompose

The temperature range at which CH decomposed was chosen to be between 400 °C and 550 °C. This temperature range differs slightly from the reported temperature range by various researchers. Table 5.2 list the observed temperature range at which CH

decompose in various researches. The same analytical procedure was repeated except that the temperature range at which CH decompose was selected to be 380 °C to 600 °C. The coefficients for the quadratic polynomial to interpolate the rate of decomposition for C-S-H gel remained the same for both analyses. The final decomposition profile for both analyses was exactly the same, which indicate that the range of temperature range at which CH decompose does not influence the decomposition profile for both C-S-H gel and CH. The analytical procedure requires that the extrapolation of the quadratic polynomial to match the DTG results to ensure continuity. The decomposition profile obtained using the analytical procedure in the previous section did not change as long as the rise in DTG due to decomposition of CH occurred within the temperature limits of 380 °C to 600 °C.

Table 5.2: Observed Temperature Range at which CH Decompose

Source	Temperature Range (°C)
Bazant and Kaplan (1996)	450 - 550
Harmathy (1970)	380 - 600
Taylor (1990)	425 - 550

Figure 5.12: DTG of Pure CH

A TGA analysis was performed on a laboratory grade CH (purity at least 95%) at 10 °C/min to determine the influence of other types of CH on the temperature range at which CH decompose. The plot of DTG for pure CH given in Figure 5.12 shows that decomposition of CH occurred within the range 400 °C to 500 °C, which is within the assumed range of 400 °C to 550 °C. The difference in observed temperature by various researchers at which CH decomposed is probably due to the difference in experimental methodology which is discussed in Section 5.2. Hence, it can conclude that the assumed temperature range is both valid and conservative.

5.3.2 Influence of Mix Proportions

The decomposition profile of various mix proportions is presented in Figure 5.13 using the same procedure as stated in the previous section. All profiles showed similar trends and indicate that decomposition profile of various phases was independent of the mix proportions which includes w/c and inclusion of pozzolana. The effects of mix proportions is removed since the procedure considers the percentage of total mass loss at elevated temperature with respect to the percentage of total mass loss at the end of decomposition (900 °C).

The decomposition profile in Figure 5.13 for silica fume blended cement paste (BCP40) and normal cement paste (HCP40) was also observed to be the same. The presence of silica fume reacts with CH release from the chemical reactions of cement powder to form additional amorphous hydrates. Pozzolanic reaction alters the volume of each phase in the specimen but not the behaviour of decomposition. The proposed method derives the decomposition profile from the ratio of percentage of total mass loss and it eliminates the volume effect of each phase. Hence, pozzolanic reaction does not affect the decomposition profile of hydration products.

Figure 5.13: Decomposition Profile for Various Mix Proportion

5.3.2.1 W/C Ratio & Degree of Hydration

In general, different w/c values will result in a hardened cement paste with different volumes of hydration products and pores. The total volume of hydration products in hardened cement paste is generally higher for low w/c (HCP35) when compared with high w/c (HCP45) at the same degree of hydration. Since hydration products release moisture when they decompose, hardened cement paste with a large volume of hydration products will experience high total mass loss when steam escapes into the atmosphere. The degree of hydration is an important parameter which governs the volume of hydrates in hardened cement paste. It is an index ($0 < \alpha < 1$) to show the fraction of cement powder which had completed the hydration process. Specimens with a high degree of hydration generally have more hydrates when compared with specimen of a low degree of hydration (same mix proportions), leading to a higher total mass loss.

Unreacted cement powder and silica fume, which does not release non-evaporable moisture when heated, appear as dead weight and do not affect the ratio of the

percentage of total mass loss at elevated temperature with respect to the percentage of total mass loss at the end of decomposition. Deriving the decomposition profile of the various phases from the percentage of total mass loss has the effect of equating unit volume to each phase, thereby removing the effect of different phase volume within the hardened cement paste.

Effects of w/c, degree of hydration and inclusion of silica fume in hardened cement does not influence decomposition profile of hydration products. The total mass loss of chemically bound moisture can be determined if the volume of each phase is known.

5.3.2.2 Volume Ratio of Amorphous Hydrates to CH

The volume ratio of amorphous hydrates to CH is important if the decomposition profile is to be applied to blended cement paste. In this research, the decomposition profile was observed to be independent of the volume ratio of the hydration products because the effects of various phases were identified in DTG. Table 5.3 shows the simulated volumetric ratio of each phase for the various test specimens after 28 days of curing at 20 °C and 100% relative humidity using CemMicro (Ji, 2003). The volume ratio of amorphous hydrates to CH is typically constant at 4.012 for normal cement paste. This is due to the volume stoichiometry relationship of the chemical reactions used in Jennings and Tennis's Equations.

Table 5.3: Predicted Volumetric Ratio of Various Phases using CemMicro

Specimen ID	V_{C-S-H}	V_{AFm}	$V_{amorphous}$	V_{CH}	$V_{amorphous}/V_{CH}$
HCP28	0.371	0.178	0.549	0.137	4.012
HCP35	0.405	0.194	0.599	0.149	4.012
HCP40	0.414	0.198	0.612	0.153	4.012
HCP45	0.412	0.198	0.610	0.152	4.012
BCP40	0.482	0.175	0.657	0.093	7.075

However, the volume ratio of amorphous hydrates to CH for silica fume blended cement paste increases from 4.012 to approximately 7.075. The increase in volume ratio is due to the occurrence of pozzolanic reaction which consumes CH released from the reaction of cement powder to form additional amorphous hydrates. Since the

decomposition profile is independent of the volume ratio of amorphous hydrates to CH, it can also be applied to other types of blended cement paste such as Fly Ash (FA) and Ground Granulated Blastfurnace Slag (GGBS) with various percentage of cement replacement. The total mass loss due to decomposition of hydration products can be determined if the volumetric ratio of each phase is known.

5.3.3 Total Mass Loss at Thermal Equilibrium

Heating scenario can vary significantly from household fire to industrial fire. This poses a problem for both engineers and researchers when trying to predict fire resistance of the concrete element using different heating rate in heat and mass transfer simulation. It was observed from this investigation that the total mass loss experienced in the specimen in transient heating is dependent on the temperature increment instead of rate of heating. This observation was also reported by Castellote *et al.* (2004) in their investigation of microstructural investigation of heated hardened cement paste. The type of specimen used in the investigation does not have an effect on total mass loss if thermal equilibrium is satisfied. This would imply that the decomposition profile for the hydration products obtained in this research can be applied to different heating scenario if the temperature profile within the heated specimen is known.

Ground specimens (particle size $< 150 \mu\text{m}$) instead of cubes are generally used in TGA. The advantage of using ground specimen is that specimens can reach thermal equilibrium in a shorter duration and it does not restrict the escape of moisture. Since ground specimen is small in size, thermal gradient between exposed surface and centre core will be small in transient heating. Ground specimen does not restrict moisture release due to the decomposition of hydration products as the distance moisture molecules have to travel before reaches atmosphere is short. Therefore, the instantaneous total mass recorded will corresponds to the total mass reading at steady state. The main effect of using large size fragment will be the occurrence of large thermal gradient within the specimen during transient heating. Only the surface of the fragment is heated and experience decomposition. The total mass reading which consists of a small portion of decomposed amorphous hydrates and a large portion of

unheated hardened cement paste makes quantification of the mass loss of various phases difficult.

Table 5.4: Total Mass Remaining (%) At Elevated Temperature for HCP35

Temperature (°C)	Ground	Fragment	Mass Ratio
105	92.169	92.163	1.000
200	86.900	88.441	0.983
400	82.044	83.770	0.979
600	76.507	79.449	0.963
800	75.952	77.911	0.975

An investigation on the effects of various heating program on total mass loss was conducted. The total mass loss of both fragments (approximately 5 mm³) and ground specimens are approximately the same if the fragments have attained thermal equilibrium. Table 5.4 shows the percentage of total mass remaining in the specimen at elevated temperature. The percentage of total mass remaining for ground specimens is obtained from TGA while fragment specimens is obtained after holding the targeted temperature for an addition of two hours in an electric furnace. The rate of heating used in both tests is fixed at 10 °C /min. The mass loss in fragment is typically slight less than mass of ground specimen. The maximum difference in mass for both types of specimen occurred at 600 °C at 3.7%. Hence, it can be concluded that the mass loss experienced by the various phases using different types of heating is dependent on the temperature increment and not rate of heating if the condition of thermal equilibrium within the specimen is satisfied.

5.3.4 Effects of Decomposition on Physical Structure of Amorphous Hydrates

Hydration begins when cement particles comes in contact with water. Amorphous hydrates of various shapes and size start to form and conglomerate. This will lead to different degree of hydration for various sizes of cement particles. Cement particle expands when hydrated, occupying the spaces that is previously occupied by water. Hardened cement paste is hardly homogeneous as hydrated cement particle and pores are randomly distributed within the volume enclosed. Due to the complexity of hardened cement paste, certain assumptions were made in order to determine the mechanism of decomposition.

5.3.4.1 Physical and Chemical Properties of C-S-H Gel

C-S-H gels are irregular in shape. An accurate theoretical derivation on the decomposition function would require treating each C-S-H gel as unique object with specific geometric shape. This poses difficulty in obtaining geometric properties of each C-S-H gel and in computation. Assumptions are made to simplify derivation of the decomposition profile. C-S-H gel particles are assumed to be spherical and colloidal in nature (Figure 2.2). This assumption is made in order to be consistent with the assumptions made in C-S-H models such as Powers-Brunauer model and Munich model (Jennings *et al.*, 1996). Dark spots in Figure 2.2 represent C-S-H gels while 'C' marks the capillary pores in hardened cement paste.

The volume of amorphous hydrates (including gel pores) was observed to increase by 220% when compared with unreacted cement particle (Breugel, 1995). This will correspond to an increase in diameter by 30.06%. The simplified amorphous hydrate structure which shows the boundary before and after hydration is given in Figure 5.14. The average diameter of C-S-H gel is reported to be 20 nm (Jennings, 2000; Ji, 2003).

Figure 5.14: Simplified Amorphous Hydrate Structure

Chemical composition, like C-S-H gel size, also varies from particle to particle. It is difficult to measure the chemical composition of a cement particle due to the small size. Hence, it is assumed that the chemical composition of each C-S-H gel is homogeneous. This implies that every C-S-H gel experience the same rate of decomposition. The degree of hydration is also assumed to be one, which means that the cement particles have completed the hydration process. This is to simplify the derivation by removing the effects of unreacted cement particles residing in the C-S-H gels.

5.3.4.2 Decompose Depth

The decomposition profile of amorphous hydrates presented in Figure 5.11 shows that the amorphous hydrates experience high rate of decomposition in the early stages of heating and approaches zero towards the end of decomposition at 900 °C. The decompose depth, δ_i , at various elevated temperature can then be determined by equating the percentage reduction in volume of each C-S-H gel to the decomposition profile of amorphous hydrate. It is assumed that the amorphous hydrate boundary will reduce back to the original cement particle boundary when moisture molecules break off from the amorphous hydrates. The calculated decompose depth at various elevated temperature is shown in Figure 5.15. However, if the degree of hydration is less than 1, the volume increase in the amorphous hydrate will be less than 220%. Specimens with high degree of hydration will experience a high rate of change in radius. The volume of amorphous hydrate that will decompose when heated will correspond to the net increase in volume during hydration. C-S-H gel structure remains the same with less water molecules surrounding the core of unreacted cement particle.

Figure 5.15: Decompose Depth at Various Elevated Temperature

The behaviour of decompose depth at various elevated temperature is due to the water molecules which are chemically bound at the outer edge of each gel as shown in Figure 5.16. Moisture molecules residing in C-S-H gel starts to evaporate when heat is supplied. The loss in moisture molecule starts from the surface (which contains the most) and propagates towards the centre of the C-S-H gel. This will lead to a simultaneous reduction in radius and surface area of each C-S-H gel.

Figure 5.16: Simplified C-S-H Gel Structure (Odler, 1998)

Hence, it can be concluded that moisture molecules released during the decomposition of C-S-H gel causes shrinkage. The effect is greatest during the initial stages of decomposition and decreases to zero at 900 °C regardless of the degree of hydration.

5.4 Predicting Non-Evaporable Moisture Loss for Different Mix Proportion

Non-evaporable moisture is released during the decomposition of various phases. However, different mix proportion with different volumetric ratio of various phases will produce different non-evaporable moisture loss. The lack of works relating non-evaporable moisture release and mix proportion limits the application of heat and mass transfer simulation. The total mass of non-evaporable moisture release is calculated by observing the flowchart given in Figure 5.17. The total mass of non-evaporable moisture release is dependent on the volume of amorphous hydrates and CH in the

specimen and can be determined by using existing microstructure hydration model. V_{Other} is assumed to be the volume corresponding to AFm phase.

Figure 5.17: Flow Chart for Determining Non-Evaporable Moisture Loss

Once the volume of various phases are determined, Equation (5.6) is then used to calculate the total mass loss of chemically bound moisture per unit volume of hardened cement paste (kg/m^3) for $T > 105^\circ\text{C}$.

$$w_d \text{ (kg/m}^3\text{)} = k_m \left(\sum_{i=a,c,p} f_i(T) V_i k_i \rho_{i,w} \right) \quad (5.6)$$

The subscript i denotes the AFm hydrates (a), C-S-H hydrates less gel pores (c) and portlandite (p) phase in hardened cement paste. The decomposition function, $f_i(T)$, is obtained from Figure 5.11. The same decomposition profile is applied for both AFm and C-S-H hydrates. The volumetric ratio of each phase, V_i , can be calculated using

available hydration model of cement paste. The volumetric ratio of moisture within a phase, k_i , is determined using volume stoichiometry relationship. Density of moisture in the phase, $\rho_{i,w}$, is assumed to be 1000 kg/m³ (Bazant and Kaplan, 1996). The regression constant (k_m) was determined to be 0.791 from experimental results.

A total of three k_i is required in Equation (5.4). The molar volume for AFm hydrate, C-S-H hydrate, CH and water are 22.9, 12.8, 3.31 and 1.8 (10⁻⁵ m³/mol) respectively (Jennings and Tennis, 1994). The volumetric ratio of moisture is calculated by taking the ratio of the volume of moisture in one mole of each phase over the molar volume of that phase and the values are given below.

$$k_a = \frac{8 \times 1.8}{22.9} = 0.6288, k_c = \frac{3 \times 1.8}{12.8} = 0.4219, k_p = \frac{1.8}{3.31} = 0.5438$$

The regression coefficient was calibrated by fixing the predicted mass loss of fully hydrated cement paste with established non-evaporable water content relationship given in Equation (5.7) and Equation (5.8). The non-evaporable moisture content for a fully hydrated specimen is approximated to be 23% by mass of anhydrous cement (Neville, 1996). Hence, only specimens HCP40 and HCP45 were used to calibrate k_m .

$$k_m = \left(0.23 + \frac{\text{LOI}}{100} \right) \left(\frac{C}{W_n} \right) \quad (5.7)$$

$$W_n = \sum_{i=a,c,p} V_i k_i \rho_{i,w} \quad (5.8)$$

Table 5.5: Calculation of k_m

Specimen ID	C (kg/m ³)	W_n (kg/m ³)	k_m
HCP40	1393.805	423.493	0.791
HCP45	1302.999	395.902	0.791

Table 5.5 shows the result of the computation. The same procedure does not apply to BCP40 due to the alteration of the volume ratio of amorphous hydrates to CH (Table

5.3) by pozzolanic reaction. However, the same regression coefficient obtained for normal hardened cement paste can be applied to blended hardened cement paste.

Figure 5.18 to Figure 5.22 show the comparison of non-evaporable moisture loss using Hilsdorf's Equation, Tenchev's Equation and the proposed equation (Equation (5.6)) with experimental results. The sudden moisture release occurring at approximately 400 °C due to the decomposition of CH was simulated. It can be observed that Equation (5.6) gives the best prediction for both normal and blended hardened cement paste. Generally for hardened cement paste, both Hilsdorf's and Tenchev's Equation slightly underestimate the mass of non-evaporable moisture loss throughout the range of elevated temperature except that Tenchev's Equation tends to overestimate the mass of non-evaporable moisture loss significantly at temperatures greater than 600 °C. Neither Hilsdorf's nor Tenchev's equations are able to predict non-evaporable moisture for BCP40 accurately due to the pozzolanic reaction in blended hardened cement paste. The effect of pozzolanic reaction is considered in Equation (5.6) through the use of volumetric ratio of hydration products in the formulation.

Figure 5.18: Non-Evaporable Moisture Loss for HCP28

Figure 5.19: Non-Evaporable Moisture Loss for HCP35

Figure 5.20: Non-Evaporable Moisture Loss for HCP40

Figure 5.21: Non-Evaporable Moisture Loss for HCP45

Figure 5.22: Non-Evaporable Moisture Loss for BCP40

The proposed equation can also be extended to both cement mortar and concrete. The key difference between hardened cement paste, cement mortar and concrete is the inclusion of sand and aggregate into the mix proportion. Sand and aggregates does not react with cement powder to produce more hydrates. Instead, water residing on the surface and pores of sand and aggregates will increase the effective water content of the design mix. This will generally increase the rate of hydration and affect the quantity of non-evaporable moisture released during heating. Water content of sand and aggregates used in the cement mortar and concrete should be measured and taken into account as part of the total water added into the design mix.

5.5 Summary

An analytical procedure was used to derive the decomposition profile of amorphous hydrates and calcium hydroxide. Decomposition profiles for the various phases in normal and blended hardened cement paste were observed to be the same. Decomposition of amorphous hydrates was most rapid at the early stages of heating and approached zero at 900 °C. Crystalline calcium hydroxide decomposed within the range 400 °C to 550 °C. Decomposition of amorphous hydrate will lead to a reduction in radius. Specimens with high degree of hydration will experience a higher rate of change in radius than specimens with low degree of hydration.

A non-linear model to predict non-evaporable moisture based on the findings of the decomposition profiles of hydration products was proposed. The quantity of non-evaporable moisture loss can be predicted if the volumetric ratio of each phase is known. Both predicted and experimental results of non-evaporable moisture loss are in accordance. Non-evaporable moisture loss for both normal and blended hardened cement paste were better predicted using the proposed method than existing methods.

Chapter 6: Residual Porosity of Hardened Cement Paste

6.1 Introduction

Mechanical properties of concrete such as compressive strength and durability are dependent on the porosity of concrete. Porosity is a measure of the total volume of pores within an enclosed volume. At elevated temperature, porosity generally starts to increase (Harmathy, 1970; Khoury, 1992). This is because the space previously filled by chemically bound moisture within the hydration products becomes available when heated and connects with capillary pores. This will lead to a reduction in mechanical properties and may cause concrete elements to fail in the event of a fire.

The relationship between porosity and elevated temperature is used in the simulation of heat and mass transfer in heated concrete elements (Bazant and Thonguthai, 1979; Majumdar *et al.*, 1995; Tenchev *et al.*, 2001). The objective of the simulation is to predict the occurrence of explosive spalling. The impacts of porosity on explosive spalling are two fold: 1) High porosity would reduce pore pressure as there is a larger space to contain vapour and 2) High porosity would increase the permeability of heated concrete as it allows vapour to escape from heated concrete. Therefore, there is a need to establish a porosity-temperature model to facilitate research on spalling.

Limited works were published on the behaviour of porosity of hardened cement paste subjected to elevated temperature. The analysis on the pore size distribution is also scarce. As such, researchers often adopt published porosity-temperature profile to simulate heat and mass transfer in heated concrete. However, such profiles may not be applicable as the concrete used in the simulation is different from published results. Difficulties in predicting residual porosity also arise when mineral admixtures such as pozzolanas are added into the mix proportions. Mineral admixtures alter the microstructure of concrete and have an effect on change in porosity at elevated temperature.

Ideally, the porosity of concrete at elevated temperature should be used in the simulation of heat and mass transfer. No experimental works have been conducted due to the limitation of porosimetry test. Instead, Bazant and Thonguthai (1979) suggested that porosity of heated concrete can be predicted by adding initial porosity of unheated concrete with the percentage change in volume due to moisture loss associated with the dehydration of C-S-H gel and decomposition of the portlandite. The feasibility of using porosity calculated from chemically bound moisture loss is yet to be established.

This chapter forms part of the study of the microstructural changes in hardened cement paste subjected to elevated temperature. The objective of this chapter is to determine the behaviour of porosity in hardened cement paste after subjected to elevated temperature. A model for predicting residual porosity for various mix proportion subjected to elevated temperature is proposed. The residual porosity of four different types of hardened cement paste heated to various elevated temperatures was evaluated. The proposed model is verified using residual porosity obtained from this research. The feasibility of using porosity of heated concrete derived from loss of chemically bound moisture is also investigated.

6.2 Development of A Model for Residual Porosity

6.2.1 Proposed Model for Hardened Cement Paste

Porosity of cement mortar and concrete after exposing to elevated temperature were reported by researchers (Janotka and Bagel, 2002; Luo *et al.*, 2000; Poon *et al.*, 2001; Vodak *et al.*, 2004) but models to predict porosity subjected to elevated temperature is scarce. In order to integrate the behaviour of porosity at elevated temperature into the simulation of heat and mass transfer, Tenchev *et al.* (2001) modelled the change in porosity using a cubic polynomial based on the residual porosity data by Luo *et al.* (2000). The equation to predict porosity subjected to elevated temperature is given as:

$$n_T = n_0 \times \begin{cases} 1 & , T < 100^\circ\text{C} \\ aT^3 + bT^2 + cT + d & , 100^\circ\text{C} \leq T \leq 800^\circ\text{C} \\ 3 & , T > 800^\circ\text{C} \end{cases} \quad (6.1)$$

where n_T , n_0 and T refer to porosity subjected to elevated temperature (m^3/m^3), initial porosity before heating (m^3/m^3) and temperature ($^{\circ}\text{C}$) respectively. The regression coefficients of a , b , c and d were not given and dependence with mix proportion was not identified. Attempts to determine the regression constant was unsuccessful due to insufficient experimental data published in Luo's *et al.* (2000) paper. Equation (6.1) is expressed as a function of initial porosity, which implicitly means that the change in porosity due to elevated temperature is dependent on the volume of hydrates existing within the specimens. Therefore, factors affecting volume of hydrates such as mix proportion and degree of hydration should be included in the model.

An equation that addresses the above limitations is proposed in this section. Residual porosity obtained from MIP test was used to calibrate the proposed model. The proposed equation to predict residual porosity for hardened cement paste subjected to elevated temperature (n_T) is given below.

$$n_T = n_0 + \Delta n_T, 20^{\circ}\text{C} \leq T \leq 800^{\circ}\text{C} \quad (6.2)$$

$$\Delta n_T = k_1 V_{hyd} \left(\frac{T - T_0}{100} \right)^{k_2} \quad (6.3)$$

where n_0 , T_0 , T and V_{hyd} are porosity of unheated hardened cement paste (%), initial temperature ($^{\circ}\text{C}$), elevated temperature ($^{\circ}\text{C}$) and volumetric ratio of hydration products excluding gel pores respectively. The derivation of n_0 and V_{hyd} will be discussed later. k_1 and k_2 was found to be 2.35 and 1.37 respectively. The equation is simple and is able to be applied to various mix proportions.

The total change in porosity (Δn_T) due to elevated temperature expressed in Equation (6.3) is dependent on the temperature increment $\left(\frac{T - T_0}{100} \right)$. This implies that the porosity profile within a transient heated specimen is dependent on the temperature contour instead on the rate of heating. Only the rate of change in porosity on the surface exposed to direct heat with respect to time can be predicted using chain rule if the rate

of change in porosity with respect to a change in temperature $\left(\frac{dn_T}{dT}\right)$ and rate of heating $\left(\frac{dT}{dt}\right)$ are known. $\frac{dn_T}{dT}$ is calculated using central difference method as shown in Equation (6.4). $\Delta n_{T+\Delta T/2}$ and $\Delta n_{T-\Delta T/2}$ is calculated by replacing T with $T + \Delta T/2$ and $T - \Delta T/2$ respectively into Equation (6.3).

$$\frac{dn_T}{dT} = \frac{\Delta n_{T+\Delta T/2} - \Delta n_{T-\Delta T/2}}{\Delta T} \quad (6.4)$$

By applying the chain rule, the rate of change in porosity on surface exposed to direct heat with respect to time (t) can be calculated using Equation (6.5).

$$\frac{dn_T}{dt} = \frac{dn_T}{dT} \frac{dT}{dt} \quad (6.5)$$

6.2.2 Derivation of n_0 and V_{hyd}

Porosity generally increases when subjected to elevated temperature. Since the space previously filled by chemically bound water becomes available upon heating, it can be deduced that the change in total porosity will be dependent on the volume of hydrates in unheated state. Specimens having high cement content and high degree of hydration generally contain more hydration products which lower n_0 in unheated hardened cement paste. Experimental investigations conducted in this research shows that specimens with large volume of hydration products experience larger increase in total porosity. Hence, there is a necessity to include the volumetric ratio of hydration products into the proposed model.

V_{hyd} is preferred instead of using water/cement ratio (w/c) in Equation (6.3). W/c only states the proportion of water and cement by mass used in concrete making and does not give any indication on the microstructure of the specimen. In concrete making, the volume of water and cement in mix proportions is often less than the volume of sand and aggregate. The behaviour of porosity of concrete subjected to elevated temperature

is independent of sand and aggregate since sand and aggregate does not introduce additional pores into concrete when heated and are excluded from the formulation. It is also difficult to introduce a correction factor that couple with w/c to represent the effective volume of concrete contributing to the change in total porosity due to difference in degree of hydration. Furthermore, the inclusion of pozzolana in concrete making cannot be accounted for in the formulation if w/c is used. Thus, the usage of w/c in the formulation greatly limits the applicability of the model.

V_{hyd} for hardened cement paste with various degree of hydration (α) can be determined using various hydration models. Corrections should also be made to the volume of C-S-H gel determined from hydration models due to the presence of gel pores. The volume of gel pores within C-S-H gel was reported to be about 28% and 19% for C-S-H gel produced from normal cement hydration and pozzolanic reaction, respectively (Copeland and Hayes, 1953; Ji, 2003). This is because the volume of gel pores is already accounted for in porosity measurement and should be removed from the volume of C-S-H gel to avoid double counting.

Figure 6.1: Effects of V_{hyd} on Δn_T (Equation 6.3)

The influence of V_{hyd} on Δn_T given in Equation (6.3) is shown in Figure 6.1. It can be observed that specimens with higher V_{hyd} experience a larger increase in porosity after subjected to various elevated temperature. The calculation of n_0 and V_{hyd} for various mix proportion can be classified into 2 categories.

Case 1: Normal Hardened Cement Paste

n_0 is to be determined from unheated hardened cement paste using MIP. If such data is unavailable, it can be approximated using hydration model. V_{hyd} is calculated using Equation (6.6).

$$V_{hyd} = V_a + V_c + V_p \quad (6.6)$$

where V_a , V_c and V_p are volumetric ratio of AFm phase, C-S-H gel less gel pores and calcium hydroxide in hardened cement paste calculated using volume stoichiometry relationship given in Appendix B respectively. However, the use of hydration model to calculate n_0 and V_{hyd} may be a difficult task for practising engineers. Hence, Figure 6.2, Figure 6.3 and Table B.2 which show the effects of w/c and α on n_0 and V_{hyd} calculated using Appendix B can be used to simplify the task. Results from the calculation are only applicable to hardened cement paste with $0.2 \leq w/c \leq 0.6$. Since n_0 and V_{hyd} are observed from Figure 6.2 and Figure 6.3 to vary linearly with α , linear interpolation can be used to determine intermediate values that are not shown.

It is recommended that α to be calculated by taking the ratio of total mass loss between 105 °C and 1050 °C measured from experiment over the total mass loss for a fully hydrated cement paste which is approximated to be 23% by mass of anhydrous cement (Lam *et al.*, 2000; Powers and Brownyard, 1946). This is to avoid errors introduced by the presence of unreacted cement powder in specimens having $w/c \leq 0.38$. Specimens with $w/c \leq 0.38$ cannot attain complete hydration even after long period of curing (Neville, 1996). Unreacted cement powder present in hardened cement paste for $\alpha < 1$ remains as fillers within the specimen and does not affect the change in porosity.

Figure 6.2: Effects on W/c and α on n_0

Figure 6.3: Effects on W/c and α on V_{hyd}

Using the method of taking the ratio of total mass loss between 105 °C and 1050 °C with total mass loss between 105 °C and 1050 °C after a year of curing (Ji, 2003) will produce a high value of α and overestimate V_{hyd} .

Alternatively, it is also possible to determine the volumetric ratio of the hydration products for fully hydrated cement paste ($w/c > 0.38$) if the volume of pores within hardened cement paste is known. A fully hydrated cement paste consists of only hydration products and pores. V_{hyd} can be calculated by taking the difference between the unit bulk volume of specimen and volume of pores as shown in Equation (6.7).

$$V_{hyd} = 1 - \frac{n_0}{100}, \alpha \approx 1 \text{ and } w/c > 0.38 \quad (6.7)$$

Thus, the volumetric ratio of hydration products for hardened cement paste can be determined if w/c and α are known. Good predictions for the various types of hardened cement paste were achieved using Equation (6.2) as shown in Figure 6.4 to Figure 6.7.

Figure 6.4: Experimental and Predicted Porosity for HCP28

Figure 6.5: Experimental and Predicted Porosity for HCP35

Figure 6.6: Experimental and Predicted Porosity for HCP40

Figure 6.7: Experimental and Predicted Porosity for HCP45

Case 2: Blended Hardened Cement Paste

Pozzolanas are often added into the mix proportions to create blended hardened cement paste which has higher compressive strength than normal hardened cement paste. Water/binder ratio (w/b) is used to describe the mix proportions of cement and pozzolana instead of w/c. The type and amount of pozzolana added to design mix affects the volume of hydrates formed. The common types of pozzolana added into the design mix are Silica Fume (SF), Ground Granulated Blastfurnace Slag (GGBS) and Fly Ash (FA). The typical chemical and physical properties for Ordinary Portland Cement (OPC) and pozzolana are given in Table 6.1.

The percentage of replacement in SF tends to be lower than GGBS and FA. Pozzolanic reaction is dependent on the chemical and physical properties of each particle. Mix proportion with high percentage replacement of cement may not produce sufficient calcium hydroxide to react with pozzolana. The remaining unreacted pozzolana, being small in particle size, will remain in the concrete as fillers and reduces the volume of

pores in unheated blended hardened cement paste. Hence, the determination of V_{hyd} in Case 2 is more difficult than in Case 1 and requires the use of hydration model.

The calculation of V_{hyd} in blended hardened cement paste is different from normal hardened cement paste. V_c , which typically occupying more than 50% of V_{hyd} , requires a reduction factor when calculating V_{hyd} . It was observed from experimental results that BCP40 experienced a smaller increase in residual porosity than HCP40 despite having the same porosity at unheated state. The gel porosity, which corresponds to 19% for C-S-H gel formed under pozzolanic reaction, contribute less to total porosity after subjected to elevated temperature when compared with 28% for C-S-H gel formed under normal cement hydration. V_{hyd} for blended hardened cement paste is to be determined using Equation (6.8).

$$V_{hyd} = V_a + \left(1 - \left(\frac{V_{c,poz}}{V_{c,nor} + V_{c,poz}} \right) \left(\frac{0.72}{0.81} \right) \right) V_c + V_p \quad (6.8)$$

where $V_{c,poz}$ and $V_{c,nor}$ refer to volumetric ratio of C-S-H gel including gel pores form under pozzolanic and normal cement hydration respectively.

The probable combination of w/b, percentage of replacement of cement with pozzolana, chemical and physical properties of pozzolana and α are too many. To simplify the process of determining n_0 and V_{hyd} , a series of tables in Appendix B showing the relationship of w/b, α and percentage of pozzolana replacement of cement can be used. Linear interpolation can be used to determine n_0 and V_{hyd} for w/b, α and percentage of cement replacement not listed in the tables. The results were generated using CemMicro and the chemical and physical properties of the materials used in mix proportion are listed in Table 6.1. Equation (6.7) can also be used to determine V_{hyd} for specimens with $\alpha \approx 1$. Good predictions were achieved (Figure 6.8) using the reduction factor given in Equation (6.8).

Table 6.1: Chemical and Physical Properties of OPC and Pozzolana

	OPC	SF	GGBS	FA
CaO	64.34	0.24	44.80	5.70
SiO ₂	20.25	99.12	34.40	44.90
Al ₂ O ₃	3.84	0.31	9.00	35.40
Fe ₂ O ₃	3.33	0.63	2.58	4.90
SO ₃	3.03	0.30	2.26	0.70
MgO	2.13	0.74	4.43	1.20
K ₂ O	0.33	0.92	0.50	1.00
Na ₂ O	0.21	0.27	0.62	1.00
Specific Surface Area (m ² /kg)	-	20,000	599	528
Specific Gravity	3.15	2.2	2.79	2.1

Figure 6.8: Experimental and Predicted Porosity for BCP40

6.2.3 Breakdown of Gel and Capillary Pores

An alternative method is required to predict the behaviour of gel pores after subjected to elevated temperature. This information is required in heat and mass transfer simulation which govern the permeability coefficient. The sum of gel pores at residual state ($n_{T,gel}$) can be predicted using Equation (6.9). The change in sum of gel pores at elevated

temperature ($\Delta n_{T, gel}$) is expressed as a function of the inverse of volumetric ratio of C-S-H gel (V_c) and a cubic polynomial calibrated from experimental data as given in Equation (6.10). $n_{0, gel}$ can either be determined from experiment or hydration model. V_c is to be calculated from hydration model or lookup using the tables attached in Appendix B. For degree of hydration not listed in the tables, $n_{0, gel}$ and V_c can be calculated using linear interpolation. Both experimental and predicted residual gel pores are in accordance as shown in Figure 6.9.

$$n_{T, gel} = n_{0, gel} + \Delta n_{T, gel} \quad (6.9)$$

$$\Delta n_{T, gel} = \frac{1}{V_c'} \left[-0.0181 \left(\frac{T - T_0}{100} \right)^3 + 0.2037 \left(\frac{T - T_0}{100} \right)^2 - 0.6845 \left(\frac{T - T_0}{100} \right) \right] \quad (6.10)$$

$$V_c' = \left(1 - \left(\frac{V_{c, poz}}{V_{c, nor} + V_{c, pox}} \right) \left(\frac{0.72}{0.81} \right) \right) V_c \quad (6.11)$$

Figure 6.9: Experimental and Predicted Residual Gel Pores

The sum of capillary pores ($n_{T, cap}$) can be calculated by taking the difference of n_T and $n_{T, gel}$ as given in Equation (6.9). Figure 6.10 shows the experimental and predicted residual capillary pores are in accordance.

$$n_{T, cap} = n_T - n_{T, gel} \quad (6.12)$$

Figure 6.10: Experimental and Predicted Residual Capillary Pores

6.2.4 Proposed Model for Cement Mortar and Concrete

The model proposed in the previous section can also be extended to cement mortar and concrete. The main difference between hardened cement paste, cement mortar and concrete is the inclusion of sand and aggregates into the mix proportion. The method to determine the residual porosity for heated cement mortar and concrete requires the understanding of experimental methodology related to MIP. MIP can be conducted on various types of cement-based materials. However, aggregates within the concrete are removed and porosity of the cement mortar is measured (Figure 6.11). This is because if sand is separated from hardened cement paste, the resultant hardened cement paste is

often flaky and unsuitable to be used in MIP. Sand is generally homogeneous and does not contain pores. Hence, the porosity in cement mortar measured using MIP represents the volume of pores within hardened cement paste.

Figure 6.11: Location of Specimen Used in MIP

The overall residual porosity for cement mortar ($n_{T,B}$) can be calculated using Equation (6.13).

$$n_{T,B} = n_{0,B} + k_1 V_{hyd,B} \left(\frac{T - T_0}{100} \right)^{k_2}, \quad 20^\circ\text{C} \leq T \leq 800^\circ\text{C} \quad (6.13)$$

$$V_{hyd,B} = \left(\frac{n_{0,B}}{n_0} \right) V_{hyd} \quad (6.14)$$

where the terms $n_{0,B}$, n_0 and $V_{hyd,B}$ refer to the unheated porosity of cement mortar (%), unheated porosity of hardened cement paste (%) and volumetric ratio of hydration products in a cement mortar system respectively. Correction factor for pozzolanic C-S-H gel shown in Equation (6.11) also applies to V_{hyd} . Both regression constant k_1 and k_2 remain the same at 2.35 and 1.37 respectively. Equation (6.14) is used to determine $V_{hyd,B}$ in a cement mortar if $n_{0,B}$ and n_0 are obtained from experimental investigation.

The term $\frac{n_{0,B}}{n_0}$ in Equation (6.14) calculates the volumetric ratio of hydration products

in the cement mortar system. Alternatively, $\frac{n_{0,B}}{n_0}$ can be predicted using Equation (6.15).

$$\frac{n_{0,B}}{n_0} = \frac{V_C + V_P + V_W}{V_C + V_P + V_W + V_S} \quad (6.15)$$

The terms V_C , V_P , V_W and V_S refer to volumetric ratio of Ordinary Portland Cement (OPC), volumetric ratio of pozzolana, volumetric ratio of water and volumetric ratio of sand in a cement mortar system respectively. Equation (6.15) assumes that the constituents of cement mortar are well mixed and is homogeneous. If $n_{0,B}$ in Equation (6.13) is unavailable, it can be calculated using Equation (6.15). n_0 can be predicted using tables attached in Appendix B if required. It can be observed from Equation (6.15) that $n_{0,B} = n_0$ and $V_{hyd,B} = V_{hyd}$ if $V_S = 0$. The formulation attempts to calculate $V_{hyd,B}$ by applying a reduction factor corresponding to the ratio of the volume of hydration products that will decompose when subjected to elevated temperature in a cement mortar system.

The proposed model to predict residual porosity for various types of cement mortar was verified with published results from various researchers (Poon *et al.*, 2001; Xu *et al.*, 2001). The data for porosity and predicted porosity are provided in Appendix A. Figure 6.12 shows the comparison between the porosity and predicted porosity. The two linear lines represent the linear trend line for two sets of data: 1) porosity data (hollow diamond) subjected to a maximum of 800 °C and 2) porosity data (solid diamond) subjected to a maximum of 650 °C which exclude the last data point at 800 °C in Appendix A. Figure 6.12 shows good correlation between predicted and measured porosity up to 650 °C. Equation (6.13) tends to underestimate residual porosity subjected to 800 °C. It was observed from published data by Poon *et al.* (2001) that residual porosity experienced a rapid increase after exposing to 650 °C. No explanation was made except that the rapid increase in residual porosity is responsible for the rapid decrease in residual compressive strength.

Figure 6.12: Comparison between Porosity and Predicted Porosity

Therefore, the net effect on total change in porosity is generally lower in cement mortar than in hardened cement paste by the volumetric ratio of hydration products. Sand, being siliceous in nature, is thermally stable until $573\text{ }^{\circ}\text{C}$ where α - β quartz (SiO_2) conversion takes place and increase the length of siliceous inclusions by 1.2% (Harmathy and Allen, 1973; Schneider, 1982). However, the reduction factor used in Equation (6.13) and (6.14) is taken at the unheated state. Hence, the formulation of $n_{0,B}$ and $V_{hyd,B}$ does not consider the volume increase in siliceous inclusion occurring at $573\text{ }^{\circ}\text{C}$.

The porosity-temperature relationship for concrete is required in heat and mass transfer simulation. However, such models are scarce. Researchers often used the porosity-temperature relationship for hardened cement paste in the simulation to predict pore pressure development in a concrete which is incorrect. Due to the experimental limitation of MIP, a theoretical derivation of the porosity-temperature for concrete is proposed. The same concept applied to cement mortar is also applied to predict porosity of concrete subjected to elevated temperature. The volumetric ratio of cement mortar in

concrete ($V_{B,A}$) is multiplied to $n_{T,B}$ to predict residual porosity of concrete ($n_{T,C}$) as given in Equation (6.16).

$$n_{T,C} = V_{B,A}(n_{T,B}), \quad 20\text{ }^{\circ}\text{C} \leq T \leq 800\text{ }^{\circ}\text{C} \quad (6.16)$$

$$V_{B,A} = \frac{V_C + V_P + V_W + V_S}{V_C + V_P + V_W + V_S + V_A} \quad (6.17)$$

V_A refers to the volumetric ratio of aggregates in the mix proportion. The thermal effects of inclusions are neglected in the determination of $V_{B,A}$ as the ratio is taken at the unheated state. $V_{B,A}$ can be calculated using Equation (6.17). Concrete is assumed to be homogeneous throughout. It can be concluded that the order of residual porosity from largest to smallest is hardened cement paste, cement mortar and concrete. Researchers (Tenchev *et al.*, 2001) tend to implement residual porosity of cement mortar instead of concrete to model heat and mass transfer in heated concrete. This may lead to overestimation of porosity at elevated temperature and underestimation of pore pressure since pressure is inversely proportional to volume of pore (Ideal Gas Law).

Gel porosity for cement mortar and concrete can be calculated by modifying V_c with the volumetric ratio of hydration products in cement mortar and concrete system respectively. Capillary porosity can be calculated by taking the difference between total porosity and gel porosity.

6.2.5 Influence of ITZ on Residual Porosity

The interface between aggregate and hardened cement paste is generally known as interface transition zone (ITZ). It extends from the surface to approximately 12 μm to 20 μm away from the face of sand and aggregate (Garboczi *et al.*, 1995; Shane *et al.*, 2000; Winslow *et al.*, 1994). Porosity within the ITZ of concrete is generally higher than hardened cement paste and has a distribution as shown in Figure 6.13.

Figure 6.13: Distributions of Pores in Aggregate-Paste Interface (Scrivener and Nemati, 1996)

The presence of ITZ does not change the hydration process. However, the water content in this region is typically higher than the paste itself (Shane *et al.*, 2000). This is because cement particles are unable to pack itself densely around the aggregate during mixing and water tends to fill this zone. This would mean the w/c ratio is higher than the mix proportion in ITZ and lower in hardened cement paste based on the conservation of mass of water in the mix proportion. Therefore, porosity within ITZ is generally higher than hardened cement paste.

Addition of pozzolana, particularly silica fume, into concrete will help in reducing the porosity and permeability when compared with a normal concrete. This is because silica fume is about 100 times smaller than cement particles (Neville, 1995). Silica fume will help in filling the voids between the aggregate and cement particle and reducing ITZ.

When concrete is subjected to elevated temperature, pores within the hardened cement paste widen due to the loss of non-evaporable moisture. Since the unheated porosity within the ITZ is higher than hardened cement paste, it implies that there is less hydration products existing within ITZ when compared with hardened cement paste. Based on the proposed Equations (6.2) and (6.3), the increase in porosity will be higher

in hardened cement paste than hardened cement paste in the ITZ due to the higher percentage of hydration products. Therefore, it can be concluded that the effect of ITZ on porosity and permeability in heated concrete should be decreasing as the temperature increase.

6.3 Analytical Derivation of Porosity at Heated State

Researchers (Bazant and Thonguthai, 1979; Harmathy, 1993) proposed to use chemically bound moisture loss at elevated temperature to calculate porosity in concrete at heated state. The principle behind the analytical derivation is based on the observation that loss of chemically bound moisture can lead to a reduction in volume at heated state. The analytical derivation proposed by them is able to address the limitations in existing porosity measurement techniques. Firstly, the analytical derivation is capable of calculating heated porosity that is required in heat and mass transfer simulation of concrete. Secondly, porosity calculated from loss of chemically bound moisture includes the volume of pores that are isolated and undetectable in MIP. Hence, this section investigates the difference in porosity for both methods.

The porosity of heated specimen based on the mass loss profile obtained from TGA ($n_{T,moist}$) for HCP35 is calculated using Equation (6.18). Figure 6.14 shows the result of the calculation. n_{105} , $w_{d,T}$ and ρ_L refer to porosity of specimen heated to 105 °C (%), mass of chemically bound moisture (kg/m³) and density of moisture (1000 kg/m³) (Bazant and Kaplan, 1996) respectively.

$$n_{T,moist} = n_{105} + \frac{w_{d,T}}{\rho_L} \times 100, 105^\circ\text{C} \leq T \leq 800^\circ\text{C} \quad (6.18)$$

Figure 6.14: Comparison of Heated and Residual Porosity for HCP35

Porosity of cement mortar and concrete of various mix proportions at heated state using Equation (6.18) can also be predicted by determining the volumetric ratio of hydration products for cement paste used in the mix proportion. The mass of chemically bound moisture can be predicted using the formulation proposed in Chapter 5.

Comparison of porosity at heated and residual state is conducted at temperature greater than 105 °C as loss of chemically bound moisture occurs at temperature above 105 °C. Porosity calculated using Equation (6.18) from chemically bound moisture loss is noticeably higher than the residual porosity measured from MIP. The largest difference occurs at 500 °C with 60% more porosity at heated state than measured porosity. The difference in porosity is due to the occurrence of shrinkage experienced in hardened cement paste when it loses chemically bound moisture. Shrinkage will lead to the formation of cracks within the specimen. These cracks do not form part of the volume of pores in MIP because mercury can easily intrude into the specimen at very low pressure even before the volume of pores is first measured. Hence, porosity obtained from MIP is lower than the analytical derivation. It can be deduced that such crack does

not lead to an increase in pore pressure when analysing explosive spalling as vapour pressure is released from the cracks. Pore pressure built up can only occur in uncracked location. In addition, Ideal Gas Law states an inverse relationship between gas pressure and volume. Overestimating the volume of pores in heated concrete will lead to an underestimation of pore pressure which may be unconservative in the analysis of explosive spalling. Hence, porosity-temperature behaviour obtained from MIP should be used in the analysis of explosive spalling instead of using analytical derivation based on non-evaporable moisture loss.

6.4 Conclusion

The volumetric ratio of hydration products is identified as an important parameter in the determination of residual porosity of heated hardened cement paste. The formulation established in hardened cement paste is extended to cement mortar and concrete using the volume of hydration products in cement mortar and concrete respectively. Both predicted and experimental results of residual porosity for hardened cement paste are in accordance. Residual porosity for hardened cement paste is the largest, followed by cement mortar and concrete. This is due to the presence of sand and aggregate in the mix proportion. The use of residual porosity of cement mortar instead of concrete in heat and mass transfer should be avoided as it will lead to underestimation of pore pressure due to overestimation in pore volume. Porosity calculated from loss in chemically bound moisture should not be used in the analysis of explosive spalling since it will underestimate pore pressure build up.

Chapter 7: Modelling of Heat and Mass Transfer in Cement-Based Materials

7.1 Introduction

The increase in terrorist activities and natural disasters around the world is presenting new challenges to both engineers and researchers. Fire, the aftermath of disaster, can present more danger to people trapped in buildings. This is because fire continues for a period of time till the exhaustion of available fuel or extinguishment by fire fighters. During this period, the surfaces of structural elements experience a rapid increase in temperature. Mechanical properties of building materials will deteriorate when exposed to elevated temperature and possibly collapse. Therefore, there is an increase in emphasis in determining the fire resistance of structural elements.

Fire resistance is commonly defined as the ability of an element in a structure to function satisfactorily whilst subjected to a prescribed load and temperature for a specified period of time. It is usually rated in hours (Eurocode 2 ENV 1992-1-2, 1996; Malhotra, 1982). A prescriptive method of designing concrete element for fire resistance given in AS 3600 (Section 5: 2001), BS 8110 (Part 1: Section 3:1985) and Eurocode 2 (ENV 1992-1-2: 1996) is through the use of concrete cover to limit heat transfer. An improved method of determining the fire resistance of a concrete element is to perform full scale heating on the actual concrete element. However, both methods do not consider the occurrence of spalling which is frequently experienced in rapidly heated environment. Once spalling occurs, concrete cover is removed and the reinforcements are exposed to direct heat. The concrete element will experience rapid reduction in load bearing capacity and will experience earlier failure than the rated fire resistance of that element (Ali *et al.*, 2001; Bailey, 2002; Dotreppe *et al.*, 1996). Spalling clearly pose a problem in predicting fire resistance of concrete elements.

Another problem with prescriptive fire resistance design is that the isotherms given in design guides are often limited to T-flange and I-flange beams (FIP/CEB Report: 1978) or rectangular cross sections. This limits the applicability of fire resistance design.

Numerical simulation to predict fire resistance is often seen as an alternative to experiment. The advantage of using numerical simulation is the ability to predict fire resistance of irregular cross section concrete elements and saving in cost of conducting experiments. A two stage procedure is commonly used for numerical studies such as FPRCBC-T and VULCAN (Huang *et al.*, 1999) and SAFIR (Franssen *et al.*, 2000). Firstly, isotherms within heated sections are predicted using Fourier's law of heat conduction. The second stage is to determine the mechanical properties of the heated section at various locations and calculate the effective load bearing capacity during the duration of heating. Hence, predicting isotherm within heated concrete elements is an integral part in fire resistance prediction.

Moisture is generally viewed as the main cause for spalling. The use of Fourier's law of heat conduction which is based on the conservation of energy is inadequate when predicting isotherm within heated sections as the presence of free water and non-evaporable moisture was observed to delay heat transfer. This will lead to an underestimation of thermal gradient and thermal stress within the heated section. Furthermore, evaporation of moisture within heated section can also lead to pore pressure increase which interacts with thermal stress to induce spalling. Therefore, a model capable of determining both isotherm and pore pressure build up simultaneously would be much preferred for use in fire resistance prediction. The effect of moisture is more prominent in hardened cement paste than in concrete as sand and aggregate does not contribute to non-evaporable moisture release at elevated temperature. This characteristic can be used to verify the proposed heat and mass transfer model.

This chapter presents the derivation of a numerical model to simulate heat and mass transfer in cement-based materials. The objective of this chapter is to formulate a model capable of predicting temperature distribution, gas pressure and spalling within heated section. The influence of different mix proportion on heat and mass transfer are investigated. Both models on non-evaporable moisture loss and behaviour of porosity at elevated temperature obtained in this research will be incorporated into the simulation. Some limitations on temperature dependent properties were addressed in this research.

7.2 Proposed Model and Formulation

A non-linear transient heat and mass transfer model is proposed to predict isotherm, gas pressure and spalling within heated sections. Non-evaporable moisture loss and behaviour of porosity at elevated temperature are dependent on the w/c ratio, degree of hydration and chemical composition of OPC. These two parameters were investigated in the early part of this research as pore pressure is dependent on vapour molecules and volume of pores as stated in Ideal Gas Law. The general workflow of the model is given in Figure 7.1.

The model is broken up into components. Various assumptions were made with regards to the individual component. The advantage of this method is to facilitate future improvement to the model in the event of improvement in other field of research which can be incorporated into this model. Limitations in heat and mass transfer models developed by other researchers are addressed in this chapter. The following sections will provide details on the workings of the individual components.

Figure 7.1: General Workflow of the Model

7.3 Physical Structure of Concrete

Concrete is a multi phase material. The breakdown of the physical structure of concrete is used in the formulation of heat and mass transfer equations, non-evaporable moisture loss and behaviour of porosity at elevated temperature. Properties are assumed to be isotropic. The physical structure of concrete consists of skeleton and pores as shown in Figure 7.2. The skeleton system can be further broken down into various phases which include hardened cement paste, sand and aggregates. The composition of the skeleton

system is summarised in Table 7.1. The microstructure of hardened cement paste consists of AFm hydrate, C-S-H gel, calcium hydroxide and unreacted particles (OPC, pozzolana). Non-evaporable moisture is residing within the hardened cement paste.

Figure 7.2: Breakdown of Skeleton Volume in Concrete

Table 7.1: Various Types of Skeleton System

Type	Skeleton System
Hardened Cement Paste	$V_{pore} + V_{bind}, V_{sand} = V_{agg} = 0$
Cement Mortar	$V_{pore} + V_{bind} + V_{sand}, V_{agg} = 0$
Concrete	$V_{pore} + V_{bind} + V_{sand} + V_{agg}$

The breakdown of the pore system is shown in Figure 7.3. Both gas (V_G) and liquid (V_L) phase fill the pore space within the pores of concrete resulting from cement and pozzolanic reaction. Liquid phase refers to the free water present in concrete. The binary gas mixture within the pores of concrete includes air and vapour molecules only.

Figure 7.3: Breakdown of Pore Volume in Concrete

7.4 Formulation of Equations for Heat and Mass Transfer

The objective of the model is to predict temperature distribution and gas pressure within cement-based materials. Conservation of energy, mass of free water, mass of vapour and mass of dry gas will be used to determine the governing equations for the model. The equations are coupled and require to be solved simultaneously. The heated section will be discretised into smaller elements and the unknown variables will be determined at the nodes. The model presented here is an improved version of Harada and Terai's (1997) and Tenchev's *et al.* (2001) models where the limitations of temperature dependent material properties are resolved.

7.4.1 Governing Equations

7.4.1.1 Energy

The conservation of energy is the most important equation in all heat and mass transfer models. Heat is transferred from the hot to cold surface by conduction. In transient heating, the rate of increase in internal energy is equal to the rate of energy gained within a system. All phases (solid skeleton, free water, water vapour and dry air) within heated hardened cement paste, cement mortar and concrete will experience the same rate of energy increase. Therefore, the basic Fourier's Law of heat conduction is

extended to incorporate the effects of all phases within the boundaries of hardened cement paste, cement mortar and concrete and is given in Equation (7.1).

$$(\rho C) \frac{\partial T}{\partial t} = \nabla(k \nabla T) - (\rho C \nu) \nabla T - \lambda_e \dot{E} - \lambda_d \frac{\partial w_{d,T}}{\partial t} \quad (7.1)$$

where ρC , T , t , k , ν , λ_e , λ_d , $\dot{E}$ and $w_{d,T}$ refer to overall specific heat capacity, temperature, time, effective thermal conductivity, migration velocity, latent heat of evaporation, specific heat of dehydration of bounded water, rate of evaporation of free water and mass of non-evaporable moisture per unit volume of hardened cement paste, cement mortar and concrete respectively. The left hand side term denotes the rate of change of internal energy of the system. The terms on the right in the order of left to right represent the energy transferred by conduction, energy transported by convection resulting from flow of fluid, energy required to vaporise liquid water without an increase in temperature and energy required to vaporise non-evaporable moisture respectively. Convective heat transfer of fluid within the system is assumed to be zero in the formulation. This is because all the free water has uniform temperature within a system and behaves like conduction instead of convection. Free water transported from neighbouring locations and non-evaporable moisture released into the system impedes heat transfer. They are accounted for as the last two negative terms of Equation (7.1). The equations for temperature dependent parameters used in Equation (7.1) will be discussed in the later sections.

7.4.1.2 Free Water

Free water is an important phase in hardened cement paste, cement mortar and concrete. They have large specific heat capacity and impede heat transfer. Conservation of mass of free water requires the rate of change in mass of free water to be equal to change in overall mass of free water within the system. Free water is assumed to be transferred using Darcy's law under the action of pressure induced flow. At 105 °C, vaporisation of free water occurs and reduces the mass of free water in the system. This is accounted for with a negative term $\dot{E}$. Non-evaporable moisture is also released into the system at

temperature greater than 105 °C in the form of free water before it vaporise. This will lead to an increase in the total mass of free water in the system and is accounted for by adding the term $\frac{\partial w_{d,T}}{\partial t}$ into the total rate of change in mass of free water.

$$\frac{\partial M_L}{\partial t} = -\nabla[M_L v_L] - \dot{E} + \frac{\partial w_{d,T}}{\partial t} \quad (7.2)$$

$$v_L = -\frac{K}{\mu_L} \nabla P_L \quad (7.3)$$

where M_L , v_L , K , μ_L and P_L refer to mass of free water per unit volume of concrete, migration velocity of free water, intrinsic permeability of concrete, dynamic viscosity of liquid phase and pressure of liquid phase respectively. v_L is governed by Darcy's Law and can be determined using Equation (7.3) (Harmathy, 1993; Martys and Ferraris, 1997). Derivation of permeability is discussed in the later section.

7.4.1.3 Vapour

Both air and vapour exist in gaseous state and fill the pores within the system. The governing equation is presented in Equation (7.4). There are two sources that affect the rate of change in mass of vapour per unit volume of hardened cement paste, cement mortar and concrete: 1) vapour being transported due to pressure induced flow (Darcy's Law) and diffusion induced flow (Fick's Law) as shown in the first and second term on the right hand side of Equation (7.5) and 2) vapour being generated within unit volume of hardened cement paste, cement mortar and concrete due to phase change of free water into steam.

$$\frac{\partial(V_G \tilde{M}_V)}{\partial t} = -\nabla J_V + \dot{E} \quad (7.4)$$

$$J_V = V_G \tilde{M}_V v_G - V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{M}_V}{\tilde{M}_G} \right) \quad (7.5)$$

$$\nu_G = -\frac{KK_G}{\mu_G} \nabla P_G \quad (7.6)$$

$$D_{AV} = \frac{D_T}{1 + \frac{l_m}{d}} \quad (7.7)$$

$$D_T = 1.89 \times \frac{(273.15 + T)^{2.072}}{P_G} \times 10^{-5} \quad (7.8)$$

$$K_G = 1 - \frac{M_L}{n_T} \quad (7.9)$$

where V_G , $\tilde{M}_V$, ν_G , $\tilde{M}_G$, D_{AV} , K_G , μ_G , P_G , M_L and n_T are volume of gas mixture within unit volume of concrete, mass of vapour in unit volume of binary gas mixture, migration velocity of gas, mass of gas in unit volume of binary gas mixture, diffusion coefficient of air or vapour in a gaseous mix in pores of concrete, relative permeability of gaseous phase through concrete, dynamic viscosity of gaseous phase, pressure of gaseous phase, mass of liquid and porosity subjected to elevated temperature respectively. D_{AV} is calculated using Knudsen's diffusion in pores (Daian *et al.*, 1996) where d is the characteristic size smaller than the mean free path (l_m) of vapour molecules which is approximately 150 nm. V_G is multiplied with $\tilde{M}_V$ and $\tilde{M}_G$ to convert the mass of vapour and gas molecules in unit volume of gaseous mix into unit volume of concrete. Diffusion induced flow is dependent on the mass concentration of two types of molecules $\frac{\tilde{M}_V}{\tilde{M}_G}$ in two different finite volume. The term $D_{AV} \nabla \left(\frac{\tilde{M}_V}{\tilde{M}_G} \right)$ represent the mass of vapour been diffused in a unit volume of binary gas mixture. Hence, the term $V_G \tilde{M}_G$ is multiplied to $D_{AV} \nabla \left(\frac{\tilde{M}_V}{\tilde{M}_G} \right)$ in order to convert mass of vapour being diffused in unit volume of gaseous mix into unit mass of air being diffused in unit volume of concrete. The term K_G is to account of the reduction in intrinsic permeability if the pores are filled with liquid. P_G can be calculated using Dalton's Law by summing both air and vapour pressure.

7.4.1.4 Dry Air

The formulation of the governing equation for vapour shown in Equation (7.10) is very similar with air as presented in Equation (7.4) with the exception of the rate of evaporation term. The mass of air in unit volume of concrete is denoted by $V_G \tilde{M}_A$.

$$\frac{\partial(V_G \tilde{M}_A)}{\partial t} = -\nabla J_A \quad (7.10)$$

$$J_A = V_G \tilde{M}_A \nu_G - V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{M}_A}{\tilde{M}_G} \right) \quad (7.11)$$

7.4.2 Coupling of Governing Equations

Many of the parameters required in the governing equations are temperature dependent. Hence, a change in temperature will affect mass transport behaviour. Furthermore, mass transport of various phases within concrete also interacts with energy conservation equation. The approach to determine the unknown variables such as temperature and gas pressure at various locations within concrete is to solve the governing equations simultaneously. It is possible to reduce the set of four governing equations into three equations by substituting Equation (7.2) into Equation (7.1), (7.4) and (7.10). The three unknown variables to be solved are temperature, gas pressure and mass of vapour per unit volume of binary gas mixture. The algebraic manipulations are provided in Appendix C. The general form of the simultaneous equations is given as Equation (7.12). The terms in $[C]$ and $[K]$ are listed as follows.

$$[C] \frac{\partial}{\partial t} \{\Phi\} = \nabla \cdot ([K] \nabla \{\Phi\}) \quad (7.12)$$

$$\begin{aligned}
 C_{TT} &= \rho C + (\lambda_d + \lambda_e) \frac{\partial w_{d,T}}{\partial T} - \lambda_e \frac{\partial M_{L,T}}{\partial T} & C_{TV} &= -\lambda_e \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} & C_{TP} &= 0 \\
 C_{MT} &= \tilde{M}_v \frac{\partial V_{pore,T}}{\partial T} + \left(1 - \frac{\tilde{M}_v}{\rho_L}\right) \frac{\partial M_{L,T}}{\partial T} - \frac{\partial w_{d,T}}{\partial T} & C_{MV} &= V_G + \left(1 - \frac{\tilde{M}_v}{\rho_L}\right) \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} & C_{MP} &= 0 \\
 C_{AT} &= \frac{\partial V_{pore,T}}{\partial T} \tilde{M}_A - \frac{\tilde{M}_A}{\rho_L} \frac{\partial M_{L,T}}{\partial T} - \frac{V_G P_G}{R_A T^2} & C_{AV} &= -\frac{R_v}{R_A} V_G - \frac{\tilde{M}_A}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} & C_{AP} &= \frac{V_G}{R_A T} \\
 K_{TT} &= k & K_{TV} &= 0 & K_{TP} &= -\lambda_e M_L \left(\frac{K}{\mu_L} \right) \\
 K_{MT} &= \left(\frac{V_G D_{AV} \tilde{M}_v P_G}{\tilde{M}_G R_A T^2} \right) & K_{MV} &= \left(\tilde{M}_A + \frac{R_v}{R_A} \tilde{M}_v \right) \frac{V_G D_{AV}}{\tilde{M}_G} & K_{MP} &= \frac{K K_G V_G \tilde{M}_v}{\mu_G} - \frac{D_{AV} V_G \tilde{M}_v}{\tilde{M}_G R_A T} + M_L \frac{K}{\mu_L} \\
 K_{AT} &= -\frac{V_G D_{AV} \tilde{M}_v P_G}{\tilde{M}_G R_A T^2} & K_{AV} &= \left(-\tilde{M}_A - \frac{R_v}{R_A} \tilde{M}_v \right) \frac{V_G D_{AV}}{\tilde{M}_G} & K_{AP} &= \frac{K K_G}{\mu_G} V_G \tilde{M}_A + \frac{V_G D_{AV} \tilde{M}_v}{\tilde{M}_G R_A T}
 \end{aligned}$$

There are four derivative terms residing in $[C]$. They can be approximated using Equations (7.13) to (7.16). ΔT and $\Delta \tilde{M}_v$ are taken as 0.1% of T and $\tilde{M}_v$. The value is determined based on the requirement of simulating the plateau in temperature-time profile relating to the latent heat of evaporation of free water which is observed in heating experiments at approximately 105 °C. Specifying a value too large will result in a short holding period and vice versa.

$$\frac{\partial w_{d,T}}{\partial T} = \frac{w_{d,(1+\Delta T)T} - w_{d,T}}{\Delta T} \quad (7.13)$$

$$\frac{\partial V_{pore,T}}{\partial T} = \frac{V_{pore,(1+\Delta T)T} - V_{pore,T}}{\Delta T} \quad (7.14)$$

$$\frac{\partial M_{L,T}}{\partial T} = \frac{M_{L,(1+\Delta T)T} - M_{L,T}}{\Delta T} \quad (7.15)$$

$$\frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} = \frac{M_{L,(1+\Delta \tilde{M}_v)\tilde{M}_v} - M_{L,\tilde{M}_v}}{\Delta \tilde{M}_v} \quad (7.16)$$

7.4.3 Boundary Conditions

The three unknown variables to be solved are temperature, gas pressure and mass of vapour in unit volume of binary gas mixture. Finite Element method is used to solve the three governing equations. Integration by parts method is used to reduce the second order partial differential equation into first order partial differential equation in the finite element formulation. This procedure will result in the creation of a boundary term which consists of two end conditions for each of the equation that is being solved. Therefore, a total of three boundary conditions are required to solve the governing equations which correspond to conservation of energy, conservation of mass of vapour and conservation of mass of air. There are generally two types of boundary conditions used in this model. The first type of boundary condition known as Dirichlet boundary condition is prescriptive which means that the variables are known at either ends of the domain. The other type of boundary condition known as Neumann boundary condition means that the flux at either ends of the domain is known.

There are also two scenarios for the end conditions of each governing equation. The line of symmetry can be used in objects such as cylinder and cubes. In this case, the sum of flux at this point will be zero. Dirichlet and Neumann boundary condition is to be applied on the heated surface. The other case will be modelling a wall or slab in a one dimensional heat transfer. Heat is been supplied on one face and transfer to the cooler surface. Both Dirichlet and Neumann boundary conditions are to be applied on both sides of the wall or slab. The following section describes the formulation of the boundary conditions for the various governing equations.

7.4.3.1 Energy

Heat energy is transferred into and out off the boundary surface via the action of convection and radiation. Heat flux been transferred by free water does not occur at the boundary surface at the heated surface is dried up rapidly during heating. Free water at the boundary wall losses heat via convection and radiation. The equation to define heat flux at heated and cooler surface is given in Equation (7.17) and (7.18) respectively.

$$-k \frac{\partial T}{\partial n} = h_{qr} (T_{\infty} - T) \quad (7.17)$$

$$-k \frac{\partial T}{\partial n} = h_{qr} (T - T_{\infty}) \quad (7.18)$$

$$h_{qr} = h_q + h_r \quad (7.19)$$

$$h_r = e\sigma \left[(T + 273.15)^2 + (T_{\infty} + 273.15)^2 \right] \times [(T + 273.15) + (T_{\infty} + 273.15)] \quad (7.20)$$

where T_{∞} , h_{qr} , h_q , h_r , e and σ refer to surrounding temperature, combined convective and radiation heat transfer coefficient, convective heat transfer coefficient (25 W/(m².°C)), radiation heat transfer coefficient, emissivity of boundary surface (0.6) and Stefan-Boltzman constant (5.67x10⁻⁸ W/(m².K⁴)) respectively.

7.4.3.2 Vapour

Mass of vapour is been transfer via the action of mass convection along the surface of the boundary. The formulation of the equation of the boundary condition for vapour at heated and cooler surface is similar with Equation (7.17) and (7.18) respectively.

$$-J_V \cdot n = \beta (\tilde{M}_V - \tilde{M}_{V,\infty}) \quad (7.21)$$

$$-J_V \cdot n = \beta (\tilde{M}_{V,\infty} - \tilde{M}_V) \quad (7.22)$$

$$-J_V \cdot n = K_{VT} \frac{\partial T}{\partial n} + K_{VV} \frac{\partial \tilde{M}_V}{\partial n} + K_{VP} \frac{\partial P_G}{\partial n} \quad (7.23)$$

where n , β , $\tilde{M}_{V,\infty}$, $\tilde{M}_V$ are the direction normal to mass convection, mass convection coefficient, mass of vapour in unit volume of surrounding gas and mass of vapour at the surface boundary respectively. β is calculated using Equations (7.24) and (7.25). Equation (7.24) is also known as Chilton-Colburn Analogy.

$$\beta = \frac{h_q}{(\rho C)_A} \left(\frac{D_{AV,\infty}}{\alpha_A} \right)^{\frac{2}{3}} \quad (7.24)$$

$$D_{AV,\infty} = 1.89 \times \frac{(273.15 + T_\infty)^{2.072}}{P_{G,\infty}} \times 10^{-5} \quad (7.25)$$

$D_{AV,\infty}$, $(\rho C)_A$, α_A and T_∞ refer to the diffusion coefficient of air or vapour in a gaseous mix, specific heat capacity of air, thermal diffusivity of air and surrounding gas temperature respectively.

7.4.3.3 Air

The unknown variable to be solved using the conservation of mass of dry air is gas pressure. Fire often occurs in an isobaric condition. Hence, Dirichlet boundary condition is applied to both boundary surfaces and is presented in Equation (7.26). $P_{G,\infty}$ corresponds to atmospheric pressure at 0.1 MPa.

$$P_G = P_{G,\infty} \quad (7.26)$$

Since the heated environment is isobaric, there are no pressure gradient between the heated surface and surrounding environment. It can be deduced that the mass flux of air due to convection $\left(\frac{\partial P_G}{\partial n} \right)$ is zero.

7.4.3.4 Assembling Boundary Terms

The next step is to implement the boundary conditions derived from the previous section into the finite element formulation. Neumann boundary condition is substituted into the boundary term resulting from integration by parts. Implementation of Dirichlet boundary condition for gas pressure will be discussed in the later section. The boundary condition at heated surface for mass of vapour is dependent on temperature and requires to be solved simultaneously with the boundary condition for energy as shown in Equation (7.27). The boundary term for gas pressure is excluded in Equation (7.27) as it is constant and independent of temperature and mass of vapour.

$$\begin{Bmatrix} \frac{\partial T}{\partial n} \\ \frac{\partial \tilde{\rho}_V}{\partial n} \end{Bmatrix} = \begin{bmatrix} K_{TT} & 0 \\ K_{VT} & K_{VV} \end{bmatrix}^{-1} \begin{bmatrix} h_{qr} & 0 \\ 0 & \beta \end{bmatrix} \begin{Bmatrix} T \\ \tilde{\rho}_V \end{Bmatrix} - \begin{bmatrix} K_{TT} & 0 \\ K_{VT} & K_{VV} \end{bmatrix}^{-1} \begin{Bmatrix} h_{qr} T_\infty \\ \beta \tilde{\rho}_{V,\infty} \end{Bmatrix} \quad (7.27)$$

Equation (7.27) can be rewritten as Equation (7.28) where the unknown variables is represented by $\{\Phi\}$ and the terms on the right hand side as $\{R_\infty\}$ and $[R_K]$.

$$\frac{\partial \Phi}{\partial n} = [R_K] \{\Phi\} - \{R_\infty\} \quad (7.28)$$

$$[R_K] = \begin{bmatrix} K_{hT} & K_{h\tilde{M}_V} & 0 \\ K_{\beta T} & K_{\beta\tilde{M}_V} & 0 \\ 0 & 0 & 0 \end{bmatrix}, \text{ where } \begin{bmatrix} K_{hT} & K_{h\tilde{M}_V} \\ K_{\beta T} & K_{\beta\tilde{M}_V} \end{bmatrix} = \begin{bmatrix} K_{TT} & 0 \\ K_{VT} & K_{VV} \end{bmatrix}^{-1} \begin{bmatrix} h_{qr} & 0 \\ 0 & \beta \end{bmatrix} \quad (7.29)$$

$$\{R_\infty\} = \begin{Bmatrix} R_{T,\infty} \\ R_{V,\infty} \\ 0 \end{Bmatrix}, \text{ where } \begin{Bmatrix} R_{T,\infty} \\ R_{V,\infty} \end{Bmatrix} = \begin{bmatrix} K_{TT} & 0 \\ K_{VT} & K_{VV} \end{bmatrix}^{-1} \begin{Bmatrix} h_{qr} T_\infty \\ \beta \tilde{\rho}_{V,\infty} \end{Bmatrix} \quad (7.30)$$

There are two cases to model the cooler boundary condition depending on the geometry of the heated concrete.

Case 1: Heating on all sides (e.g. column, cylinder, cube)

At the line of symmetry, the sum of flux will be equal. Hence, the other boundary condition can be modelled as given in Equation (7.31).

$$\frac{\partial \Phi}{\partial n} = \{0\} \quad (7.31)$$

Case 2: Heating on one face (e.g. slab, wall)

Heat and mass of vapour are loss to the surrounding at the cooler boundary surface. The formulation of the boundary condition is the same with Equation (7.28) as provided in Equation (7.32).

$$\frac{\partial \Phi}{\partial n} = [R_K] \{\Phi\} - \{R_\infty\} \quad (7.32)$$

7.4.4 Finite Element Formulation

The general form of the simultaneous equation is solved using Finite Element method. The objective of the formulation is to discretise the entire domain into small elements. Unknown variables at the nodes of the elements will then be solved using numerical approach at various time steps. Galerkin weighted residual method is used to reduce the second order partial differential equations to first order partial differential equations. The unknown variables are expressed as a function of the shape function (N) as shown in Equations (7.33) to (7.35).

$$T = [N] \{T^e\} \quad (7.33)$$

$$\tilde{M}_v = [N] \{\tilde{M}_v^e\} \quad (7.34)$$

$$P_G = [N] \{P_G^e\} \quad (7.35)$$

Hence, all the unknowns can be represented by a term $\{\Phi^e\}$ as shown in Equation (7.36).

$$\{\Phi\} = [\bar{N}] \{\delta\} \quad (7.36)$$

$$[\bar{N}] = \begin{bmatrix} [N] & 0 & 0 \\ 0 & [N] & 0 \\ 0 & 0 & [N] \end{bmatrix} \quad (7.37)$$

$$\{\delta\} = \begin{Bmatrix} T^e \\ \tilde{M}_v^e \\ P_G^e \end{Bmatrix} \quad (7.38)$$

Galerkin weighted residual method is applied to Equation (7.12).

$$\int_{\Omega} [\bar{N}] \left[[C] \frac{d}{dt} \{\Phi\} - \nabla([K] \nabla \{\Phi\}) \right] d\Omega = 0 \quad (7.39)$$

$$\int_{\Omega} [\bar{N}] [C] \frac{d}{dt} \{\Phi\} d\Omega - \int_{\Omega} [\bar{N}] \nabla([K] \nabla \{\Phi\}) d\Omega = 0 \quad (7.40)$$

Integration by parts is then carried out for the second derivative term in Equation (7.40). The superscript (L) and subscript (0) on the first term on the right hand side represent the boundary condition for the cooler and heated surface respectively.

$$\int_{\Omega} [\bar{N}] \nabla([K] \nabla \{\Phi\}) d\Omega = [\bar{N}] [K] \nabla \{\Phi\} \Big|_0^L - \int_{\Omega} [K] \nabla \{\Phi\} [\nabla \bar{N}] d\Omega \quad (7.41)$$

Substituting Equation (7.41) back into Equation (7.40).

$$\begin{aligned} \int_{\Omega} [\bar{N}] [C] \frac{d}{dt} \{\Phi\} d\Omega + \int_{\Omega} [K] \nabla \{\Phi\} [\nabla \bar{N}] d\Omega &= [\bar{N}] [K] \nabla \{\Phi\} \Big|_0^L \\ \int_{\Omega} [\bar{N}] [C] \frac{d\Phi}{dt} d\Omega + \int_{\Omega} [K] \nabla \{\Phi\} [\nabla \bar{N}] d\Omega &= [\bar{N}] [K] \nabla \{\Phi\} \Big|_L - [\bar{N}] [K] \nabla \{\Phi\} \Big|_0 \end{aligned} \quad (7.42)$$

Substituting Equation (7.32) and (7.36) into Equation (7.42).

$$\begin{aligned} &\int_{\Omega} [\bar{N}]^T [C] \frac{d[\bar{N}]\{\delta\}}{dt} d\Omega + \int_{\Omega} [K] \nabla([\bar{N}]^T \{\delta\}) [\nabla \bar{N}] d\Omega \\ &= [\bar{N}]^T [K] (\{R_{\infty}\} - [R_K] [\bar{N}]\{\delta\}) \Big|_L - [\bar{N}]^T [K] ([R_K] [\bar{N}]\{\delta\} - \{R_{\infty}\}) \Big|_0 \\ &\int_{\Omega} [\bar{N}]^T [C] [\bar{N}] d\Omega \frac{d\{\delta\}}{dt} + \int_{\Omega} [\nabla \bar{N}]^T [K] [\nabla \bar{N}] d\Omega \{\delta\} + [\bar{N}]^T [K] [R_K] [\bar{N}]_L \{\delta\} + [\bar{N}]^T [K] [R_K] [\bar{N}]_0 \{\delta\} \\ &= [\bar{N}]^T [K] \{R_{\infty}\} \Big|_L + [\bar{N}]^T [K] \{R_{\infty}\} \Big|_0 \end{aligned} \quad (7.43)$$

Therefore, the final form of equation to solve is Equation (7.44).

$$[C'] \frac{d\{\delta\}}{dt} + [K']\{\delta\} = \{R'\} \quad (7.44)$$

7.4.5 Finite Difference Method

The finite difference method is used to solve the initial boundary value problem in the time domain. Both $[C']$ and $[K']$ are function of $\{\delta\}$ and require to be evaluated using $\{\delta\}$ from the previous time step.

$$\dot{K}\{\delta\} = {}^n\dot{R} \quad (7.45)$$

$$\dot{K} = \theta[K'] + \frac{1}{\Delta t}[C'] \quad (7.46)$$

$${}^n\dot{R} = \left[\frac{[C']}{\Delta t} - (1 - \theta)[K'] \right] \{\delta\}^{n-1} + (1 - \theta)\{\delta\}^{n-1} + \theta\{\delta\}^n \quad (7.47)$$

n and Δt represents current time step and size of time step respectively. θ is a finite difference coefficient which define the type of finite difference scheme used. A value of 0.5 is selected for θ which corresponds to Crank-Nicolson implicit method. The benefit of such a scheme is that the approximation is unconditional stable and no limit on the size of time step. However, such method requires iteration within each time step. Iteration stops when the difference in $\{\delta\}$ of all nodes in the model between convergence iteration is less than a predefined error term given in Equation (7.48) or convergence iteration stops after it reaches a predefined integer.

$$\Delta_i^n \delta = \frac{\text{norm}({}_i^n \delta - {}_{i-1}^n \delta)}{\text{norm}({}_i^n \delta)} < 10^{-9} \quad (7.48)$$

i and norm refer to the number of steps for convergence iteration and norm of a vector respectively. In this model, maximum i is selected to be five. Specifying a large value for maximum i does not ensure that the convergence criterion will be satisfied due to

non-linear behaviour and rounding up errors in $[C']$ and $[K']$. This will result in wastage in computational time. Dirichlet boundary condition for gas pressure is applied at this stage by specifying the corresponding value into $\{^n\delta\}$. An example of the formulation is provided in Equation (7.49). Corrections to $\dot{K}$ and $^n\dot{R}$ are then made as shown in Equation (7.49).

$$\begin{bmatrix} \dot{K}_{11} & \dot{K}_{12} & \dot{K}_{13} \\ \dot{K}_{21} & \dot{K}_{22} & \dot{K}_{23} \\ \dot{K}_{31} & \dot{K}_{32} & \dot{K}_{33} \end{bmatrix} \begin{Bmatrix} ^n\delta_1 \\ ^n\delta_2 \\ ^n\delta_3 \end{Bmatrix} = \begin{Bmatrix} ^n\dot{R}_1 \\ ^n\dot{R}_2 \\ ^n\dot{R}_3 \end{Bmatrix} \quad (7.49)$$

$$\begin{bmatrix} \dot{K}_{11} & \dot{K}_{12} \\ \dot{K}_{21} & \dot{K}_{22} \end{bmatrix} \begin{Bmatrix} ^n\delta_1 \\ ^n\delta_2 \end{Bmatrix} = \begin{Bmatrix} ^n\dot{R}_1 - ^n\delta_3 \dot{K}_{13} \\ ^n\dot{R}_2 - ^n\delta_3 \dot{K}_{23} \end{Bmatrix} \quad (7.50)$$

The convergence criterion in Equation (7.48) is checked without considering the nodal value of the Dirichlet boundary term.

7.4.6 Shape Function

A two node linear element is used to interpolate the unknown variable within the element. The shape function and differential of the shape function are provided below. The accuracy of approximation improves if the size of each element is small when using two node linear elements. The shape function and derivative of the shape function is given in Equation (7.51) and (7.52) respectively.

$$N_1(x) = 1 - \frac{x}{L}, \quad N_2(x) = \frac{x}{L} \quad (7.51)$$

$$\nabla N_1 = \frac{\partial N_1}{\partial x} = -\frac{1}{L}, \quad \nabla N_2 = \frac{\partial N_2}{\partial x} = \frac{1}{L} \quad (7.52)$$

The shape matrixes of each element used in Equation (7.44) are determined as follow.

$$\begin{aligned}\int_0^L [N]^T [C] [N] d\Omega &= \int_0^L \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} [C] \begin{bmatrix} N_1 & N_2 \end{bmatrix} d\Omega \\ &= [C] \int_0^L \begin{bmatrix} N_1 N_1 & N_1 N_2 \\ N_1 N_2 & N_2 N_2 \end{bmatrix} d\Omega\end{aligned}\quad (7.53)$$

$$\int_0^L N_1 N_1 d\Omega = \int_0^L \left(1 - \frac{x}{L}\right)^2 d\Omega = \left(-\frac{L}{3}\right) \left(1 - \frac{x}{L}\right)^3 \Big|_0^L = 0 - \left(-\frac{L}{3}\right) = \frac{L}{3}\quad (7.54)$$

$$\int_0^L N_1 N_2 d\Omega = \int_0^L \left(1 - \frac{x}{L}\right) \left(\frac{x}{L}\right) d\Omega = \int_0^L \left(\frac{x}{L} - \frac{x^2}{L^2}\right) d\Omega = \left(\frac{x^2}{2L} - \frac{x^3}{3L^2}\right) \Big|_0^L = \frac{L}{2} - \frac{L}{3} = \frac{L}{6}\quad (7.55)$$

$$\int_0^L N_2 N_2 d\Omega = \int_0^L \left(\frac{x}{L}\right)^2 d\Omega = \int_0^L \frac{x^2}{L^2} d\Omega = \frac{x^3}{3L^2} \Big|_0^L = \frac{L}{3}\quad (7.56)$$

$$\begin{aligned}\int_0^L [\nabla N]^T [K] [\nabla N] d\Omega &= \int_0^L \begin{bmatrix} \nabla N_1 \\ \nabla N_2 \end{bmatrix} [K] \begin{bmatrix} \nabla N_1 & \nabla N_2 \end{bmatrix} d\Omega \\ &= [K] \int_0^L \begin{bmatrix} \nabla N_1 \nabla N_1 & \nabla N_1 \nabla N_2 \\ \nabla N_1 \nabla N_2 & \nabla N_2 \nabla N_2 \end{bmatrix} d\Omega\end{aligned}\quad (7.57)$$

$$\int_0^L \nabla N_1 \nabla N_1 d\Omega = \int_0^L \left(-\frac{1}{L}\right)^2 d\Omega = \left(\frac{x}{L^2}\right) \Big|_0^L = \frac{1}{L} - 0 = \frac{1}{L}\quad (7.58)$$

$$\int_0^L \nabla N_1 \nabla N_2 d\Omega = \int_0^L \left(-\frac{1}{L}\right) \left(\frac{1}{L}\right) d\Omega = \int_0^L \left(-\frac{1}{L^2}\right) d\Omega = \left(-\frac{x}{L^2}\right) \Big|_0^L = -\frac{1}{L} - 0 = -\frac{1}{L}\quad (7.59)$$

$$\int_0^L \nabla N_2 \nabla N_2 d\Omega = \int_0^L \left(\frac{1}{L}\right)^2 d\Omega = \frac{x}{L^2} \Big|_0^L = \frac{1}{L} - 0 = \frac{1}{L}\quad (7.60)$$

$$\begin{aligned}[N]^T [K] [R_K] [N] \Big|_L &= [K] [R_K] \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} \begin{bmatrix} N_1 & N_2 \end{bmatrix} \Big|_L \\ &= [K] [R_K] \begin{bmatrix} N_1 N_1 & N_1 N_2 \\ N_1 N_2 & N_2 N_2 \end{bmatrix} \Big|_L = [K] [R_K] \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}\end{aligned}\quad (7.61)$$

$$\begin{aligned}
 [N]^T [K] [R_K] [N] \Big|_0 &= [K] [R_K] \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} \begin{bmatrix} N_1 & N_2 \end{bmatrix} \Big|_0 \\
 &= [K] [R_K] \begin{bmatrix} N_1 N_1 & N_1 N_2 \\ N_1 N_2 & N_2 N_2 \end{bmatrix} \Big|_0 = [K] [R_K] \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}
 \end{aligned} \tag{7.62}$$

$$[N]^T [K] \{R_\infty\} \Big|_L = [K] \{R_\infty\} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} \Big|_L = [K] \{R_\infty\} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{7.63}$$

$$[N]^T [K] \{R_\infty\} \Big|_0 = [K] \{R_\infty\} \begin{bmatrix} N_1 \\ N_2 \end{bmatrix} \Big|_0 = [K] \{R_\infty\} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{7.64}$$

7.5 Thermal Properties of Hardened Cement Paste and Concrete

7.5.1 Non-Evaporable Moisture Loss

Non-evaporable moisture loss impedes heat transfer, resulting in large thermal gradient if not accounted for in heat transfer analysis. Non-evaporable moisture loss at temperature greater than 105 °C was observed to be non-linear and dependent on temperature and volumetric ratio of the hydration products. The equation to calculate non-evaporable moisture loss in hardened cement paste is given in Equation (7.65). The correction factor K_c is to convert the volumetric ratio of hydration products in unit volume of hardened cement paste to unit volume of cement mortar or concrete.

$$M_{d,T} = 0.791 K_c \left(\sum_{i=a,c,p} f_i(T) V_i k_i \rho_{i,w} \right) \tag{7.65}$$

$$K_c = \frac{V_C + V_P + V_W}{V_C + V_P + V_W + V_{sand} + V_{agg}} \tag{7.66}$$

The subscript i denotes the AFm hydrates (a), C-S-H gels less gel pores (c) and calcium hydroxide (p) phase in hardened cement paste. The decomposition function, $f_i(T)$, is obtained from Chapter 5. The same decomposition profile is applied for both AFm and C-S-H gel. Volumetric ratio of each phase (V_i) can be calculated using Appendix B.

The volumetric ratio of moisture within AFm hydrate, C-S-H gel and calcium hydroxide is 0.629, 0.422 and 0.544 respectively. Density of moisture in the phase ($\rho_{i,w}$) is assumed to be 1000 kg/m³. V_C , V_P and V_w refer to volume of cement, pozzolana and water per unit volume of hardened cement paste respectively.

7.5.2 Porosity at Elevated Temperature

Pore pressure is dependent on both temperature and volume of pores. Ideal Gas Law states that pressure increase when temperature rises within a fix volume as shown in Equation (7.67).

$$P_i = R_i \tilde{M}_i T \quad (7.67)$$

The subscript i represents either air (a) or vapour (v) phase. R_i is a gas constant corresponds to 287 J/(kg°K) for air and 461.5 J/(kg°K) for vapour. $\tilde{M}_i$ represents the mass of the phase per unit volume of binary mixture while T is temperature in Kelvin.

Porosity of hardened cement paste increases when heated. This is because the space previously filled by chemically bound moisture within the hydration products becomes available when heated and connects with capillary pores. Therefore, an increase in the amount of chemically bound moisture released at elevated temperature will also lead to an increase in porosity. The equation to predict porosity for hardened cement paste is given in Equation (7.68). Details to calculate V_{hyd} are provided in Chapter 6 and Appendix B.

$$n_T = K_c \left[n_0 + 2.35 V_{hyd} \left(\frac{T - T_0}{100} \right)^{1.37} \right] \quad (7.68)$$

where n_0 , n_T , T_0 and T are initial volume of pore in per unit volume of hardened cement paste, volume of pore subjected to elevated temperature per unit volume of

hardened cement paste, initial temperature (°C) and elevated temperature (°C) respectively.

7.5.3 Thermal Conductivity

Thermal conductivity is a measure of the ability to transfer heat. A material with high thermal conductivity will transfer heat from the hotter region to the cooler region very rapidly, resulting in small thermal gradient and vice versa. It behaves non-linearly with temperature. Thermal conductivity for siliceous, calcareous and light weight concrete shown in Figure 7.4 can be calculated using Equation (7.69), (7.70) and (7.71) respectively as provided in ENV 1994-1-2.

Figure 7.4: Thermal Conductivity of Various Types of Concrete

$$k = 2.0 - 0.24 \left(\frac{T}{120} \right) + 0.012 \left(\frac{T}{120} \right)^2 \quad (7.69)$$

$$k = 1.6 - 0.16 \left(\frac{T}{120} \right) + 0.008 \left(\frac{T}{120} \right)^2 \quad (7.70)$$

$$k = \begin{cases} 1 - \frac{T}{1600}, & 20^\circ\text{C} \leq T \leq 800^\circ\text{C} \\ 0.5, & T > 800^\circ\text{C} \end{cases} \quad (7.71)$$

Generally, thermal conductivity for various types of concrete decreases with temperature except a rise that is calculated by Harmathy (1993) in a poreless hardened cement paste.

7.5.4 Specific Heat

Specific heat is a measure of energy required to raise the temperature of unit mass of substance by unit temperature. It also behaves non-linearly with temperature. The proposed model requires specific heat of concrete to be modelled as various phases which includes solid skeleton, liquid, air and vapour. The equation to define the specific heat for both normal and light weight concrete given in ENV 1994-1-2 is shown in Equation (7.72) and Equation (7.73) respectively.

$$C_s = 900 + 80 \left(\frac{T}{120} \right) - 4 \left(\frac{T}{120} \right)^2 \quad (7.72)$$

$$C_s = 840 \quad (7.73)$$

Figure 7.5 shows the specific heat of solid skeleton for hardened cement paste and concrete that is implemented in the heat and mass transfer model calculated using Equation (7.72) and (7.73). Moist hardened cement paste is not the same with saturated hardened cement paste. It means that the non-evaporable moisture is residing within moist hardened cement paste while saturated hardened cement paste implies free water filling the pores of hardened cement paste.

In the formulation of the heat and mass equation, mass of non-evaporable moisture loss is modelled separately from the skeleton volume. Hence, specific heat of dry hardened cement paste is used in the formulation. The peak in specific heat for moist hardened cement paste occurring between 400 °C and 600 °C corresponds to the energy required to vaporise moisture due to the release of non-evaporable moisture resulting from the

decomposition of calcium hydroxide. Hence, the overall specific heat capacity (ρC) of heated concrete is calculated using Equation (7.74).

Figure 7.5: Specific Heat of Hardened Cement Paste and Concrete

$$\rho C = \rho_s C_s + M_L C_L + V_G \tilde{M}_V C_V + V_G \tilde{M}_A C_A \quad (7.74)$$

C_i refers specific heat of various phases (i). The temperature dependent C_A , C_L and C_V can be obtained from Cengel (1998).

7.5.5 Free Water Content

The mass of free water in unit volume of concrete residing within the pores shown in Equation (7.75) is dependent on temperature and vapour pressure (Bazant and Thonguthai, 1979). It was observed in this research that free water ceased to exist within heated hardened cement paste at temperature greater than 374.14 °C. P_V and P_{sat} represents pressure vapour calculated using Equation (7.67) and using International

Association for the Properties of Water and Steam (IAPWS) Industrial Formulation for the Thermodynamic Properties of Water and Steam respectively.

$$M_L = \begin{cases} M_{cem} \left(\frac{P_V}{P_{sat}} \frac{{}^0M_L}{M_{cem}} \right)^{\frac{1}{m(T)}}, & \frac{P_V}{P_{sat}} \leq 0.96 \\ {}^0M_L \left[1 + 0.12 \left(\frac{P_V}{P_{sat}} - 1.04 \right) \right], & \frac{P_V}{P_{sat}} \geq 1.04 \end{cases} \quad (7.75)$$

$$m(T) = 1.04 - \frac{(T + 10)^2}{(T + 10)^2 + 22.3({}^0T + 10)^2} \quad (7.76)$$

0M_L and 0T refer to initial conditions for M_L and T respectively. M_{cem} denotes the mass of OPC per unit volume of concrete. The term $\frac{P_V}{P_{sat}}$ is used to define the state of saturation within concrete. A value less than 0.96 denotes non-saturated concrete while a value greater than 1.04 represents saturated concrete where all pores are filled with free water. Linear interpolation is used to determine M_L for $0.96 \leq \frac{P_V}{P_{sat}} \leq 1.04$.

7.5.6 Intrinsic Permeability

Behaviour of intrinsic permeability of hardened cement paste subjected to elevated temperature is taken to be the normalised critical diameter square that is obtained from MIP. The square function was selected based on the equation proposed by Katz and Thompson (1986) provided in Equation (4.6) to calculate intrinsic permeability. The normalised intrinsic permeability of the various specimens are marked in cross as shown in Figure 7.6. The solid line which corresponds to the normalised critical diameter square for HCP35 is used in analytical model to predict temperature and gas pressure distribution within SP1 to SP5 as they have the same design mix.

Investigation on the behaviour of intrinsic permeability of cement mortar and concrete subjected to elevated temperature are scarce. Therefore, quantification of the behaviour of intrinsic permeability of cement mortar and concrete is unavailable. It is

recommended that further researches on the investigation of widening of critical diameter in heated cement mortar and concrete to be conducted to improve the accuracy of the proposed heat and mass transfer model.

Due to this limitation, it is assumed that the behaviour of intrinsic permeability of cement mortar and concrete are the same with heated cement paste when investigating heat and mass transfer in cement mortar and concrete until further researches have been conducted in this area.

Figure 7.6: Behaviour of Intrinsic Permeability

7.6 Spalling Criterion

In the model, spalling occurs when tensile stress is greater than the tensile strength of concrete. Both parameters are required to be determined at every time step since they are dependent on temperature and gas pressure. It occurs throughout heating if this condition is satisfied, resulting in a cycle of pressure build up and spalling until tensile stress is less than tensile strength of concrete.

7.6.1 Tensile Stress

The use of pore pressure as a criterion for spalling is not applicable as pore pressure acts as a hydrostatic pressure within the pores causing both circumferential and radial stresses. Hence, Ichikawa and England (2001) proposed to calculate tensile stress using the principal of hollow shell. By assuming that the pores are spherical in shape, Equation (7.77) can be used to calculate the maximum circumferential tensile stress in a sphere.

$$\sigma_T' = \frac{(1 + 2n_T)}{2(1 - n_T)} P_g \quad (7.77)$$

where σ_T' , n_T and P_g refer to maximum circumferential stress (Pa), volume of pores ($\text{m}^3 \text{ m}^{-3}$) and pore pressure.

7.6.2 Tensile Strength

The behaviour of tensile strength of concrete subjected to elevated temperature was derived from the works by Carette *et al.* (1982). They conducted experiments to determine the residual compressive and tensile strength of concrete subjected to various elevated temperature. Tensile splitting strength was observed to increase when heated to temperatures less than 200 °C and decrease at temperatures beyond 200 °C. The w/c of test specimens used by Carette *et al.* (1982) was 0.45 and 0.60. Figure 7.7 shows the relationship between normalised split-tensile strength and temperature. The equation to describe the non-linear behaviour of tensile splitting strength, $\sigma_{T,T}$, is given in Equation (7.78).

$$\sigma_{T,T} = \sigma_T \left(-1.85 \times 10^{-11} T^4 + 2.69 \times 10^{-8} T^3 - 1.46 \times 10^{-5} T^2 + 2.19 \times 10^{-3} T + 0.958 \right) \quad (7.78)$$

σ_T refers to the unheated tensile capacity of concrete. It should be noted that Ichikawa and England (2001) determined the occurrence of spalling by assuming a uniform

tensile strength of 5 MPa across the range of temperature. This value is much higher than the data obtained by Carette *et al.* (1982). Therefore, using the data obtained from Carette *et al.* (1982) instead of Ichikawa and England (2001) to predict spalling should be more appropriate.

Figure 7.7: Residual Split-Tensile Strength of Concrete (Carette *et al.*, 1982)

The tensile strength of concrete at heated and residual state is assumed to be the same. From experimental investigations on the heated and residual compressive strength of concrete, researchers generally observed that the cracks formed during cooling lowers the residual compressive strength. Hence, it can be deduced that the residual tensile strength of concrete is lower than hot tensile strength. The overall effect on the occurrence of spalling is conservative.

7.7 Summary

The details of the formulation of the heat and mass transfer model are provided in this chapter. The governing equations were derived based on the conservation of energy and mass of various phases within hardened cement paste and concrete. The model is also

capable of simulating heat and mass transfer using different boundary conditions. Properties of various phases within concrete are non-linear and both stiffness and mass matrix is required to be determined for each time step. The effect of moisture on thermal properties is separated from the skeleton to avoid errors in computation. Numerical approach is used to solve the governing equations. Finite Element formulation is used to discretise the domain while Finite Difference scheme is used to solve the unknown variables at various time steps. The model is then implemented into computer using Matlab. Verification of the model and sensitivity analysis of mix proportion on isotherm, pore pressure and spalling will be discussed in the next chapter.

Chapter 8: Numerical Analysis of Experimental Data

8.1 Overview

The proposed heat and mass transfer model involves solving three coupled differential equations simultaneously. Non-linear behaviour of material properties increases the difficulty in solving the model. Predicting heat and mass transfer in hardened cement paste is more difficult than concrete. This is because the presence of moisture in concrete is generally lower than hardened cement paste. Errors in governing equations and non-linear thermal properties of concrete do not result in significant difference between experimental and simulated results for concrete but not for hardened cement paste. The analytical model proposed in Chapter 7 is solved using numerical approach. This chapter presents the verification of the proposed heat and mass transfer simulation model. Temperature profiles obtained in this research are used to verify the unknown variables at different time step.

8.2 Implementation in Matlab

Due to the complexity of the equations, the analytical model is implemented and solved using personal computer. The program was developed within Matlab environment because of its wide selection of built-in functions and ability to solve matrix problems. External toolbox is not required for this program. Results of the simulation can be displayed graphically to understand the transfer of heat and migration of vapour. The display is continuously updated once calculation at each time step is successfully completed. A screen shot of the running of the simulation and flow chart of the program in Matlab is shown in Figure 8.1 and Figure 8.2 respectively.

A cycle of calculating the unknown variables and testing of error term is repeated at every time step until the maximum simulation duration is reached. The process of determining the non-linear material properties such as mass of liquid in specimen, mass of non-evaporable loss, porosity, volumetric ratio of gas in hardened cement paste,

thermal conductivity and specific heat capacity for each element is most computational intensive and requires a large percentage of the computational time.

Figure 8.1: Screen Shot of Simulation in Progress

The inputs required at the start of the program are the volumetric ratio of hydration products in cement mortar/concrete system, initial temperature, initial porosity and initial permeability. Volumetric ratio of hydration products and initial porosity can be obtained using Appendix B. The program starts with generating the non-evaporable moisture loss profile at every 1 °C interval for the required mix proportion to facilitate interpolation during calculation of non-evaporable moisture loss for each element at each time step. Non-linear material properties for each element such as thermal conductivity, specific heat, mass of free liquid, mass of non-evaporable moisture, heated porosity, diffusion coefficient, volume of gas and volume of liquid are calculated using average nodal temperature, nodal mass of vapour and nodal gas pressure located at both ends of each element. Global matrices are then assembled with the appropriate boundary conditions.

Figure 8.2: Flow Chart of Program

Solutions at each time step are solved using finite difference method. Final output from each run includes temperature distribution, mass of air and vapour distribution, gas pressure, volumetric ratio of gas and liquid, liquid water distribution and tensile stress. The occurrence of spalling is not determined at this stage of computation and the simulation continues until the required time step. Once the calculation is completed, the tensile stress is compared with tensile strength to determine the occurrence of spalling.

The key difference of this program from other models (Ahmed and Hurst, 1997; Arita *et al.*, 2000; Consolazio *et al.*, 1998) is the ability to simulate the two plateaus in temperature-time domain which corresponds to the evaporation of evaporable and non-evaporable moisture in hardened cement paste. From experiments conducted in this research, it was observed that evaporation of free water and non-evaporable moisture released by the decomposition of calcium hydroxide impedes heat transfer. This implies that the occurrence of the two plateaus is independent of rate of heating. The ability to simulate the two plateaus will improve the accuracy in predicting temperature distribution within heated cement-based materials. As a result, transient thermal stress and strain can be better predicted and improve the ability to predict fire resistance of concrete elements.

8.3 Results of Numerical Simulations

Several simulations were carried out to verify the proposed models with experimental results provided in Chapter 4 (SP1 to SP5). Different rate of heating, targeted temperature and initial moisture content (Table 4.4) were used in the simulation to calculate heat and gas pressure distribution within SP1 to SP5 and are shown in Figure 8.3 to Figure 8.7 respectively. Mass of vapour refers to vapour existing within the pores of the hardened cement paste and is calculated by multiplying mass of vapour in unit volume of gas with volume of gas in unit volume of hardened cement paste obtained from simulation. The specimens were discretised at every 4 mm interval with a time step of 10 seconds. Dirichlet boundary conditions for heat transfer were specified at the surface exposed to heat. It can be observed from the results of the simulation that the temperature remains stagnant during evaporation of free water at 100 °C. The location at

Chapter 8: Numerical analysis of experimental data

which temperature starts to deviate from 100 °C demarcates dry and moist condition in hardened cement paste.

Figure 8.3: Simulation Results for SP1

Figure 8.4: Simulation Results for SP2

Chapter 8: Numerical analysis of experimental data

Figure 8.5: Simulation Results for SP3

Figure 8.6: Simulation Results for SP4

Figure 8.7: Simulation Results for SP5

For unsaturated specimens (SP1 & SP5), vapour released by evaporable and non-evaporable moisture are able to migrate freely further into the depth of the specimen without causing a peak in gas pressure. The remaining specimens which are saturated experience the phenomenon “moisture clog”, which can be identified by a peak and rapid decrease to zero from the plot of mass of vapour along the direction of heat transfer. This implies that vapour was restrained from migrating into the depths of the specimen and accumulates at the quasi-saturated front.

Pore pressure starts to build up and tensile stress increases. The intersection of the thick (strength) and thin (stress) line in the plot of tensile stress/strength against distance from heated surface at various duration of heating satisfy the condition for spalling. No explosive spalling was observed during experimental investigations. However, numerous cracking sounds could be heard between 10 to 60 minutes from start of heating which coincides with the intersection points in the plots.

Rate of heating was observed to have an influence on pore pressure development. Generally, specimens with high rate of heating (SP3, 30 °C/min) experience a higher pore pressure development (0.40 MPa) than lower rate of heating (SP4, 20 °C/min) at 0.2 MPa for the same moisture content. This is because vapour does not have sufficient time to diffuse and migrate through the networks of pores and escape into the atmosphere.

8.4 Validation of Computer Model

It is important to validate the results from the program. Simulation results were verified using the following two approaches: 1) compare temperature profile with experimental obtained readings and 2) verify spalling criterion with experimental observations. Comparison of gas pressure with existing literature was performed to verify the accuracy of the heat and mass transfer program.

8.4.1 Comparing Temperature Profile

The temperature profile calculated from the program is verified with experimental results obtained in this research. Details of the mix proportions and volumetric ratio of hydration products are given in Chapter 3 and Chapter 4 respectively. The simulation was run using 18 elements with a time step of 10 seconds. Since heat is been transfer from external surface to centre of the specimens, heat and mass flux at the centre of the specimens will be zero. Figure 8.8 to Figure 8.12 shows the comparison of temperature profiles between simulation (thick line) and experiment (broken line) at various locations within heated cement paste. The program is able to predict the temperature profile reasonably well. The prediction of thermal gradient between heated surface and centre of specimen are in accordance.

Figure 8.8: Comparison of Temperature Distributions for SP1 **Figure 8.9: Comparison of Temperature Distributions for SP2**

Figure 8.10: Comparison of Temperature Distributions for SP3

Figure 8.11: Comparison of Temperature Distributions for SP4

Figure 8.12: Comparison of Temperature Distributions for SP5

Two plateaus were also simulated when modelling the behaviour of evaporable and non-evaporable moisture loss during transient heating. While decomposition of calcium hydroxide observed from non-evaporable moisture loss test occur within 400 °C to 500 °C, the corresponding plateau in temperature measurement test occurred at approximately 530 °C. This delay only occurs to non-evaporable moisture and not applicable to evaporable moisture. Researchers (Kalifa *et al.*, 2000; Tenchev *et al.*, 2001) commonly observed that evaporable moisture tends to evaporate at 200 °C instead at 100 °C. This is due to the built up of vapour pressure, which results in a higher evaporation temperature (Irvine, 1976). However, gas pressure obtained from simulation results for hardened cement paste are in the range of 0.2 - 0.4 MPa which corresponds to an evaporation temperature of 120 °C - 140 °C respectively (Irvine, 1976). Due to the low gas pressure build up, the plateau due to evaporable moisture observed from experimental investigations remained at 100 °C instead at 200 °C.

The difference in temperature at which decomposition of calcium hydroxide occurs is probably due to transient heating. In mass loss tests performed using TGA (ground

specimens) and electric furnace (fragment specimens), non-evaporable moisture released from decomposition of calcium hydroxide have sufficient time to escape into the atmosphere without causing delay in rise of temperature within specimen. In analysing transient heat and mass transfer through structural sections, non-evaporable moisture released from decomposition of calcium hydroxide are restrained from escaping into the atmosphere regardless of rate of heating. This cause an increase in specific heat at a later period after non-evaporable moisture is released into the pores of the specimen. Nevertheless, the ability to model the occurrence of plateaus is an improvement from existing techniques.

8.4.2 Comparison Between Models

The accuracy of the proposed heat and mass transfer model was compared with Ichikawa and England's (2001) model. This model was selected as Ichikawa and England attempted to validate their simulation results with experimental data. Temperature and gas pressure distribution calculated using the proposed heat and mass transfer model was superimposed over the graph by Ichikawa and England (2001) as shown in Figure 8.13. The experimental data was obtained from a one dimensional heating scenario with all sides sealed against moisture loss. Temperature and gas pressure were measured at 5 positions within the cylindrical sample. The mix proportion of the concrete used in the experiment is provided in Table 8.1. Material models used in the proposed heat and mass transfer model were derived from the mix proportion given in Table 8.1. Effects of pozzolanic reaction on material models resulting from the inclusion of GGBS were also considered.

While the governing equations in the two models are different, the plot of gas pressure against temperature (Figure 8.13) at various positions in heated concrete from both models is quite similar. Temperature and gas pressure distributions calculated using the proposed model is able to simulate experimental data more accurately than Ichikawa and England's model. Therefore, it can be concluded that the proposed model can be used to analyse the occurrence of explosive spalling due to presence of moisture within heated specimen.

Figure 8.13: Comparison between Experimental Data, Ichikawa and England's (2001) (—) model and Proposed Model (---)

Table 8.1: Mix proportion of Concrete Used in Experiment (Ichikawa and England, 2001)

Cement		Inclusions : Cement		Water : Cement
Sulphate Resisting Portland Cement	GGBS	Sand	Aggregate	Water
0.5	0.5	1.46	2.51	0.39

* Initial Porosity = 8.41%, $\alpha = 0.645$

8.4.3 Verify Spalling Criterion

While the occurrence of explosive spalling was not present, numerous cracking sounds could be heard 10 to 60 minutes from start of heating. From Figure 8.3 to Figure 8.7, tensile stress intersects tensile strength at various times from start of heating. This indicates that spalling criterion is met and spalling has occurred. Spalling would cause cracking in heated section and generate cracking sound during the process. This helps to verify the spalling criterion.

Despite having large thermal gradient within heated specimens, it was deduced that thermal stress does not contribute significantly to spalling in this research. There are two conditions before thermal stress can be developed: 1) presence of thermal difference between various depth of the heated specimen and 2) presence of at least two or more structural restraint in the direction of expansion such as pin or fix joint at both ends of the specimen. The presence of thermal difference would lead to an increase in length of the heated specimen without an increase in stress. If there are no structural restraint to limit the change in length, thermal stress would remain zero. The setup of the thermal distribution experiment focus on the effect of gas pressure on spalling while minimising thermal stress. However, this does not imply that thermal stress does not play a part in explosive spalling in buildings and tunnels.

8.5 Discussion

8.5.1 Effects of W/C on Temperature and Gas Pressure

Numerical simulations were conducted for HCP28, HCP35, HCP40 and HCP45 to understand the difference in temperature and gas pressure development in pores for various mix proportions when exposed to elevated temperature. All parameters and initial conditions are held constant except for the difference in the microstructure which are provided in Chapter 4. All specimens experience the same curing duration and environment. Degree of hydration for different specimens was determined experimentally. Different profiles for non-evaporable moisture loss and porosity at elevated temperature were used for different specimens in the simulation. A 150 mm slab was subjected to heating at 30 °C/min until the maximum of 800 °C where it remained constant. The slab was discretised into 50 elements and heat and mass transfer was evaluated at every 10 seconds interval.

Figure 8.14 shows the temperature distribution within the heated slab at various intervals. A single line for each time interval is plotted in Figure 8.14 as it is observed that the temperature distribution is independent of w/c. Generally, heat propagates further into the slab and escapes at the cooler surface through convection and radiation. A kink in the temperature distribution profile starts to develop at approximately 10

minutes and 100 °C due to the evaporation of evaporable moisture. Thermal gradient and gas pressure reach the maximum after heating for approximately 30 minutes.

Figure 8.14: Temperature Profile for Various Mix proportions

The gas pressure profiles of various specimens in pores of heated section after heating for 30 minutes are shown in Figure 8.15. Gas pressure in pores develops most rapidly at approximately 100 °C due to the evaporation of evaporable moisture. Once heated beyond 100 °C, the release of non-evaporable moisture into the pores of the heated section further increases gas pressure. The peak will continue to increase and migrate further into the depths of the slab. Generally, HCP28 experiences the highest gas pressure build up at all times, followed by HCP35, HCP40 and HCP45 in descending order. Hence, low permeability in hardened cement paste restricts both evaporable and non-evaporable moisture migration and has the largest impact on gas pressure.

Figure 8.15: Gas Pressure Profile for Various Mix proportions (30 min)

The most probable depth of spalling occurs at approximately 20 mm to 30 mm away from the heated surface as it is the location of the peak in gas pressure profile. The temperature range at which spalling occurs cannot be established as it is dependent on the rate of heating. The usage of w/c to quantification spalling will be valid if the degree of hydration is also known. Microstructure model can be used to predict non-evaporable moisture content and behaviour of porosity increase. Heat and mass transfer model can then be used to determine the gas pressure build up. This would be the preferred method instead of using prescriptive guidelines to minimise occurrence of spalling.

8.5.2 Effects of Pozzolana on Temperature and Gas Pressure

Pozzolanas are typically included in mix proportion to create concrete with enhanced properties. It is generally believed that the addition of silica fume into concrete mix proportions lowers permeability in concrete and increase the risk of spalling. A numerical analysis was conducted to understand the temperature and gas pressure development in specimens having the same water/binder ratio (w/b). Mix proportion

and volumetric ratio of HCP40 (0 % silica fume replacement) and BCP40 (10 % silica fume replacement) listed in Chapter 4 are used in the simulation. All parameters except the microstructure of the specimens and discretization in space and time are the same with the previous section. Temperature profiles for both specimens (Figure 8.16) are very similar at various intervals. Hence, it can be concluded that the addition of silica fume into mix proportions does not influence temperature distributions.

Figure 8.16: Temperature Profile of HCP40 and BCP40

However, similar temperature distribution within heated specimen does not imply similar gas pressure distribution. The peak in gas pressure occurs at approximately 30 mm away from the face of heating after heating for 30 minutes. Gas pressure distribution in BCP40 is slightly higher than HCP40. This is because the change in porosity in BCP40 is less than HCP40. A smaller volume of pores will result in high pore pressure build up. Generally, researchers believed that blended cement concrete have much lower permeability. However, permeability of HCP40 and BCP40 are very close to each other and does not have a significant impact on pore pressure build up. Compressive strength and w/b should not be used to quantify occurrence of spalling as

both specimens have similar strength. The results from the parametric analysis on the use of pozzolana in mix proportion is in accordance with the general observations that the use of pozzolana increase gas pressure build up and lead to an increase in risk of spalling.

Figure 8.17: Gas Pressure Profile of HCP40 and BCP40

8.5.3 Effect of Degree of Hydration on Temperature and Gas Pressure

The other parameter that can affect volumetric ratio of hydration products is degree of hydration. As hydration progress further, more hydrates will be formed and initial porosity gets reduced. This lead to a greater quantity of non-evaporable moisture and a larger increase in porosity when subjected to elevated temperature. The effect of non-evaporable moisture and porosity on gas pressure build up is different. A large quantity of non-evaporable moisture can lead to an increase in gas pressure build up while a large increase in porosity can lower gas pressure build up. The microstructure of HCP40 ($w/c=0.4$) at various degree of hydration was calculated using Appendix B and tabulated in Table 8.2. Information in Table 8.2 is used to generate the non-evaporable moisture

profile (Figure 8.18) and behaviour of porosity subjected to elevated temperature (Figure 8.19) for various degree of hydration. Both non-evaporable moisture and increase in porosity for degree hydration 0.7 and 0.8 is 16.6% and 33.3% higher than 0.6.

Table 8.2: Microstructure at Different Degree of Hydration

α	n_0	V_a	V_c	V_p	V_{hyd}
0.6	0.328	0.151	0.227	0.116	0.495
0.7	0.290	0.176	0.265	0.136	0.577
0.8	0.252	0.202	0.303	0.155	0.659

Figure 8.18: Non-Evaporable Moisture Profile for HCP40 at Various Degree of Hydration

Figure 8.19: Porosity Profile for HCP40 at Various Degree of Hydration

Figure 8.20: Gas Pressure Profile for HCP40 at Various Degree of Hydration

The same heating scenario and descritization is being applied in this analysis. The results of the analysis are shown in Figure 8.20. Maximum gas pressure is observed to build up at the interface of dry and moist region which is approximately 40mm. Evaporation of free water at 100 °C at this location causes maximum temperature gradient with the surface temperature. Gas pressure build up in specimen having high degree of hydration (0.8) is about 0.176 MPa higher than specimen with low degree of hydration (0.6). Non-evaporable moisture released during heating migrates in both directions along the path of heat transfer. Vapour from evaporable and non-evaporable moisture accumulates around the interface of dry and moisture region and increase gas pressure. Porosity around the region does not increase as the temperature is held constant for a period of time and unable to relieve gas pressure. Hence, it can be concluded that high degree of hydration can lead to a higher gas pressure build up due to the increase in non-evaporable moisture within the hardened cement paste.

8.5.4 Effect of Different Types of Cement on Temperature and Gas Pressure

Different types of cement are manufactured to suit different construction needs. The different types of cement will affect volumetric ratio of hydration products and subsequently affect the quantity of non-evaporable moisture and change in porosity due to elevated temperature. A sensitivity analysis was performed on unsaturated hardened cement paste using different compound composition as listed in Table 8.3 to determine the influence on temperature distribution and gas pressure build up. The w/c and degree of hydration are held constant at 0.4 and 0.8 respectively. The microstructure of the different types of cement calculated using Appendix B is tabulated in Table 8.4.

Table 8.3: Compound Composition of Different Types of OPC (Neville, 1996)

Cement	C_3S	C_2S	C_3A	C_4AF	Remark
Type I	49	25	12	8	OPC
Type II	46	29	6	12	Modified Cement
Type III	56	15	12	8	Rapid Harden
Type IV	30	46	5	13	Low Heat
Type V	43	36	4	12	Sulphate Resisting

Table 8.4: Microstructure of Different Cement

Cement	n_0	V_a	V_c	V_p	V_{hyd}	$W_{d,T}$ (kg/m ³)
Type I	0.260	0.206	0.322	0.124	0.652	263.38
Type II	0.263	0.197	0.331	0.120	0.648	260.40
Type III	0.250	0.230	0.298	0.133	0.661	271.31
Type IV	0.273	0.187	0.356	0.096	0.639	253.12
Type V	0.273	0.166	0.355	0.118	0.639	251.87

The analysis was conducted by assuming a constant heating rate of 30 °C/min (maximum of 800 °C) through a slab of thickness 150 mm. The slab is discretised into 50 elements and heat and mass transfer is evaluated at every 10 seconds interval. The temperature distribution and maximum gas pressure envelop is presented in Figure 8.21 and Figure 8.22 respectively.

Figure 8.21: Temperature Distribution of Various Types of Cement

It was observed from the analysis that the temperature distributions for different types of cement are the same. Hence, only 1 temperature distribution profile was plotted at different time interval in Figure 8.21. The kink which appears at 100 °C at 15 mm (10

min) away from the heated face denotes the evaporation of evaporable moisture and separates dry and moist region within the heated slab. This kink continues to appear throughout different interval and at various depths of the slab. After 10 min of heating, heat only managed to transfer 60 mm away from the heated face. Maximum temperature gradient is reached after 30 min of heating and it corresponds to the difference in the maximum temperature and room temperature at 120 mm away from face of heating.

Figure 8.22: Maximum Gas Pressure Envelop of Various Types of Cement

Table 8.5: Peak Gas Pressure for Different Cement

Cement	Peak Gas Pressure (MPa)
Type 3	0.868
Type 1	0.850
Type 2	0.843
Type 4	0.828
Type 5	0.820

The profiles of maximum gas pressure envelope for different cement (Figure 8.22) are similar. Peak in gas pressure build up occurs at 30 mm from face of heating. Table 8.5 shows the peak gas pressure for different types of cement in descending order. The

difference in gas pressure between the highest (Type 3) and lowest (Type 5) is approximately 5.9%. The high volume of hydrates and low initial porosity within Type 3 hardened cement paste is responsible for the higher gas pressure build up. While Type 3 cement experiences the highest peak in gas pressure, it does not ensure the occurrence the spalling. Hence, it is concluded that the temperature and gas pressure distributions within heated sections manufactured with different cement types does not differ significantly provided that the chemical compounds of the different types of cement conforms to Table 8.3.

8.5.5 Effect of Using Specific Heat of Dry and Moist Hardened Cement Paste

In the model, specific heat of hardened cement paste is the sum of specific heat of various phases within the hardened cement paste. In Chapter 7, there are two profiles that describe the specific heat of hardened cement paste. One is approximately a linear line which describes the specific heat of dry hardened cement paste while the other profile has a peak in specific heat at approximately 500 °C to describe moist hardened cement paste. If the profile for moist hardened cement paste is used, mass of non-evaporable moisture used in the governing equations is to be taken as zero to avoid double counting in calculating overall specific heat.

The specific heat of moist hardened cement paste is generally higher than dry hardened cement paste as shown in Figure 7.5. This will result in slower heat transfer within the specimen. An additional simulation run for SP2 was conducted using specific heat of moist hardened cement paste to determine the influence on temperature distribution within the specimen and the result is shown in Figure 8.23. Heat transfer predicted using moist specific heat is faster than dry specific heat as the amount of vapour in SP2 is reduced. Temperature profile predicted using moist and dry specific heat intersects at 300 °C. Thereafter, temperature predicted by using moist specific heat is less than dry specific heat. Instead of simulating a plateau at approximately 530 °C, the peak in specific heat of moist hardened cement paste cause a gradual change in rate of change in temperature at the centre of SP2.

Figure 8.23: Temperature Profile of SP2

The peak in specific heat occurring at 500 °C is dependent on the quantity of calcium hydroxide present in the specimen. Therefore, it can be deduced that the use of specific heat of moist hardened cement paste would not be appropriate for blended hardened cement paste due to the low volumetric ratio of calcium hydroxide existing in the specimen. Hence, the recommended approach to predict temperature distribution in heated hardened cement paste is to use the sum of specific heat of various phases present within the section.

8.5.6 Effect of Non-Evaporable Moisture Loss on Heat and Mass Transfer

This section looks into the effect of using a simplified bi-linear non-evaporable moisture loss (Tenchev *et al.*, 2001) on pore pressure development in hardened cement paste. Simulation results using bi-linear and non-linear non-evaporable moisture loss are shown in Figure 8.24. All other parameters used in the simulation were kept constant. The difference in using a bi-linear and non-linear non-evaporable moisture loss is the

absence of the plateau in the temperature-time profile corresponding to the decomposition of calcium hydroxide at approximately 530 °C.

Figure 8.24: Comparison of Simulation Results for SP2

The differences in the two non-evaporable moisture loss profiles were discussed in Chapter 5. Generally, bi-linear non-evaporable moisture loss tends to be underestimated for temperature less than 600 °C and overestimated for temperature greater than 600 °C. Underestimating non-evaporable moisture would result in a reduction in specific heat capacity of the heated section. As a result, temperature within heated section rises rapidly. This led to overestimation of the temperature distribution within the heated section which can be observed from Figure 8.24 and underestimate thermal stress.

The other limitation of using bi-linear equation is the prediction of non-evaporable moisture loss for blended hardened cement paste. Bi-linear equation tends to underestimate the quantity of non-evaporable moisture due to the lower amount of OPC used in unit volume of hardened cement paste and concrete. Underestimation is most severe for hardened cement paste than concrete. This will also lead to reduction in

specific heat capacity, followed by overestimation in temperature distribution within heated specimen and underestimation of thermal stress. Therefore, predicting non-evaporable moisture loss using microstructure model improves the accuracy of the heat and mass transfer model. This also shows the importance of relating analysis of spalling with microstructure of the heated section.

8.6 Summary

The computer model was verified by comparing experimental results obtained in this research as well as from other investigations. Cement-based materials were modelled as phases such as skeleton matrix, liquid and vapour. Microstructure models were also incorporated by calculating non-linear non-evaporable moisture loss and pore structure behaviour using volumetric ratio of hydration products. These two parameters were found to have the largest impact on both temperature and gas pressure development in heated hardened cement paste. The strength of this model is its ability to model the two plateaus occurring in the temperature-time profile corresponding to the evaporation of evaporable and non-evaporable moisture at approximately 100 °C and 450 °C respectively. Therefore, both thermal gradient and thermal stress can be predicted more accurately. This will improve the accuracy of temperature distributions in heated cement-based materials. The use of bi-linear equation proposed by Tenchev *et al.* (2001) is unable to simulate the plateau corresponding to the evaporation of moisture released from the decomposition of calcium hydroxide and tends to underestimate thermal gradient.

Parametric analyses were also conducted on specimens of various w/b. Current method of quantifying spalling such as high compressive strength, low w/c ratio and blended hardened cement paste are unable to address the fundamental cause of spalling. The smaller change in porosity for silica fume blended hardened cement paste compared with normal hardened cement paste is responsible for the increase in gas pressure build up within the specimen which also increases the risk of spalling. Analysis results shows that hardened cement paste using Type 3 cement may have a slight increase in risk of spalling. Effect of non-evaporable moisture on risk of spalling in specimens having high degree of hydration is more significant than the change in porosity.

Chapter 9: Conclusions and Recommendations

9.1 Summary and Conclusions

The occurrence of spalling was investigated using microstructural approach. This research addressed some of the problems relating to quantification of spalling using parameters such as compressive strength, water/cement ratio (w/c) and blended hardened cement paste. When concrete is subjected to elevated temperature, both non-evaporable moisture loss and behaviour of porosity are of primary concern in the analysis of spalling. Through experiments, non-evaporable moisture loss and behaviour of porosity were observed to be dependent on the volumetric ratio of hydration products. Volumetric ratio of hydration products is selected as the basis of modelling as it allows models develop using this approach to be independent of chemical composition of Ordinary Portland Cement (OPC) and pozzolana, water/cement ratio (w/c) and degree of hydration. Hardened cement paste was selected in the experiment instead of concrete to ensure that the state of homogeneity is maintained within the specimen.

Experiments such as mass loss test, porosity and temperature measurements were conducted in this research. The condition of thermal equilibrium was ensured throughout the experiments. Non-linear change in non-evaporable moisture loss and porosity subjected to elevated temperature were observed. Models were developed and verified for non-evaporable moisture loss and porosity subjected to elevated temperature. The models can be extended to different mix proportion including normal and blended hardened cement paste, cement mortar and concrete.

An analytical model for heat and mass transfer which incorporate material models established in this research is proposed. In the model, concrete is identified as phases which include solid skeleton, liquid, air and vapour. Finite element and finite difference method were used to discretised concrete into elements and solve the governing equations at various time intervals respectively. The results of the simulation were verified with temperature distributions obtained from experiments. Parametric analyses

were conducted to better understand the common parameters used to quantify occurrence of spalling.

The following lists the major conclusions made from this research.

1. Presence of pozzolana lowers the quantity of non-evaporable moisture due to the consumption of calcium hydroxide to produce C-S-H gel. The approach of predicting non-evaporable moisture loss by separating the effects of amorphous hydrates and calcium hydroxide allows the model to be extended to both normal and blended hardened cement paste.
2. Total porosity subjected to elevated temperature for blended hardened cement paste is lower than normal hardened cement paste of the same w/b. This is because C-S-H gel formed by pozzolanic reaction is denser than normal cement hydration. There is less gel pores in total porosity when the specimen is exposed to elevated temperature. If porosity is analytically derived using mass loss of hardened cement paste, it will be overestimated. This can lead to underestimation of pore pressure.
3. Two plateaus were observed in the plot of temperature against various depth of the specimen. The first plateau corresponds to the evaporation of evaporable moisture residing on pore walls at 100 °C while the second plateau corresponds to the evaporation of non-evaporable moisture at 530 °C. The duration of the first plateau is dependent on the initial moisture content of the specimen and rate of heating. The duration of the second plateau is observed to be dependent on the rate of heating and volume of hydration products.
4. Non-evaporable moisture loss and behaviour of pore widening, which is indirectly affected by degree of hydration, can affect gas pressure build up in hardened cement paste. Hardened cement paste of low w/c subjected to the same curing condition generate higher gas pressure. The degree of hydration should also be considered when using w/c to quantify spalling.
5. Parametric analysis conducted on normal and blended hardened cement paste used in this research showed that compressive strength, inclusion of pozzolana and w/c are unsuitable parameters to be used to quantify spalling. The use of pozzolana in mix proportion also increase gas pressure build up because of smaller increase in total porosity when subjected to elevated temperature.

6. The use of specific heat of moist hardened cement paste is unable to model the second plateau occurring at 530 °C corresponding to decomposition of calcium hydroxide. Instead, it creates a gentle positive gradient in the temperature profile. Thermal gradient tends to be underestimated for temperature less than 300 °C and overestimated thereafter.
7. The use of bi-linear model for non-evaporable moisture loss is also unable to model the second plateau occurring at 530 °C which corresponds to the decomposition of calcium hydroxide. This was improved by using the non-linear non-evaporable moisture loss model proposed in this research. As a result, thermal distribution, thermal stress and ultimately fire resistance can be better predicted.

9.2 Recommendations for Future Research

The following recommendations for future research are made based on the findings of this research.

1. The proposed model to predict non-evaporable moisture loss and behaviour of porosity for Fly Ash (FA) and Ground Granulated Blastfurnace Slag (GGBS) blended hardened cement paste requires experimental verification. Effects of inclusion such as sand and aggregates on moisture loss need to be verified.
2. The behaviour of porosity at temperature larger than 800 °C should also be investigated. ISO fire curve is the preferred fire load for analysing fire resistance of concrete sections and the maximum temperature specified in the fire load can reach in excessive of 800 °C after 23 minutes of heating.
3. The study on the effects of microstructure on non-linear thermal conductivity and specific heat of hardened cement paste should be conducted to improve the accuracy of the analytical model for heat and mass transfer.
4. Investigation on gas pressure distribution in heated concrete needs to be conducted. Permeability of concrete should also be determined for validating the analytical heat and mass transfer model.
5. The effect of interfacial transition zone in concrete on permeability and gas pressure development due to elevated temperature needs to be investigated. Further improvements to the heat and mass transfer equations should also be made to incorporate the effects of interfacial transition zone.

6. Spalling test involving mix proportion of different volume of sand and aggregate but constant w/c should be conducted to verify the increase in risk of spalling. Specimens of different geometry and sizes should also be tested to determine the influence on risk of spalling.
7. Works on applying fracture mechanics into the analysis of spalling should be conducted. The effect of cracks on pore pressure development needs to be established to further improve the understanding of spalling.

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Appendix A

Summary of Reported Mix proportion and Residual Porosity

*Mix proportion is expressed in the order of cement, water, pozzolana (type), fine aggregate, coarse aggregate

Reference	W/B (ID)	Mix proportion (kg/m ³)*	Temp (°C)	Porosity (%)	Predicted Porosity (%)
Poon <i>et al.</i> (2001)	0.3 (HS-CC)	500,150,-, 758,927	20	9.52	9.52
			600	18.32	17.55
			800	29.13	21.57
	0.3 (HS-SF5)	475,150,25(SF), 710,1066	20	7.68	7.68
			600	13.71	15.29
			800	22.21	19.10
	0.3 (HS-SF10)	450,150,50(SF), 620,1151	20	5.73	5.73
			600	9.87	13.07
			800	32.71	16.75
	0.3 (HS-FA20)	400,150,100(FA), 618,1147	20	7.73	7.73
			600	12.77	13.77
			800	23.31	16.80
	0.3 (HS-FA30)	350,150,150(FA), 615,1143	20	6.69	6.69
			600	11.28	8.97
			800	21.96	10.12
	0.3 (HS-FA40)	300,150,200(FA), 613,1139	20	6.23	6.23
			600	10.63	10.77
			800	22.46	13.04
	0.3 (HS-BS30)	350,150,150(GGBS), 616,1145	20	6.29	6.29
			600	12.71	12.96
			800	23.01	16.31
	0.3 (HS-BS40)	300,150,200(GGBS), 615,1142	20	6.02	6.02
			600	11.21	10.27
			800	24.42	12.40
	0.5 (NS-CC)	390,195,-, 768,917	20	14.82	14.82
			600	26.56	23.11
			800	42.12	27.27
	0.5 (NS-FA30)	273,195,117(FA), 626,1133	20	12.17	12.17
			600	20.29	17.61
			800	31.09	20.33
	0.5 (NS-FA40)	234,195,156(FA), 625,1129	20	11.71	11.71
			600	18.78	16.34
			800	29.98	18.65

Reference	W/B (ID)	Mix proportion (kg/m ³)*	Temp (°C)	Porosity (%)	Predicted Porosity (%)
Poon <i>et al.</i> (2001)	0.5 (NS-BS30)	273,195,117(GGBS), 626,1135	20	11.46	11.46
			600	19.39	18.64
			800	28.89	22.23
	0.5 (NS-BS40)	234,195,156(GGBS), 625,1132	20	11.08	11.08
			600	17.87	17.36
			800	27.79	20.51
Xu <i>et al.</i> (2001)	0.5 (C-0.5-00)	410,205,-, 609,1132	20	21.19	21.19
			250	23.20	23.84
			450	26.88	27.43
			650	32.10	31.72
	0.5 (C-0.5-25)	307.5,205,102.5(FA), 576,1132	20	22.21	22.21
			250	24.00	23.95
			450	27.79	26.31
			650	31.10	29.12
	0.5 (C-0.5-55)	184.5,205,225.5(FA), 536,1132	20	23.98	23.98
			250	24.89	25.03
			450	27.84	26.44
			650	31.54	28.14
	0.3 (C-0.3-00)	500,150,-, 724,1086	20	13.94	13.94
			250	14.16	16.25
			450	18.05	19.39
			650	24.24	23.14
	0.3 (C-0.3-25)	375,150,125(FA), 683,1086	20	12.99	12.99
			250	13.55	14.51
			450	16.99	16.57
			650	23.05	19.03
	0.3 (C-0.3-55)	225,150,275(FA), 634,1086	20	19.89	19.89
			250	22.21	20.80
			450	26.60	22.04
			650	29.00	23.52

**Chemical Compositions of OPC & Pozzolanas by
Poon *et al.* (2001) and Xu *et al.* (2001)**

	OPC	FA	GGBS	SF
SiO ₂	19.61	56.79	38.14	90.26
CaO	63.15	<3.00	35.77	3.18
Al ₂ O ₃	7.33	28.21	6.53	0.63
Fe ₂ O ₃	3.32	5.31	0.4	0.33
MgO	2.54	5.21	13.65	0.33
Na ₂ O	-	-	0.36	-
K ₂ O	-	-	0.40	-
SO ₃	2.13	0.68	-	0.4
L.O.I.	2.97	3.90	0.76	4.84
Specific Gravity	3.16	2.31	2.52	2.31
Specific Surface (m ² /kg)	352	412	470	-

Appendix B

Equations to Determine Volumetric Ratio of Hydration Products in Hardened Cement Paste

Normal Cement Paste

Water/cement ratio (w/c) and degree of hydration (α) are the two inputs required to predict the volumetric ratio of hydration products. The volumetric ratio of hydration products namely AFm hydrate, C-S-H hydrate and portlandite is calculated using Bogue's Phase Fraction relationship and volume stoichiometry relationship (Jennings and Tennis 1994). The volume of cement powder and water used in mix proportion can be calculated using Equation (B.1) and (B.2) respectively. The sum of the volume of cement powder and water is equal to one.

$$V_{cem} = \frac{1}{1 + \rho_{cem}(w/c)} \quad (B.1)$$

$$V_{wat} = 1 - V_{cem} \quad (B.2)$$

where V and ρ refer to volume and specific density respectively. The subscript *cem* refers to cement powder while *wat* refers to water. The following set of equations from Equations (B.3) to (B.9) which was derived from Equations (2.5) to (2.8) is then used to determine the volumetric ratio of hydration products and pores in hardened cement paste after calculating the phase composition using Bogue's Equations.

$$V_{c,nor} = V_{cem} \times \alpha \times \left([C_3S] \times \frac{3.2}{3.15} \times 1.521 + [C_2S] \times \frac{3.2}{3.28} \times 2.077 \right) \quad (B.3)$$

$$V_{p,nor} = V_{cem} \times \alpha \times \left([C_3S] \times \frac{3.2}{3.15} \times 0.61 + [C_2S] \times \frac{3.2}{3.28} \times 0.191 \right) \quad (B.4)$$

$$V_{a,nor} = v_{nor} V_{cem} \alpha_{nor} - V_{c,nor} - V_{p,nor} \quad (B.5)$$

$$V_{u,nor} = V_{cem} (1 - \alpha_{nor}) \quad (B.6)$$

$$V_{exp,nor} = (v_{nor} - 1) V_{cem} \alpha_{nor} \quad (B.7)$$

$$V_{cap,nor} = V_{wat} - V_{exp,nor} \quad (B.8)$$

$$V_{gel} = 0.28V_{c,nor} \quad (B.9)$$

where α_{nor} , $[C_3S]$, $[C_2S]$ and v_{nor} refer to the degree of hydration, mass ratio of C_3S and mass ratio of C_2S and ratio of volumetric expansion of hydrated products to unhydrated cement. v_{nor} is assumed to be 2.2.

Blended Cement Paste

There are two types of reaction occurring with the blended cement paste. Normal cement hydration begins when anhydrous cement powder is mixed with water to produce hydration products. Pozzolanic reaction takes place when calcium hydroxide formed during cement hydration reacts with pozzolana to form additional C-S-H gel. Unlike normal cement paste, a portion of the cement by weight (x) is been replaced with pozzolana. Hence, it is necessary to determine the percentage of pozzolana by volume (y) in cement and pozzolana mix.

$$x = \frac{M_{poz}}{M_{poz} + M_{cem}} \quad (B.10)$$

$$y = \frac{x / \rho_{poz}}{x / \rho_{poz} + (1 - x) / \rho_{cem}} \quad (B.11)$$

where M and ρ are mass and specific density respectively while the subscript poz and cem refer to pozzolana and cement powder respectively. The volume of total solid in blended cement paste (V_{sol}) used during mixing can be determined using Equation (B.12). Water/binder ratio (w/b) instead of w/c is used in the calculation of V_{sol} due to the inclusion of pozzolana.

$$V_{sol} = \frac{(1 - x) / \rho_{cem} + x / \rho_{poz}}{w / b + (1 - x) / \rho_{cem} + x / \rho_{poz}} \quad (B.12)$$

$$V_{wat} = 1 - V_{sol} \quad (B.13)$$

$$V_{poz} = yV_{sol} \quad (B.14)$$

$$V_{cem} = (1 - y)V_{sol} \quad (B.15)$$

Hydration products due to cement reaction can be calculated using Equations (B.3) to (B.9). Pozzolanic reactions are observed to consume calcium hydroxide to form additional C-S-H gel. The volume of additional C-S-H gel and reduction in calcium hydroxide due to pozzolanic reaction ($V_{c,poz}$ and $V_{p,poz}$ respectively) can be determined using (B.16) and (B.17). Both Equation (B.16) and (B.17) was derived from Equation (2.10) and (2.11).

$$V_{c,poz} = 3.77 \times V_{SiO_2} \times \alpha_{poz} \quad (B.16)$$

$$V_{p,poz} = (1.35V_{SiO_2} + 1.33V_{Al})\alpha_{poz} \quad (B.17)$$

where V_{SiO_2} and V_{Al} are the volume fraction of silica and alumina phases in pozzolana respectively. Therefore, the total C-S-H gel and calcium hydroxide in the system can be calculated using Equation (B.18) and (B.19) respectively.

$$V_c = V_{c,nor} + V_{c,poz} \quad (B.18)$$

$$V_p = V_{p,nor} - V_{p,poz} + V_{p,nor(GGBS)} \quad (B.19)$$

The term V refers to the volumetric ratio of the phase. The first subscript c and p refer to C-S-H gel and calcium hydroxide respectively while the second subscript denotes the chemical reaction either normal cement hydration (nor) or pozzolanic reaction (poz). Some pozzolana such as GGBS possesses high CaO content and increases the calcium hydroxide available to pozzolanic reaction during mixing. They are accounted for with the term $V_{p,nor(GGBS)}$ which can be determined using Equation (B.20).

$$V_{p,nor(GGBS)} = 1.982V_{CaO} \quad (B.20)$$

V_{CaO} refers to the volumetric ratio of CaO in GGBS. The coefficient 1.982 is determined from the volume stoichiometry relationship shown in Equation (B.21). The details of the calculation are provided in Table B.1.

Table B.1: Calculation of Volume Stoichiometry

Phase	CaO	H_2O	$Ca(OH)_2$
Mass (%)	75.690	24.310	100.000
Mass (kg)	56.079	18.011	74.09
Density (kg/m ³)	3345	1000	2230
Volume (m ³)	0.017	0.018	0.033
Normalised Volume	1	1.074	1.982

The gel pores for normal cement reaction and pozzolanic reaction is reported to be 28% and 19% by volume of C-S-H gel (Bentz, 2000). Therefore, capillary and gel pores can be calculated using Equations (B.22) to (B.24). $v_{poz,c}$ and $v_{poz,p}$ are ratio of volumetric expansion of hydration products C-S-H gel (4.6) and calcium hydroxide (2.08) from pozzolanic reaction respectively (Bentz and Garboczi, 1991).

$$V_{cap} = V_{wat} - V_{nor,exp} - V_{poz,exp} \quad (B.22)$$

$$V_{poz,exp} = (v_{poz,c} - v_{poz,p} - 1)V_p \alpha_p \quad (B.23)$$

$$V_{gel} = 0.28V_{c,nor} + 0.19V_{c,poz} \quad (B.24)$$

The probable combination of w/b, percentage of replacement of cement with pozzolana, chemical and physical properties of pozzolana and α are too many. To simplify the task of determine the volumetric ratio of the hydration products, a series of lookup tables attached in this appendix can be used. n_0 and V_{hyd} refer to volumetric ratio of pores and volumetric ratio of sum of hydration products respectively. Linear interpolation is to be used for mix proportions not listed in the tables.

Table B.2: V_{hyd} and n_0 for Normal Cement Paste

W/C	α_{nor}	V_a	V_c^*	V_p	V_{hyd}	n_0
0.2	0.000	0.000	0.000	0.000	0.000	0.387
	0.202	0.070	0.106	0.054	0.230	0.280
	0.400	0.140	0.210	0.107	0.457	0.175
	0.525	0.183	0.275	0.141	0.600	0.109
0.3	0.000	0.000	0.000	0.000	0.000	0.486
	0.301	0.088	0.133	0.068	0.289	0.352
	0.600	0.176	0.264	0.135	0.575	0.220
	0.788	0.231	0.346	0.177	0.755	0.136
0.4	0.000	0.000	0.000	0.000	0.000	0.558
	0.301	0.076	0.114	0.058	0.248	0.443
	0.600	0.151	0.227	0.116	0.495	0.328
	1.000	0.252	0.378	0.194	0.824	0.176
0.5	0.000	0.000	0.000	0.000	0.000	0.612
	0.300	0.066	0.100	0.051	0.217	0.511
	0.600	0.133	0.199	0.102	0.434	0.411
	1.000	0.221	0.332	0.170	0.723	0.277
0.6	0.000	0.000	0.000	0.000	0.000	0.654
	0.298	0.059	0.088	0.045	0.192	0.565
	0.600	0.118	0.178	0.091	0.387	0.475
	1.000	0.197	0.296	0.152	0.645	0.355

* Volume of C-S-H gel excludes gel pores

Table B.3: V_{hyd} and n_0 for SF Blended Cement Paste

W/B	α_{nor}	5% Replacement					10% Replacement					15% Replacement				
		V_a	V_c^*	V_p	V_{hyd}	n_0	V_a	V_c^*	V_p	V_{hyd}	n_0	V_a	V_c^*	V_p	V_{hyd}	n_0
0.2	0.000	0.000	0.000	0.000	0.000	0.381	0.000	0.000	0.000	0.000	0.377	0.000	0.000	0.000	0.000	0.372
	0.202	0.066	0.110	0.046	0.213	0.280	0.062	0.114	0.038	0.197	0.280	0.058	0.118	0.030	0.180	0.280
	0.400	0.131	0.229	0.086	0.420	0.178	0.123	0.248	0.066	0.384	0.181	0.114	0.266	0.046	0.348	0.184
	0.453	0.148	0.332	0.066	0.457	0.139	0.139	0.423	0.011	0.394	0.132	0.129	0.418	0.000	0.360	0.140
0.3	0.000	0.000	0.000	0.000	0.000	0.481	0.000	0.000	0.000	0.000	0.475	0.000	0.000	0.000	0.000	0.470
	0.301	0.083	0.137	0.058	0.268	0.353	0.078	0.141	0.049	0.248	0.354	0.073	0.145	0.040	0.228	0.355
	0.600	0.165	0.288	0.109	0.530	0.224	0.155	0.313	0.083	0.485	0.228	0.145	0.336	0.058	0.441	0.232
	0.724	0.199	0.391	0.113	0.628	0.164	0.187	0.461	0.063	0.562	0.164	0.174	0.527	0.017	0.496	0.164
0.4	0.000	0.000	0.000	0.000	0.000	0.552	0.000	0.000	0.000	0.000	0.547	0.000	0.000	0.000	0.000	0.542
	0.301	0.071	0.117	0.051	0.231	0.443	0.067	0.120	0.043	0.214	0.443	0.063	0.123	0.036	0.198	0.443
	0.600	0.142	0.238	0.099	0.460	0.333	0.134	0.248	0.082	0.425	0.337	0.125	0.258	0.065	0.391	0.341
	1.000	0.237	0.435	0.147	0.756	0.180	0.223	0.490	0.102	0.687	0.185	0.208	0.545	0.057	0.618	0.190
0.5	0.000	0.000	0.000	0.000	0.000	0.607	0.000	0.000	0.000	0.000	0.602	0.000	0.000	0.000	0.000	0.597
	0.300	0.063	0.102	0.044	0.202	0.511	0.059	0.104	0.038	0.188	0.510	0.055	0.107	0.032	0.174	0.509
	0.600	0.125	0.206	0.088	0.405	0.414	0.117	0.213	0.074	0.375	0.418	0.110	0.220	0.061	0.346	0.421
	1.000	0.208	0.382	0.130	0.664	0.280	0.196	0.431	0.090	0.604	0.283	0.183	0.480	0.050	0.544	0.286
0.6	0.000	0.000	0.000	0.000	0.000	0.649	0.000	0.000	0.000	0.000	0.644	0.000	0.000	0.000	0.000	0.640
	0.298	0.055	0.090	0.039	0.180	0.564	0.052	0.092	0.034	0.167	0.563	0.049	0.094	0.028	0.154	0.562
	0.600	0.112	0.183	0.079	0.361	0.478	0.105	0.188	0.067	0.336	0.481	0.098	0.193	0.056	0.310	0.483
	1.000	0.186	0.341	0.116	0.592	0.358	0.175	0.385	0.080	0.539	0.360	0.164	0.429	0.045	0.486	0.362

Table B.4: V_{hyd} and n_0 for GGBS Blended Cement Paste

W/B	α_{nor}	10% Replacement					20% Replacement					30% Replacement				
		V_a	V_c^*	V_p	V_{hyd}	n_0	V_a	V_c^*	V_p	V_{hyd}	n_0	V_a	V_c^*	V_p	V_{hyd}	n_0
0.2	0.000	0.000	0.000	0.000	0.000	0.383	0.000	0.000	0.000	0.000	0.380	0.000	0.000	0.000	0.000	0.378
	0.106	0.033	0.073	0.064	0.151	0.307	0.029	0.090	0.099	0.180	0.284	0.025	0.107	0.134	0.207	0.261
	0.202	0.063	0.132	0.080	0.244	0.245	0.055	0.158	0.105	0.256	0.211	0.048	0.183	0.130	0.267	0.178
	0.306	0.095	0.198	0.096	0.345	0.176	0.084	0.235	0.109	0.338	0.129	0.073	0.272	0.123	0.330	0.082
0.3	0.000	0.000	0.000	0.000	0.000	0.483	0.000	0.000	0.000	0.000	0.479	0.000	0.000	0.000	0.000	0.476
	0.201	0.053	0.108	0.068	0.205	0.370	0.046	0.128	0.091	0.216	0.343	0.040	0.147	0.113	0.227	0.317
	0.400	0.105	0.207	0.097	0.368	0.267	0.092	0.238	0.104	0.353	0.226	0.080	0.269	0.111	0.336	0.185
	0.532	0.139	0.271	0.118	0.478	0.201	0.123	0.308	0.116	0.445	0.153	0.107	0.344	0.114	0.411	0.105
0.4	0.000	0.000	0.000	0.000	0.000	0.554	0.000	0.000	0.000	0.000	0.551	0.000	0.000	0.000	0.000	0.548
	0.301	0.068	0.134	0.072	0.248	0.415	0.060	0.154	0.086	0.247	0.387	0.052	0.174	0.100	0.245	0.360
	0.599	0.135	0.256	0.113	0.461	0.289	0.119	0.285	0.110	0.428	0.250	0.104	0.313	0.108	0.393	0.212
	0.890	0.201	0.356	0.163	0.676	0.188	0.177	0.376	0.153	0.617	0.158	0.154	0.395	0.143	0.558	0.129
0.5	0.000	0.000	0.000	0.000	0.000	0.609	0.000	0.000	0.000	0.000	0.606	0.000	0.000	0.000	0.000	0.603
	0.300	0.059	0.117	0.064	0.218	0.487	0.053	0.134	0.076	0.217	0.464	0.046	0.151	0.089	0.216	0.440
	0.600	0.119	0.223	0.101	0.406	0.377	0.105	0.247	0.099	0.378	0.345	0.092	0.271	0.097	0.348	0.312
	1.000	0.198	0.346	0.160	0.665	0.254	0.175	0.359	0.149	0.605	0.231	0.153	0.372	0.139	0.546	0.208
0.6	0.000	0.000	0.000	0.000	0.000	0.651	0.000	0.000	0.000	0.000	0.648	0.000	0.000	0.000	0.000	0.645
	0.303	0.054	0.105	0.057	0.196	0.542	0.047	0.120	0.069	0.196	0.521	0.041	0.134	0.080	0.195	0.501
	0.600	0.106	0.198	0.090	0.363	0.446	0.094	0.218	0.089	0.338	0.418	0.082	0.238	0.089	0.312	0.390
	1.000	0.177	0.308	0.142	0.593	0.335	0.156	0.320	0.133	0.540	0.314	0.136	0.332	0.124	0.487	0.293

Table B.5: V_{hyd} and n_0 for FA Blended Cement Paste

W/B	α_{nor}	10% Replacement					20% Replacement					30% Replacement				
		V_a	V_c^*	V_p	V_{hyd}	n_0	V_a	V_c^*	V_p	V_{hyd}	n_0	V_a	V_c^*	V_p	V_{hyd}	n_0
0.2	0.000	0.000	0.000	0.000	0.000	0.375	0.000	0.000	0.000	0.000	0.364	0.000	0.000	0.000	0.000	0.354
	0.154	0.047	0.085	0.027	0.147	0.287	0.041	0.088	0.013	0.120	0.271	0.035	0.089	0.001	0.094	0.258
	0.300	0.091	0.166	0.051	0.285	0.203	0.079	0.174	0.023	0.231	0.180	0.067	0.178	0.000	0.181	0.163
	0.403	0.123	0.237	0.059	0.377	0.128	0.106	0.261	0.014	0.297	0.086	0.090	0.239	0.000	0.243	0.097
0.3	0.000	0.000	0.000	0.000	0.000	0.474	0.000	0.000	0.000	0.000	0.462	0.000	0.000	0.000	0.000	0.451
	0.201	0.052	0.092	0.030	0.162	0.379	0.045	0.094	0.017	0.133	0.363	0.038	0.095	0.004	0.106	0.349
	0.400	0.103	0.183	0.060	0.322	0.285	0.089	0.189	0.031	0.264	0.263	0.076	0.195	0.005	0.209	0.242
	0.613	0.157	0.301	0.078	0.484	0.160	0.137	0.330	0.021	0.385	0.110	0.117	0.309	0.000	0.314	0.118
0.4	0.000	0.000	0.000	0.000	0.000	0.545	0.000	0.000	0.000	0.000	0.534	0.000	0.000	0.000	0.000	0.523
	0.301	0.067	0.117	0.040	0.211	0.425	0.058	0.119	0.023	0.175	0.409	0.050	0.121	0.007	0.140	0.394
	0.600	0.133	0.238	0.077	0.418	0.300	0.116	0.247	0.040	0.343	0.273	0.099	0.257	0.004	0.271	0.247
	0.840	0.186	0.350	0.096	0.576	0.181	0.162	0.382	0.032	0.462	0.127	0.139	0.368	0.000	0.375	0.127
0.5	0.000	0.000	0.000	0.000	0.000	0.600	0.000	0.000	0.000	0.000	0.589	0.000	0.000	0.000	0.000	0.578
	0.300	0.059	0.102	0.036	0.185	0.495	0.051	0.104	0.021	0.154	0.480	0.044	0.105	0.008	0.124	0.466
	0.600	0.117	0.206	0.070	0.369	0.388	0.102	0.211	0.040	0.306	0.367	0.088	0.217	0.011	0.245	0.346
	1.000	0.195	0.355	0.109	0.609	0.232	0.170	0.378	0.049	0.497	0.189	0.146	0.379	0.005	0.399	0.170
0.6	0.000	0.000	0.000	0.000	0.000	0.643	0.000	0.000	0.000	0.000	0.632	0.000	0.000	0.000	0.000	0.622
	0.298	0.052	0.090	0.032	0.164	0.550	0.045	0.092	0.019	0.137	0.536	0.039	0.093	0.007	0.111	0.523
	0.600	0.105	0.182	0.064	0.331	0.455	0.091	0.186	0.038	0.276	0.437	0.079	0.190	0.013	0.222	0.419
	1.000	0.174	0.317	0.097	0.544	0.314	0.152	0.338	0.044	0.445	0.274	0.131	0.344	0.002	0.355	0.251

Appendix C

Derivation of Equations for Finite Element Formulation of Heat and Mass Transfer

From the first law of thermodynamics (expressed using Fourier's law of heat conduction)

$$(\rho C) \frac{\partial T}{\partial t} = \nabla(k \nabla T) - (\rho C v) \nabla T - \lambda_e \dot{E} - \lambda_d \frac{\partial w_{d,T}}{\partial t} \quad (C.1)$$

From the conservation of mass (in order of free water, vapour and dry air)

$$\frac{\partial M_L}{\partial t} = -\nabla[M_L v_L] - \dot{E} + \frac{\partial w_{d,T}}{\partial t} \quad (C.2)$$

$$\frac{\partial(V_G \tilde{M}_V)}{\partial t} = -\nabla J_V + \dot{E} + \frac{\partial w_{d,T}}{\partial t}, J_V = V_G \tilde{M}_V v_G - V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{M}_V}{\tilde{M}_G} \right) \quad (C.3)$$

$$\frac{\partial(V_G \tilde{M}_A)}{\partial t} = -\nabla J_A, J_A = V_G \tilde{M}_A v_G - V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{M}_A}{\tilde{M}_G} \right) \quad (C.4)$$

From Equation (C.2)

$$\dot{E} = -\nabla[M_L v_L] + \frac{\partial w_{d,T}}{\partial t} - \frac{\partial M_L}{\partial t} \quad (C.5)$$

The unknowns variables are chosen to be T , $\tilde{M}_V$ and P_G . Hence, expressing all terms used in Equations (C.2) to (C.5) as a function of the unknown variables.

Common Relationships

Ideal Gas Law

$$P_A = \tilde{M}_A R_A T$$

$$P_V = \tilde{M}_V R_V T$$

Dalton's Law

$$P_G = P_A + P_V$$

$$\tilde{M}_G = \tilde{M}_A + \tilde{M}_V$$

Darcy's Law

$$v_G = -\frac{KK_G}{\mu_G} \nabla P_G$$

$$v_L = -\frac{K}{\mu_L} \nabla P_L$$

Behaviour of Mass of Non-Evaporable Moisture Loss

$$M_{d,T} = f(T)$$

Time Derivative of Mass of Non-Evaporable Moisture Loss

$$\frac{\partial w_{d,T}}{\partial t} = \frac{\partial w_{d,T}}{\partial T} \frac{\partial T}{\partial t}$$

Behaviour of Pores

$$V_{pore,T} = f(T)$$

Time Derivative of Volume of Pores

$$\frac{\partial n_T}{\partial t} = \frac{\partial n_T}{\partial T} \frac{\partial T}{\partial t}$$

Mass of Free Water

$$M_L = f(T, \tilde{M}_V)$$

Time Derivative of Mass of Free Water

$$\frac{\partial M_L}{\partial t} = \frac{\partial M_{L,T}}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial M_{L,\tilde{M}_V}}{\partial \tilde{M}_V} \frac{\partial \tilde{M}_V}{\partial t}$$

Mass of Air in Unit Volume of Binary Gas Mixture

$$\tilde{M}_A = \frac{P_A}{R_A T} = \frac{P_G - P_V}{R_A T} = \frac{P_G - \tilde{M}_V R_V T}{R_A T} = \frac{P_G}{R_A T} - \frac{R_V}{R_A} \tilde{M}_V = f(T, \tilde{M}_V, P_G)$$

Time Derivative of Mass of Air in Unit Volume of Binary Gas Mixture

$$\frac{\partial \tilde{M}_A}{\partial t} = \frac{\partial}{\partial t} \left(\frac{P_G}{R_A T} - \frac{R_V}{R_A} \tilde{M}_V \right) = \left(-\frac{P_G}{R_A T^2} \right) \frac{\partial T}{\partial t} + \left(-\frac{R_V}{R_A} \right) \frac{\partial \tilde{M}_V}{\partial t} + \left(\frac{1}{R_A T} \right) \frac{\partial P_G}{\partial t}$$

Mass Gradient of Air

$$\begin{aligned} \nabla \tilde{M}_A &= \nabla \left(\frac{P_G}{R_A T} - \frac{R_V}{R_A} \tilde{M}_V \right) = \frac{T \nabla P_G - P_G \nabla T}{R_A T^2} - \frac{R_V}{R_A} \nabla \tilde{M}_V \\ &= \left(-\frac{P_G}{R_A T^2} \right) \nabla T + \left(-\frac{R_V}{R_A} \right) \nabla \tilde{M}_V + \left(\frac{1}{R_A T} \right) \nabla P_G \end{aligned}$$

Mass Concentration Gradient of Air in Gas

$$\begin{aligned} \nabla \left(\frac{\tilde{M}_A}{\tilde{M}_G} \right) &= \frac{1}{\tilde{M}_G} \nabla (\tilde{M}_A) - \frac{\tilde{M}_A}{\tilde{M}_G^2} \nabla (\tilde{M}_G) = \frac{(\tilde{M}_A + \tilde{M}_V) \nabla (\tilde{M}_A) - \tilde{M}_A \nabla (\tilde{M}_A + \tilde{M}_V)}{\tilde{M}_G^2} \\ &= \frac{\tilde{M}_V \nabla (\tilde{M}_A) - \tilde{M}_A \nabla (\tilde{M}_V)}{\tilde{M}_G^2} \end{aligned}$$

Mass Concentration Gradient of Vapour in Gas

$$\nabla \left(\frac{\tilde{M}_V}{\tilde{M}_G} \right) = \nabla \left(1 - \frac{\tilde{M}_A}{\tilde{M}_G} \right) = -\nabla \left(\frac{\tilde{M}_A}{\tilde{M}_G} \right)$$

Air Flux

$$\begin{aligned}
 -J_A &= \frac{KK_G}{\mu_G} V_G \tilde{M}_A \nabla P_G + V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{M}_A}{\tilde{M}_G} \right) \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_A \nabla P_G + V_G \tilde{M}_G D_{AV} \frac{\tilde{M}_V \nabla(\tilde{M}_A) - \tilde{M}_A \nabla(\tilde{M}_V)}{\tilde{M}_G^2} \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_A \nabla P_G + \frac{V_G D_{AV} \tilde{M}_V}{\tilde{M}_G} \nabla(\tilde{M}_A) - \frac{V_G D_{AV} \tilde{M}_A}{\tilde{M}_G} \nabla(\tilde{M}_V) \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_A \nabla P_G + \frac{V_G D_{AV} \tilde{M}_V}{\tilde{M}_G} \left[\left(-\frac{P_G}{R_A T^2} \right) \nabla T + \left(-\frac{R_V}{R_A} \right) \nabla \tilde{M}_V + \left(\frac{1}{R_A T} \right) \nabla P_G \right] \\
 &\quad - \frac{V_G D_{AV} \tilde{M}_A}{\tilde{M}_G} \nabla(\tilde{M}_V) \\
 &= \left(-\frac{V_G D_{AV} \tilde{M}_V P_G}{\tilde{M}_G R_A T^2} \right) \nabla T + \left(-\tilde{M}_A - \frac{R_V}{R_A} \tilde{M}_V \right) \frac{V_G D_{AV}}{\tilde{M}_G} \nabla \tilde{M}_V \\
 &\quad + \left(\frac{KK_G}{\mu_G} V_G \tilde{M}_A + \frac{V_G D_{AV} \tilde{M}_V}{\tilde{M}_G R_A T} \right) \nabla P_G
 \end{aligned}$$

Vapour Flux

$$\begin{aligned}
 -J_V &= \frac{KK_G}{\mu_G} V_G \tilde{M}_V \nabla P_G + V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{M}_V}{\tilde{M}_G} \right) \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_V \nabla P_G - V_G \tilde{M}_G D_{AV} \nabla \left(\frac{\tilde{\rho}_A}{\tilde{\rho}_G} \right) \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_V \nabla P_G - V_G \tilde{M}_G D_{AV} \frac{\tilde{M}_V \nabla(\tilde{M}_A) - \tilde{M}_A \nabla(\tilde{M}_V)}{\tilde{M}_G^2} \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_V \nabla P_G - \frac{V_G D_{AV} \tilde{M}_V}{\tilde{M}_G} \nabla(\tilde{M}_A) + \frac{V_G D_{AV} \tilde{M}_A}{\tilde{M}_G} \nabla(\tilde{M}_V) \\
 &= \frac{KK_G}{\mu_G} V_G \tilde{M}_V \nabla P_G - \frac{V_G D_{AV} \tilde{M}_V}{\tilde{M}_G} \left[\left(-\frac{P_G}{R_A T^2} \right) \nabla T + \left(-\frac{R_V}{R_A} \right) \nabla \tilde{M}_V + \left(\frac{1}{R_A T} \right) \nabla P_G \right] + \frac{V_G D_{AV} \tilde{M}_A}{\tilde{M}_G} \nabla(\tilde{M}_V) \\
 &= \left(\frac{V_G D_{AV} \tilde{M}_V P_G}{\tilde{M}_G R_A T^2} \right) \nabla T + \left(\tilde{M}_A + \frac{R_V}{R_A} \tilde{M}_V \right) \frac{V_G D_{AV}}{\tilde{M}_G} \nabla \tilde{M}_V + \left(\frac{KK_G}{\mu_G} - \frac{D_{AV}}{\tilde{M}_G R_A T} \right) V_G \tilde{M}_V \nabla P_G \\
 &= K_{VT} \nabla T + K_{VV} \nabla \tilde{M}_V + K_{VP} \nabla P_G
 \end{aligned}$$

Time Derivative of Volume of Gas Mixture in Unit Volume of Concrete

$$V_G = n_T - \frac{M_L}{\rho_L}$$

$$\begin{aligned} \frac{\partial V_G}{\partial t} &= \frac{\partial n_T}{\partial t} - \frac{1}{\rho_L} \frac{\partial M_L}{\partial t} = \frac{\partial n_T}{\partial T} \frac{\partial T}{\partial t} - \frac{1}{\rho_L} \left(\frac{\partial M_{L,T}}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \frac{\partial \tilde{M}_v}{\partial t} \right) \\ &= \left(\frac{\partial n_T}{\partial T} - \frac{1}{\rho_L} \frac{\partial M_{L,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(-\frac{1}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \end{aligned}$$

Time Derivative of Mass of Air in Unit Volume of Concrete

$$\begin{aligned} \frac{\partial (V_G \tilde{M}_A)}{\partial t} &= V_G \frac{\partial \tilde{M}_A}{\partial t} + \tilde{M}_A \frac{\partial V_G}{\partial t} = V_G \left[\left(-\frac{P_G}{R_A T^2} \right) \frac{\partial T}{\partial t} + \left(-\frac{R_v}{R_A} \right) \frac{\partial \tilde{M}_v}{\partial t} + \left(\frac{1}{R_A T} \right) \frac{\partial P_G}{\partial t} \right] \\ &+ \tilde{M}_A \left[\left(\frac{\partial n_T}{\partial T} - \frac{1}{\rho_L} \frac{\partial M_{L,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(-\frac{1}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \right] \\ &= \left(\frac{\partial n_T}{\partial T} \tilde{M}_A - \frac{\tilde{M}_A}{\rho_L} \frac{\partial M_{L,T}}{\partial T} - \frac{V_G P_G}{R_A T^2} \right) \frac{\partial T}{\partial t} + \left(-\frac{R_v}{R_A} V_G - \frac{\tilde{M}_A}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + \left(\frac{V_G}{R_A T} \right) \frac{\partial P_G}{\partial t} \end{aligned}$$

Time Derivative of Mass of Vapour in Unit Volume of Concrete

$$\begin{aligned} \frac{\partial (V_G \tilde{M}_v)}{\partial t} &= V_G \frac{\partial \tilde{M}_v}{\partial t} + \tilde{M}_v \frac{\partial V_G}{\partial t} \\ &= V_G \frac{\partial \tilde{M}_v}{\partial t} + \tilde{M}_v \left[\left(\frac{\partial n_T}{\partial T} - \frac{1}{\rho_L} \frac{\partial M_{L,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(-\frac{1}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \right] \\ &= \left(\tilde{M}_v \frac{\partial n_T}{\partial T} - \frac{\tilde{M}_v}{\rho_L} \frac{\partial M_{L,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(V_G - \frac{\tilde{M}_v}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \end{aligned}$$

Substitute Equation (C.5) into Equation (C.1), and assuming $P_L = P_G$ and $\rho C v = 0$,

$$(\rho C) \frac{\partial T}{\partial t} = \nabla (k \nabla T) - \lambda_e \left(-\nabla \left[M_L \left(-\frac{K}{\mu_L} \nabla P_G \right) \right] + \frac{\partial w_{d,T}}{\partial t} - \frac{\partial M_L}{\partial t} \right) - \lambda_d \frac{\partial w_{d,T}}{\partial t}$$

LHS

$$\begin{aligned}
 & (\rho C) \frac{\partial T}{\partial t} + (\lambda_d + \lambda_e) \frac{\partial w_{d,T}}{\partial T} \frac{\partial T}{\partial t} - \lambda_e \frac{\partial M_L}{\partial T} \frac{\partial T}{\partial t} - \lambda_e \frac{\partial M_L}{\partial \tilde{M}_v} \frac{\partial \tilde{M}_v}{\partial t} \\
 &= \left(\rho C + (\lambda_d + \lambda_e) \frac{\partial w_{d,T}}{\partial T} - \lambda_e \frac{\partial M_{L,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(-\lambda_e \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \\
 &= C_{TT} \frac{\partial T}{\partial t} + C_{TV} \frac{\partial \tilde{M}_v}{\partial t} + C_{TP} \frac{\partial P_G}{\partial t}
 \end{aligned}$$

RHS

$$\begin{aligned}
 & k \nabla T + (0) \nabla \tilde{M}_v + \left(-\lambda_e M_L \left(\frac{K}{\mu_L} \right) \right) \nabla P_G \\
 &= K_{TT} \nabla T + K_{TV} \nabla \tilde{M}_v + K_{TP} \nabla P_G
 \end{aligned}$$

Substitute Equation (C.5) into Equation (C.3) , and assuming $P_L = P_G$

$$\begin{aligned}
 \frac{\partial (V_G \tilde{M}_v)}{\partial t} &= -\nabla J_v - \nabla [M_L v_L] + \frac{\partial w_{d,T}}{\partial t} - \frac{\partial M_L}{\partial t} \\
 \frac{\partial M_L}{\partial t} - \frac{\partial w_{d,T}}{\partial t} + \frac{\partial (V_G \tilde{M}_v)}{\partial t} &= \nabla (-J_v - M_L v_L)
 \end{aligned}$$

where $-J_v = K_{vT} \nabla T + K_{vV} \nabla \tilde{M}_v + K_{vP} \nabla P_G$

LHS

$$\begin{aligned}
 \frac{\partial M_L}{\partial t} - \frac{\partial w_{d,T}}{\partial t} + \frac{\partial (V_G \tilde{M}_v)}{\partial t} &= \frac{\partial M_{L,T}}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \frac{\partial \tilde{M}_v}{\partial t} - \frac{\partial w_{d,T}}{\partial T} \frac{\partial T}{\partial t} \\
 &+ \left(\tilde{M}_v \frac{\partial n_T}{\partial T} - \frac{\tilde{M}_v}{\rho_L} \frac{\partial M_{L,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(V_G - \frac{\tilde{M}_v}{\rho_L} \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \\
 &= \left(\tilde{M}_v \frac{\partial n_T}{\partial T} + \left(1 - \frac{\tilde{M}_v}{\rho_L} \right) \frac{\partial M_{L,T}}{\partial T} - \frac{\partial w_{d,T}}{\partial T} \right) \frac{\partial T}{\partial t} + \left(V_G + \left(1 - \frac{\tilde{M}_v}{\rho_L} \right) \frac{\partial M_{L,\tilde{M}_v}}{\partial \tilde{M}_v} \right) \frac{\partial \tilde{M}_v}{\partial t} + (0) \frac{\partial P_G}{\partial t} \\
 &= C_{MT} \frac{\partial T}{\partial t} + C_{MV} \frac{\partial \tilde{M}_v}{\partial t} + C_{MP} \frac{\partial P_G}{\partial t}
 \end{aligned}$$

RHS

$$\begin{aligned}
 -J_V - M_L v_L &= K_{VT} \nabla T + K_{VV} \nabla \tilde{M}_V + K_{VP} \nabla P_G + M_L \frac{K}{\mu_L} \nabla P_L \\
 &= K_{VT} \nabla T + K_{VV} \nabla \tilde{M}_V + K_{VP} \nabla P_G + M_L \frac{K}{\mu_L} \nabla P_G \\
 &= K_{VT} \nabla T + K_{VV} \nabla \tilde{M}_V + \left(K_{VP} + M_L \frac{K}{\mu_L} \right) \nabla P_G \\
 &= K_{MT} \nabla T + K_{MV} \nabla \tilde{M}_V + K_{MP} \nabla P_G
 \end{aligned}$$

From Equation (C.4),

$$\frac{\partial(V_G \tilde{M}_A)}{\partial t} = -\nabla J_A$$

LHS, T is in Kelvin

$$\begin{aligned}
 \frac{\partial(V_G \tilde{M}_A)}{\partial t} &= \left(\frac{\partial n_T}{\partial T} \tilde{M}_A - \frac{\tilde{M}_A}{\rho_L} \frac{\partial M_{L,T}}{\partial T} - \frac{V_G P_G}{R_A T^2} \right) \frac{\partial T}{\partial t} + \left(-\frac{R_V}{R_A} V_G - \frac{\tilde{M}_A}{\rho_L} \frac{\partial M_{L,\tilde{M}_V}}{\partial \tilde{M}_V} \right) \frac{\partial \tilde{M}_V}{\partial t} \\
 &\quad + \left(\frac{V_G}{R_A T} \right) \frac{\partial P_G}{\partial t} \\
 &= C_{AT} \frac{\partial T}{\partial t} + C_{AV} \frac{\partial \tilde{M}_A}{\partial t} + C_{AP} \frac{\partial P_G}{\partial t}
 \end{aligned}$$

RHS

$$\begin{aligned}
 -J_A &= \left(-\frac{V_G D_{AV} \tilde{M}_V P_G}{\tilde{M}_G R_A T^2} \right) \nabla T + \left(-\tilde{M}_A - \frac{R_V}{R_A} \tilde{M}_V \right) \frac{V_G D_{AV}}{\tilde{M}_G} \nabla \tilde{M}_V \\
 &\quad + \left(\frac{K K_G}{\mu_G} V_G \tilde{M}_A + \frac{V_G D_{AV} \tilde{M}_V}{\tilde{M}_G R_A T} \right) \nabla P_G \\
 &= K_{AT} \nabla T + K_{AV} \nabla \tilde{M}_V + K_{AP} \nabla P_G
 \end{aligned}$$

The energy and mass balance equations are combined to form a 3x3 matrix which takes up the general form given below.

$$[C] \frac{\partial}{\partial t} \{\Phi\} = \nabla \cdot ([K] \nabla \{\Phi\})$$

The notation for each cell within the matrix $[C]$ and $[K]$ is given below.

$$\begin{pmatrix} C_{TT} & C_{TV} & C_{TP} \\ C_{MT} & C_{MV} & C_{MP} \\ C_{AT} & C_{AV} & C_{AP} \end{pmatrix} \frac{\partial}{\partial t} \begin{Bmatrix} T \\ \tilde{M}_v \\ P_G \end{Bmatrix} = \nabla \cdot \left(\begin{pmatrix} K_{TT} & K_{TV} & K_{TP} \\ K_{MT} & K_{MV} & K_{MP} \\ K_{AT} & K_{AV} & K_{AP} \end{pmatrix} \nabla \begin{Bmatrix} T \\ \tilde{M}_v \\ P_G \end{Bmatrix} \right)$$