

**INFLUENCE OF MULTIPLE BLENDED BINDERS ON ENGINEERING  
PROPERTIES AND DURABILITY OF CONCRETE**

**by**

**MOHD FADZIL B ARSHAD**

**Thesis submitted in fulfillment of the requirements  
for the degree of  
Doctor of Philosophy**

**August 2010**

**INFLUENCE OF MULTIPLE BLENDED BINDERS ON ENGINEERING  
PROPERTIES AND DURABILITY OF CONCRETE**

**MOHD FADZIL B ARSHAD**

**UNIVERSITI SAINS MALAYSIA**

**2010**

**PENGARUH PEREKAT CAMPURAN BERBILANG KE ATAS SIFAT-SIFAT  
KEJURUTERAAN DAN KETAHANLASAKAN KONKRIT**

**MOHD FADZIL B ARSHAD**

**Tesis yang diserahkan untuk  
Memenuhi keperluan bagi  
Ijazah doktor falsafah**

**UNIVERSITI SAINS MALAYSIA**

**Ogos 2010**

## ACKNOWLEDGEMENTS

*With the name of Allah and His messenger Prophet Muhammad s.a.w.*

First of all the author would like to thank to Allah s.w.t. for his blessing and kindness that giving the opportunity so that this PhD thesis can be completes as it is that was only a dream once before, “Thank you Allah”.

Along the process of completing this thesis, author was sheltered by a group of people that is directly or indirectly, gives strength and supported to author in completing the task. Author would like to express his sincere appreciation to all off them especially his supervisor, Associate Professor Dr Megat Azmi Megat Johari in Civil Engineering School, for his patient, advice, continuous support and encouragement throughout the period of research and during the preparation of this thesis.

The author also wishes to thank his co-supervisors Associate Professor Dr Badorul Hisham Abu Bakar and Professor Khairun Azizi Mohd Azizli for providing grants, facilities and support for this research programme.

Thanks also extended to University Technology MARA (UiTM) for providing scholarship and School of Civil Engineering, University Science Malaysia (USM) for providing facilities and very supporting technical staff so that the research was carryout smoothly.

The author also wish to acknowledge his helping hands, Mr Ramadhansyah Putra Jaya, Mr Norhasri, Mr Fuad and Mr Ridzuan who has struggling in preparing specimens for the experiments. To Choong, Abdullahi, Ayu, Puga, Farah, Yee, Wesam, Bashir, Sheena and all others best colleagues of civil engineering postgraduates room, ACEPRO members and USM staff, the author is really appreciated each moments that been together throughout the duration of this research.

Finally, the author is very grateful to his wife, Norhayah Osman for her enduring support, loves, encouragement and patience, particularly in upbringing our children, Nor Atiqah, Mohd Ashmaan and Nor Atrisyah. Their support and presence have undoubtedly relieved the pressure of doing this research. Also, the loves, patience and prayers of his parents (Arshad Lebai Hashim and Maimunah Mohammad, Osman Awang and Aminah Ijam) and all family members will never be forgotten.

*May Allah will bless all of you. Thank you....*

## TABLES OF CONTENTS

Content	Page
Acknowledgements	i
Table of Contents	ii
List of Tables	ix
List of Figures	xi
List of Plates	xvi
List of Abbreviations	xvii
List of Publications	xviii
Abstract	xx
Abstrak	xxi

### **CHAPTER 1      INTRODUCTION**

1.1	Background study	1
1.2	Problem Statement	3
1.3	Aim and Objectives	4
1.4	Scope of research	5
1.5	Definitions of terms	6
	1.5.1 Pozzolanic Materials	6
	1.5.2 Ternary blended cement (TBC)	6
	1.5.3 Binary blended cement (BBC)	6
	1.5.4 High performance concrete	6
	1.5.5 Multi blended cement (MBC)	7
1.6	Layout of Thesis	7

### **CHAPTER 2      LITERATURE REVIEW**

2.1	Introduction	9
2.2	High performance concrete (HPC)	11
2.3	Cement for HPC	13
2.4	Ordinary Portland Cement (OPC)	14
2.5	Pozzolanic Materials	18
	2.5.1 Silica Fume (SF)	19
	2.5.1.1 Chemical Composition of Silica Fume (SF)	20
	2.5.1.2 Physical Characteristic of Silica Fume (SF)	21
	2.5.2 Fly Ash (FA)	22

2.5.2.1	Chemical composition of FA	23
2.5.2.2	Physical Properties of Fly Ash (FA)	24
2.5.3	Metakaolin (MK)	25
2.5.3.1	Chemical Composition of Metakaolin (MK)	26
2.5.3.2	Physical Properties of Metakaolin (MK)	26
2.5.4	Rice Husk Ash (RHA)	27
2.5.4.1	Chemical Composition of Rice Husk Ash (RHA)	28
2.5.4.2	Physical Properties of Rice Husk Ash (RHA)	29
2.6	Classifications of Pozzolan	29
2.7	Standard Specifications of Pozzolans	31
2.7.1	British Standard	31
2.7.2	American Standard	32
2.8	Pozzolanic Cement	34
2.9	Effect of Pozzolans on Engineering Properties of HPC	35
2.9.1	Silica Fume (SF)	36
2.9.1.1	Effects on Fresh Concrete	36
2.9.2.2	Effects on Hardened Concrete	37
2.9.2	Fly Ash (FA)	39
2.9.2.1	Effects on Fresh Concrete	39
2.9.2.2	Effects on Hardened Concrete	43
2.9.3	Metakaolin (MK)	46
2.9.3.1	Effects on Fresh Concrete	46
2.9.3.2	Effects on Hardened Concrete	47
2.9.4	Rice husk Ash (RHA)	51
2.9.4.1	Effect on fresh concrete	51
2.9.4.2	Effect on hardened concrete	52
2.10	Durability Performance	54
2.10.1	Silica Fume (SF)	57
2.10.2	Fly Ash (FA)	58
2.10.3	Metakaolin	59
2.10.4	Rice Husk Ash	61
2.11	Ternary Blended Cement (TBC)	62
2.12	Summary	64

<b>CHAPTER 3</b>	<b>MATERIALS PROPERTIES AND MIX PROPORTIONS</b>	
3.1	Introduction	65
3.2	Pozzolan materials	66
	3.2.1 Silica Fume (SF)	67
	3.2.2 Fly Ash (FA)	67
	3.2.3 Metakaolin (MK)	67
	3.2.4 Rice Husk Ash (RHA)	68
3.3	Analysis of Pozzolan Material	68
	3.3.1 Analyses on the chemical compositions	70
	3.3.2 Phase Identification and Mineralogical Composition	72
	3.3.3 Analyses of Physical Properties and Appearance	74
	3.3.4 Micrograph Appearance	76
3.4	Chemical compositions of Pozzolans	77
	3.4.1 Composition of SF	78
	3.4.2 Composition of FA	79
	3.4.3 Composition of MK	80
	3.4.4 Composition of RHA	81
3.5	Mineralogical and Phase Identification of Pozzolans	82
	3.5.1 Mineralogy of SF	83
	3.5.2 Mineralogy of FA	84
	3.5.3 Mineralogy of Kaolin and MK	85
	3.5.4 Mineralogy of RHA	85
3.6	Particle Characteristics of Pozzolans	87
	3.6.1 Density	88
	3.6.2 Fineness and Surface Area	88
3.7	Micrograph Appearance	90
3.8	Materials for Concreting	95
	3.8.1 Ordinary Portland Cement (OPC)	95
	3.8.2 Coarse Aggregates	96
	3.8.3 Fine Aggregates	97
	3.8.4 Water	98
	3.8.5 Superplasticizers	99
3.9	Concrete Design Mixes	100
3.10	Concrete Mix Proportions	100
	3.10.1 Results and Discussion	102

	3.10.1.1 Compressive Strength	102
	3.10.2 Mixes Proportions of TBC	107
	3.10.3 Compressive Strength of TBC	108
3.11	Summary	112

## **CHAPTER 4- BINDERS PROPERTIES**

4.1	Introduction	115
4.2	British Standard Requirements	116
4.3	Binders Preparations mix proportions and testing	118
	4.3.1 Binder preparations and mix proportions	118
	4.3.2 Testing and analysis	119
4.4	Results and Discussion	122
	4.4.1 Fineness and density	122
	4.4.1.1 Fineness of binders	123
	4.4.1.2 Density	124
	4.4.2 Chemical composition of binders	125
	4.4.2.1 General chemical composition	125
	4.4.2.2 Lime saturation factor	128
	4.4.2.3 Insoluble residue (IR)	129
	4.4.2.4 Magnesia content	130
	4.4.2.5 Sulphuric anhydride	130
	4.4.2.6 Loss of ignition	131
	4.4.3 Effect of binders on compressive strength	133
	4.4.4 Effect of binders on setting characteristic	135
	4.4.4.1 Water requirement	135
	4.4.4.2 Effect of binders on water requirement	137
	4.4.4.3 Setting Times	142
	4.4.4.4 Effect of binders on setting time	143
	4.4.4.5 Effect of pozzolanic materials on setting time	145
	4.4.5 Effect of binders on soundness of cement paste	148
	4.4.6 Pozzolanicity	151
	4.4.6.1 Sample preparation and pozzolanicity identification	152
	4.4.6.2 Analyses of pozzolanicity	153
	4.4.6.3 Identification of Ca(OH) <sub>2</sub> location	154
	4.4.6.4 Pozzolanicity of binders	156
4.5	Summary	161



<b>CHAPTER 5</b>	<b>ENGINEERING PROPERTIES</b>	
5.1	Introduction	163
5.2	Preparation of specimens	164
5.3	Testing	165
	5.3.1 Workability	165
	5.3.2 Compressive strength	166
	5.3.3 Surface Hardness	169
	5.3.4 Flexural strength	171
	5.3.5 Density	171
5.4	Result and Discussion	172
	5.4.1 Influence of binder types on the workability of concrete	172
	5.4.2 Influence of binders on compressive strength of concrete under standard curing	175
	5.4.2.1 Influence of SF	178
	5.4.2.2 Influence of MK	180
	5.4.2.3 Influence of RHA	182
	5.4.3 Influence of binders on compressive strength of concrete under air exposure condition	185
	5.4.4 Influence of binders on compressive strength of concrete under Sulphate exposure condition	190
	5.4.5 Influence of binders on compressive strength of concrete under Chloride exposure condition	196
	5.4.6 Effect of TBC on concrete surface hardness	200
	5.4.6.1 Influence of TBC	200
	5.4.6.2 Influence of SF	202
	5.4.6.3 Influence of MK	202
	5.4.6.4 Influence of RHA	203
	5.4.6.5 Relationship between compressive strength and surface hardness of concrete	204
	5.4.7 Influence of binders on the flexural strength of concrete	205
	5.4.8 Effect of binders to the density of concrete	207
5.5	Summary	209

## CHAPTER 6- DURABILITY PROPERTIES

6.1	Introduction	212
6.2	Methodology	213
	6.2.1 Samples preparation	213
	6.2.2 Curing and exposure conditions	214
	6.2.3 Testing	215
	6.2.3.1 Porosity and water absorption	216
	6.2.3.2 Gas Permeability	217
	6.2.3.3 Expansion and shrinkage level	220
	6.2.3.4 Carbonation determination	220
	6.2.3.5 Sulphate and chloride concentration	221
6.3	Results and Discussion	221
	6.3.1. Porosity of concrete	222
	6.3.1.1 Influence of binders on porosity of concrete under standard curing condition	222
	6.3.1.2 The influence of binders on porosity of concrete under air exposure condition	229
	6.3.1.3 The influence of binders on porosity of concrete under sulphate exposure condition	233
	6.3.1.4 Influence of binders on porosity of concrete under chloride exposure condition	237
	6.3.2 Permeability of concrete	241
	6.3.2.1 Influence of binders on permeability of concrete under standard curing condition	242
	6.3.2.2 Influence of binders on permeability of concrete under under air exposure condition	246
	6.3.2.3 Influence of binders on permeability of concrete under sulphate exposure condition	250
	6.3.2.4 Influence of binders on permeability of concrete under under chloride exposure condition	253
	6.3.3 Expansion and shrinkage of concrete	256
	6.3.3.1 Influence of binders on expansion of concrete under standard curing condition	256
	6.3.3.2 Influence of binders on expansion of concrete under air exposure condition	259

	6.3.3.3 Influence of binders on expansion of concrete under sulphate exposure condition	261
	6.3.3.4 Influence of binders on expansion of concrete under chloride exposure condition	263
	6.3.4 Influence of binders on water absorption of concrete	264
	6.3.5 Influence of binders on carbonation of concrete	267
	6.3.6 Influence of binders on sulphate concentration content in concrete matrix	271
	6.3.7 Influence of binders on Chloride concentration content in concrete matrix	273
6.4	Summary	275
	6.4.1 Influence of binders on porosity	275
	6.4.2 Influence of binders on permeability	277
	6.4.3 Influence of binders on shrinkage and swelling	278
	6.4.4 Influence of binders on water absorption	279
	6.4.5 Influence of binders on carbonation	279
	6.4.6 Influence of binders on sulphate concentration	279
	6.4.7 Influence of binders on chloride concentration	280
 <b>CHAPTER 7- CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE</b>		
7.1	Summary of conclusion	281
7.2	Properties of Materials	282
7.3	Potential of TBC binders	282
7.4	Engineering properties of TBC binders	284
7.5	Durability properties of TBC binders	288
7.6	Recommendations for future research	293
 <b>REFERENCES</b>		 295

## LIST OF TABLE

<b>Table</b>		<b>Page</b>
<b>Chapter 2</b>		
Table 2.1	BS6610: 1991 standard specification requirements of Pozzolanic cement	32
Table 2.2	BS6588: 1991 standard specifications requirement of Portland Pulverized-fuel ash cement	32
Table 2.3	Chemical requirements of pozzolanic materials (modified from ASTM C618)	33
Table 2.4	Physical requirement of pozzolanic materials (modified from ASTM C618)	33
Table 2.5	Influence of FA on freshly-mixed concrete	42
Table 2.6	Workability and setting times of MK concrete	47
<b>Chapter 3</b>		
Table 3.1	Chemical composition of Pozzolans	78
Table 3.2	Chemical Composition of supplied OPC	96
Table 3.3	Grading properties of aggregate	97
Table 3.4	Technical data of superplasticizer (Glenium C380)	100
Table 3.5	Proportion of binder for OPC and BBC concrete	102
Table 3.6	Compressive strength of HSC using BBC	103
Table 3.7	Binder mixes proportion of TBC	108

#### **Chapter 4**

Table 4.1	Standard specifications requirements	117
Table 4.2	Binders mix proportions (%)	119
Table 4.3	Concrete mixes proportions	120
Table 4.4	Fineness of binders	123
Table 4.5	Density of binders	125
Table 4.6	Chemical composition of binders	127
Table 4.7	Lime saturation factor (LSF) values of binders	128
Table 4.8	Insoluble residue (IR) of binders	129
Table 4.9	Magnesia content of binders	130
Table 4.10	Sulphuric Anhydrite content of binders	131
Table 4.11	LOI values of binders	132
Table 4.12	The percentage increase in water demand of the different binders in comparison to OPC	138

#### **Chapter 5**

Table 5.1	Details of concrete mixes proportions	165
Table 5.2	Influence of binders types on workability of concrete	173

#### **Chapter 6**

Table 6.1	Values of constants and coefficient of determination for the expressions of porosity as a function of time	226
Table 6.2	Comparison of expansion level of concrete containing blended cement under chloride exposure versus standard curing at 336 days	264

## LIST OF FIGURE

<b>Figure</b>		<b>Page</b>
<b>Chapter 2</b>		
Figure 2.1	Hydrated OPC cement paste	17
Figure 2.2	Effect of FA replacement levels and fineness on water demand ratio of mortar	40
Figure 2.3	Relation between the setting time and cement replacement by FA cement	43
Figure 2.4	Effect of FA replacement level on the concrete compressive strength	45
Figure 2.5	Effect of MK on strength development of concrete	49
Figure 2.6	Effect of MK content on values of concrete the elastic modulus of concrete	50
Figure 2.7	The effect of RHA on slump values of concrete	51
Figure 2.8	Compressive strength of concrete containing OPC, RHA and SF	54
<b>Chapter 3</b>		
Figure 3.1	XRD on mineralogical phase of SF	84
Figure 3.2	XRD on mineralogical phase of FA	85
Figure 3.3	XRD on mineralogical phase of MK and Kaolin clay	86
Figure 3.4	XRD on mineralogical phase of RHA	87
Figure 3.5	Density of OPC and pozzolanic materials	88
Figure 3.6	BET surface area of OPC and pozzolanic materials	89
Figure 3.7	Grading curve of coarse aggregate	98
Figure 3.8	Grading Curve of fine aggregate	98
Figure 3.9	Compressive strength SF concrete	104

Figure 3.10	Compressive strength FA concrete	105
Figure 3.11	Compressive strength MK concrete	105
Figure 3.12	Compression strength of RHA concrete	106
Figure 3.13	Compression strength of BBC concrete	107
Figure 3.14	Compression strength of SF based TBC concrete	109
Figure 3.15	Compression strength of MK based TBC concrete	109
Figure 3.16	Compression strength of RHA based TBC concrete	110
Figure 3.17	Compression strength of TBC concrete	111

#### **Chapter 4**

Figure 4.1	Compressive strength of TBC	134
Figure 4.2	Compressive strength of BBC	135
Figure 4.3	Water requirement of TBC	136
Figure 4.4	Water requirement of BBC	137
Figure 4.5	BET surface area vs. Water/binder ration to achieve standard consistency	137
Figure 4.6	Water requirements of TBC with SF	141
Figure 4.7	Water requirements of TBC with MK	141
Figure 4.8	Water requirements of TBC with RHA	141
Figure 4.9	Setting time of TBC	144
Figure 4.10	Setting time of BBC	145
Figure 4.11	Setting time performance of TBC with SF	147
Figure 4.12	Setting time performance of TBC with MK	147
Figure 4.13	Setting time performance of TBC with RHA	148
Figure 4.14	Soundness of TBC	149
Figure 4.15	Soundness of BBC	150
Figure 4.16	Soundness of TBC with SF	150

Figure 4.17	Soundness of TBC with MK	150
Figure 4.18	Soundness of TBC with RHA	151
Figure 4.19	XRD diffractogram of OPC at 336 days	155
Figure 4.20	XRD graph of Ca(OH) <sub>2</sub> locations	155
Figure 4.21	Ca(OH) <sub>2</sub> Intensity at 34.1° of 2 Theta axis	157
Figure 4.22	Ca(OH) <sub>2</sub> Intensity at 336 days	158
Figure 4.23	Ca(OH) <sub>2</sub> Concentration of OPC and BBC paste	158
Figure 4.24	Ca(OH) <sub>2</sub> Concentration of OPC and TBC paste	160

### **Chapter 5**

Figure 5.1	Strength development of TBC concrete	177
Figure 5.2	Relative strength of TBC concrete	177
Figure 5.3	Relative strength of BBC concrete	178
Figure 5.4	Compressive strength development of TBC with SF	179
Figure 5.5	Relative strength of TBC concrete with SF	180
Figure 5.6	Compressive strength development of TBC with MK	182
Figure 5.7	Relative strength of TBC concrete with MK	182
Figure 5.8	Compressive strength development of TBC with RHA	184
Figure 5.9	Relative strength of TBC concrete with RHA	185
Figure 5.10	Compressive strength of concrete under air exposure condition	189
Figure 5.11	Effect of air exposure condition on the concrete compressive strength	190
Figure 5.12	Compressive strength of concrete exposed to sulphate exposure condition	195
Figure 5.13	Effect of sulphate exposure on compressive strength of concrete	196
Figure 5.14	Strength reduction of concrete under sulphate exposure	196
Figure 5.15	Compressive strength of concrete exposed to chloride solution	199
Figure 5.16	Effect of chloride exposure on concrete strength	200
Figure 5.17	Effect of TBC on surface hardness of concrete	201



Figure 5.18	Effect of BBC on surface hardness of concrete	201
Figure 5.19	Surface hardness of TBC concrete with SF	203
Figure 5.20	Surface hardness of TBC concrete with MK	204
Figure 5.21	Surface hardness of TBC concrete with RHA	204
Figure 5.22	Relationship between compressive strength and rebound numbers	205
Figure 5.23	Flexural strength of TBC concrete at 28 days	207
Figure 5.24	Flexural strength of BBC concrete at 28 days	207
Figure 5.25	Development of concrete density	208
Figure 5.26	Density of TBC concrete at 336 days	208
Figure 5.27	Density of BBC concrete at 336 days	209

## **Chapter 6**

Figure 6.1	Porosity of TBC concrete	225
Figure 6.2	Porosity of BBC concrete	225
Figure 6.3	Relationship between porosity and strength of concrete	225
Figure 6.4	Effect of TBC containing SF on porosity of concrete	228
Figure 6.5	Effect of TBC containing MK	228
Figure 6.6	Effect of TBC containing RHA on porosity of concrete	228
Figure 6.7	Porosity of concrete under air exposure condition	231
Figure 6.8	Effect of air exposure condition vs standard curing on porosity of concrete	233
Figure 6.9	Porosity of concrete exposed to sulphate	236
Figure 6.10	Effect of sulphate exposure on porosity of concrete	237
Figure 6.11	Porosity reduction of concrete under sulphate exposure	237
Figure 6.12	Porosity of concrete exposed to chloride solution	240
Figure 6.13	Effect of chloride exposure on porosity of concrete	241
Figure 6.14	Permeability of TBC concrete	244

Figure 6.15	Permeability of BBC concrete	245
Figure 6.16	Relationship between permeability and compressive strength of concrete	245
Figure 6.17	Relationship between permeability with porosity of 1-year concrete	245
Figure 6.18	Permeability of concrete under air exposure condition	249
Figure 6.19	Gas Permeability of concrete exposed to sulphate	252
Figure 6.20	Permeability of concrete exposed to chloride solution	255
Figure 6.21	Effect of binders to swelling of concretes	257
Figure 6.22	Swelling of TBC concrete at 336 days under water curing	258
Figure 6.23	Swelling of BBC concrete at 336 days under water curing	259
Figure 6.24	Shrinkage of concrete exposed to air curing condition for 336 days	259
Figure 6.25	Expansion of concrete exposed to sulphate solution for 336 days	261
Figure 6.26	Expansion of concrete exposed to chloride solution	263
Figure 6.27	Water absorption of TBC concrete	266
Figure 6.28	Water absorption of BBC concrete	266
Figure 6.29	Relationship of water absorption with the porosity of concrete	266
Figure 6.30	Carbonation of concrete under air exposure condition	270
Figure 6.31	Sulphate concentration in the prepared binders	271
Figure 6.32	Chloride concentration in the different binders	274

## LIST OF PLATE

<b>Plate</b>		<b>Page</b>
<b>Chapter 3</b>		
Plate 3.1	Electrical Furnace	68
Plate 3.2	Ball Mill Apparatus	69
Plate 3.3	XRF apparatus Rigaku Rix 3000	71
Plate 3.4	35 mm Ø pallet of compress samples powder	72
Plate 3.5	XRD machine Bruker D8	73
Plate 3.6	Micromeritics 1320 helium Autopycnometer	74
Plate 3.7	Micromeritics Model 2300 Flowsorb	76
Plate 3.8	Scanning Electron Microscopy (SEM)	77
Plate 3.9	SEM micrograph of SF	92
Plate 3.10	SEM micrograph of FA	93
Plate 3.11	SEM micrograph of Kaolin clay	93
Plate 3.12	SEM micrograph of MK	94
Plate 3.13	SEM micrograph of RHA before milling process	94
Plate 3.14	SEM micrograph of RHA after milling process	95
<b>Chapter 4</b>		
Plate 4.1	Mixing machine	119
Plate 4.2	Vicat Apparatus	121
Plate 4.3	Le-Chatelier Apparatus	122
<b>Chapter 5</b>		
Plate 5.1	Cube compression machine	167
<b>Chapter 6</b>		
Plate 6.1	Permeability apparatus	218

## LIST OF ABBREVIATION

HSC	High Strength Concrete
HPC	High Performance Concrete
OPC	Ordinary Portland Cement
BBC	Binary Blended Cement
TBC	Ternary Blended Cement
SF	Silica Fume
FA	Fly Ash
MK	Metakaolin
RHA	Rice Husk Ash
ACI	American Concrete Institute
MPa	Mega Pascal
C <sub>3</sub> S	Tricalcium Silicate
C <sub>2</sub> S	Dicalcium Silicate
C <sub>3</sub> A	Tricalcium Aluminate
C <sub>4</sub> AF	Tetracalcium Aluminoferrite
C-S-H	Calcium silicate Hydrate
Ca(OH) <sub>2</sub>	Calcium Hydroxide
ASTM	American Society for Testing and Materials
BET Apparatus	Brunauer, Emmetl, and Teller Apparatus
SiO <sub>2</sub>	Silica Oxide
Al <sub>2</sub> O <sub>3</sub>	Alumina Oxide
Fe <sub>2</sub> O <sub>3</sub>	Ferum Oxide
CaO	Calcium Oxide
MgO	Magnesium Oxide
LOI	Loss of Ignition
BS	British Standard

## LIST OF PUBLICATIONS

**Mohd Fadzil A, Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A B.**(2009) Durability of Ternary Blended Cement Containing Rice Husk Ash and Fly Ash as Partial Cement Replacement Materials under Sulphate Curing Condition. 10th International Conference on Concrete Engineering and Technology 2009 (CONCET2009), Advances in Concrete Engineering and Technology, Shah Alam, Malaysia

**Mohd Fadzil A, Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A B.**(2009) Surface Hardness and Compressive Strength of Concrete Containing Ternary Blended Cement. Persidangan Kejuruteraan Awam ke 5, (AWAM'09). Kuala Lumpur

**Mohd Fadzil A, Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A B.**(2008) "Engineering Properties of Ternary Blended Cement Containing Rice Husk Ash and Fly Ash as Partial Cement Replacement Materials". International Conference on Construction and Building Technology (ICCBT08).UNiTEN. Kuala Lumpur, Malaysia.

**Mohd Fadzil A , Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A B.**(2008) "Durability of Ternary Blended Cement Containing Silica Fume and Fly Ash as Partial Cement Replacement Materials under Sulphate Curing Condition".International Seminar of Civil and Infrastructure Engineering 2008 (ISCIE08), UiTM. Shah Alam. Malaysia.

**Mohd Fadzil A, Megat Johari MA, Kairun Azizi MA, Badorul Hisham AB.**(2007), "Engineering Properties of HSC using Ternary Blended Cement Containing Metakaolin and Fly Ash as Partial Cement Replacement Materials".National seminar of Civil Engineering Research (SEPKA2007). UTM, Skudai Johor . Malaysia.

**Mohd Fadzil A, Megat Johari MA, Kairun Azizi MA, Badorul Hisham AB** (2007), "Engineering Properties of HSC using Ternary Blended Cement containing Silica Fume and Fly Ash as partial Cement Replacement Materials".Malaysian Infrastucture Technology Conference 2007 (INFRATECT2007).USM.Sungai Petani, Kedah Malaysia.

**Mohd Fadzil A, Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A.B** (2007). "Properties of Ternary Blended Cementitious System containing Rice Husk Ash and Fly ash as partial Mineral Replacement materials". World Housing Congress (WHC2007). UPM. Kuala Terengganu, Malaysia.

**Mohd Fadzil A, Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A.B Muhd Nurhasri M.S.** (2007) "Cementitious Properties of Ternary Blended Cement System with Metakaolin and Fly Ash as Minerals Replacement Materials". Persidangan Kebangsaan AWAM07. USM. Langkawi, Kedah. Malaysia.

**Mohd Fadzil A, Megat Azmi M.J, Kairun Azizi.M.A, Badorul Hisham A.B** (2006). “Properties of ternary Blended Cementitious systems containing Silica Fume and Fly Ash as partial cement replacement materials. National seminar of Civil Engineering Research (SEPKA2006). UTM, Skudai Johor . Malaysia.

**Mohd Fadzil A, Megat Azmi M.J, Badorul Hisham A B,Kairun Azizi.M.A** (2006) “Formulations of Ternary Blended Cement for High Strength Concrete”, Civil Engineering Collocium (CEC06) USM. Pulau Pinang, Malaysia.

**Mohd Fadzil A, Megat Azmi M.J, Hannan RR, Badorul Hisham A B,Kairun Azizi.M.A** (2005)“High strength concrete containing Rice Husk Ash as partially cement replacement material” South East Asia Conference on the Advancement of scientific and social research 2005 (SEA-CASSR 2005) UiTM, Perlis.

# **INFLUENCE OF MULTIPLE BLENDED BINDERS ON ENGINEERING PROPERTIES AND DURABILITY OF CONCRETE**

## **Abstract**

The influence of multiple blended binders in the forms of binary blended cement (BBC) and ternary blended cement (TBC) on the properties and performance of concrete is investigated. The mineral admixtures used are silica fume(SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). They are used to partly replace the cement by direct replacement method on mass-to-mass basis. The mix proportions of the concretes are kept nominally the same with constant water/binder ratio and the same superplasticizer content for all concrete mixes, so as to isolate the effect of each binder type. Most of the mineral admixtures used are abundantly available in the country and analyses performed indicate their compliance with standard specification requirements as pozzolan. They are used to replace ordinary Portland cement (OPC) at replacement level of 0 (control mix) to 40% (TBC mix). Analyses on the binders also exhibit their compliance with standard specification requirements which are comparable to OPC. The engineering properties of the TBC concretes are generally comparable with those of OPC and better than OPC:FA BBC concrete when cured continuously in water. The durability performance of the TBC concrete exposed to air is found to be comparable to that OPC concrete. Nonetheless when exposed to sulphate and chloride environments the durability performance seems to be more effected in comparison to the OPC concrete. This could be due to the very early exposure to the aggressive environments

**PENGARUH PEREKAT CAMPURAN BERBILANG KE ATAS SIFAT-SIFAT  
KEJURUTERAAN DAN KETAHANLASAKAN KONKRIT**

**Abstrak**

Kajian telah dijalankan berhubung pengaruh penggunaan perekat campuran berbilang dalam bentuk simen campuran binari (BBC) dan simen campuran ternari (TBC) terhadap ciri-ciri dan prestasi konkrit. Bahan tambah mineral yang digunakan ialah abu silika (SF), abu ringan (FA), metakaolin (MK) dan abu sekam padi (RHA). Bahan mineral tersebut telah digunakan sebagai bahan gantian separa kepada simen secara gantian terus berdasarkan nisbah berat simen. Bahan campuran konkrit yang sama digunakan untuk semua bancuhan dengan nisbah air/perekat yang tetap dan kandungan bahan super pemplastikkan dikekalkan bagi mengenalpasti kesan bahan mineral ke atas sifat-sifat konkrit. Bahan mineral yang digunakan merupakan bahan mineral yang banyak terdapat di dalam Negara telah dianalisis dan didapati memenuhi keperluan spesifikasi piawai untuk bahan tambah mineral dalam konkrit. Bahan mineral digunakan untuk menggantikan simen OPC dari 0 (bagi bancuhan kawalan) hingga 40%(bagi bancuhan TBC). Analisa ke atas bahan perekat yang dihasilkan adalah didapati simen campuran yang dihasilkan memenuhi spesifikasi piawai yang dirujukan bahkan ianya juga didapati setanding dengan simen OPC. Ciri-ciri kejuruteraan yang terdapat pada konkrit TBC secara amnya didapati setanding dengan konkrit OPC dan ianya juga didapati lebih baik berbanding dengan konkrit BBC dengan perekat OPC:FA. Keputusan yang diperolehi mendapati bahan mineral yang digunakan berpotensi dalam penghasilan simen campuran. Prestasi ketahananlasakkan konkrit dengan bahan perekat TBC dalam pendedahan udara didapati standing dengan konkrit OPC, walaubagaimanapun ianya didapati lebih rendah berbanding dengan konkrit kawalan apabila ia didedahkan secara terus kepada persekitaran yang mengandungi garam sulfat dan klorida.



## **CHAPTER 1 INTRODUCTION**

### **1.1 BACKGROUND OF STUDY**

In comparison to other construction materials such as timber and steel, concrete is the most widely used construction material because of its global availability, relatively cheap, flexible and versatile in term of its application, can be tailored to achieve various strength level and durability. The grade of concrete is normally based on 28 days compressive strength of the concrete. Since the application of concrete is versatile, the production of wide range of grade from the lowest (i.e 20MPa to 200 MPa) is possible. The different application would require concrete with different strength, workability and durability. Higher grade of concrete is usually utilized for high end application such as precast work, high strength concrete and etc. [ Nawy, 2001]. The blended or multi-blended cements are essential for higher grade of concrete rather than the normal grade of concrete. The disadvantage of high strength concrete is that it requires a lot of cementitious materials which is the most expensive ingredients in the concrete. Therefore, research on the production and application of blended or multi-blended cement for producing concrete is much needed.

In general, ordinary Portland cement (OPC), coarse aggregates, fine aggregates and water are the basic ingredients used in the production of normal concrete. However, the production of High Strength Concrete (HSC) or sometimes also known as High Performance Concrete (HPC) requires a proper selection of materials especially the binders that contribute to the superior performance. In addition, the production of HSC normally requires a higher content of Portland cement or binder, stronger aggregates with smaller maximum size and lower water/binder ratio (Bharatkumar et

al., 2001). Furthermore, chemical and mineral admixtures such as high range water reducer and silica fume are normally included in the production of HSC. Due to the higher consumption of OPC in the production of HSC, the search for alternative binders or cement replacement materials has thus become a challenge. The importance of using Binary Blended Cement (BBC) in HSC/HPC has been revised. To note that using BBC, other aspects especially in terms of gaining early strength, reduction of workability and high heat liberation cannot be addressed, hence the use of the multiple blended binders would be one way to address all aspects in HPC.

From the perspectives of economy, technology and ecology, cement replacement materials have an undisputed role to play in the construction industry. Small amounts of inert fillers have always been acceptable as cement additives, but if the fillers have pozzolanic properties, they impart not only technical advantages to the resulting concrete but also enables larger quantities of cement replacement to be achieved. Many of these mineral admixtures are industrial by products, and correctly considered as waste, so that the resulting benefits in terms of energy savings, economy, environmental protection and conservation of resources are substantial [Malhotra and Mehta,( 2004)].

It has been generally accepted that the roles of pozzolanic materials in concrete industry are not only to increase the strength of concrete but also at the same time to enhance the durability performance of concrete. Due to the enhancement of concrete durability, HSC has also been called as High Performance Concrete (HPC). Either the materials are used as minerals admixtures or as partial cement replacement materials in concrete mixes, they normally give positive effect on the engineering, physical and mechanical properties of concrete [Aitcin, (2003), Baalbaki et al., (1992), Ramezaniapour, (1987)].

## 1.2 PROBLEM STATEMENT

Service life of concrete has become short due to premature deterioration problems especially to the structure in severe and extreme environmental exposure conditions. Due to these problems HPC should be proposed to reduce the deterioration of concrete structure and having longer period of service life. Neville (2002) stated that the HPC concrete normally used higher content of cement (450 to 550 kg/m<sup>3</sup>) to achieve its specific target strength. Taylor (2002) reported that a concrete with high content of cement may face high heat of hydration problems that may increase the formation of micro crack and porosity that could significantly reduce the durability of concrete. In addition, the production of cement has also been reported to contribute to environmental problems caused by the extraction of raw material and CO<sub>2</sub> emission during cement manufacture (Sabir et al., 2001). In addressing these concerns and other environmental problems related to the disposal of waste industrial by products and also because of economic advantages, mixtures of Portland cement (OPC) and pozzolans known as binary blended cement (BBC) has been introduced.

The use of Binary Blended Cement (BBC) system based on industrial by products or natural pozzolan has been known to improve long-term strength and to enhance durability performance of concrete [Sabir et al.,(2001), Uzal and Turanli, (2003), Omar,(2002)]. Most of these mineral admixtures are industrial by products, and could be correctly considered as waste, so that the resulting benefits in terms of energy savings, economy, environmental protection and conservation of resources are substantial [Swamy, 1986]. With the intention of reducing environmental problems, producing low cost binder, reducing the consumption of cement by using higher replacement level of OPC, as well as achieving higher strength and durability performance, the Ternary Blended Cement (TBC) is introduced in this study. Due to

the importance of providing a new type of cement to support the concrete construction industry's demand, this research is believed to be significant. The information about TBC are still limited and this study is significant in providing more information and creating a better understanding of TBC for high strength concrete application.

Pozzolan is recognised as materials that can give positive effects on concrete properties but there is still considerable reluctance to use these materials as widely as they deserve. Malaysia has a lot of pozzolan resources. However, only a little amount of these materials are used, especially in the concrete industry. This phenomenon may be due to the lack of research done on these materials especially in the Malaysian concrete industry.

### **1.3 AIM AND OBJECTIVES**

The aim of this research was carried out and designed based on four main objectives.

The objectives are:-

- a) To identify and assess the properties of the pozzolanic materials used in the investigation so as to determine their suitability to be used as partial cement replacement materials in the production of TBC and BBC cementitious systems.
- b) To formulate and produce TBC containing pozzolanic materials available in Malaysia, to be used in the production of high strength concrete (grade C60).
- c) To investigate the engineering properties of fresh and hardened concrete containing TBC.

- d) To study the durability related properties of the TBC concrete under different curing conditions, and compare with those of OPC and BBC concretes.

#### **1.4 SCOPE OF RESEARCH**

The TBC system was formulated based on optimum 28 days compressive strength performance of concrete containing BBC at various replacement levels of the selected pozzolanic materials. A control HPC mix containing OPC was designed and prepared through series of trial mixes to have minimum compressive strength of 60 MPa at 28 days of age.

The pozzolanic materials used in this investigation were silica fume (SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). All of the pozzolanic materials used were obtained locally. Some of them are already established in the concrete industry and available in the market (SF), but some of them were produced in the laboratory to control the quality of the pozzolanic materials.

The experimental program involved studying the properties of materials used, effect of TBC system on the cementitious properties, as well as influence of TBC systems on properties of fresh concrete, engineering properties of hardened concrete and properties related to durability performance under different curing conditions. Four curing conditions were utilized namely; normal water curing, air curing, water containing sulphate and water containing chloride. The properties and performance of the HPC containing TBC system were compared with those of HPC containing BBC and OPC.

## **1.5 DEFINITION OF TERMS**

### **1.5.1 Pozzolanic materials**

Pozzolanic materials or pozzolans are siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value but in the presence of moisture, can react with lime to produce cementitious products such as calcium silicate hydrates and calcium aluminium, furnished by the hydration of the anhydrous calcium silicates present in the Portland cement [BS 6610 (1985)].

### **1.5.2 Ternary Blended cement (TBC)**

TBC is a multi component cementitious system produced by combining two types of pozzolanic materials with OPC at specified replacement level. It was prepared during the mixing process.

### **1.5.3 Binary blended cement (BBC)**

BBC is a blended cementitious system produced by combining one type of pozzolanic material with OPC at a specified replacement level. It was prepared during the mixing process.

### **1.5.4 High performance concrete (HPC)**

Hashem. et al., (2002) stated that the definition of HPC is not standardized, nevertheless several different definitions of HPC have been proposed and from all the definitions HPC can be summarized as concrete with superior properties that is not only high in strength but also have great durability performance in extreme environmental exposure.

### **1.5.5 Multi Blended Cement (MBC)**

MBC refers to blended cement either in binary system or in ternary blended system used in this investigation.

## **1.6 LAYOUT OF THESIS**

The thesis consists of seven chapters. They are introduction, literature review, material properties and mix proportions, binder properties, engineering properties, durability performance, and finally, conclusions and recommendations.

Chapter one is an introduction to the research which comprises of overview of works, problem statement, objective, scope of research and definition of terms that have been used in this investigation.

In chapter two, an introduction to the pozzolanic materials used and their performance in the production of HSC are presented. Existing knowledge on the effect of pozzolanic materials used as mineral admixture or replacement material to produce binary blended cement system in HSC, which are related to this study, are reviewed.

Chapter three outlines the pozzolanic sample preparations and productions that were used in the investigations. Details of pozzolanic materials properties used in the investigations are also described in this chapter. Subsequently, the mixing, casting, curing procedures and experimental design and program are also presented.

In chapter four, the properties of pozzolanic materials used throughout the experimental program are evaluated. The influence of different replacement levels of the pozzolanic materials on properties of binder of the ternary blended cementitious system is compared with those of BBC and OPC cementitious systems. Evaluations

are based on the tests specified by British Standard Specification for Ordinary Portland Cement, BS 12:1996.

Chapter five presents the influence of TBC system in HSC on the engineering properties compared to HSC containing BBC and OPC cementitious system. The engineering properties considered include workability, compressive strength, surface hardness and concrete uniformity.

Chapter six presents the results and discussion on the effects of pozzolanic materials used as minerals replacement in TBC compared to BBC and OPC on the durability performance of HSC. The prepared specimens were cured under different curing condition and the durability performance was assessed through the engineering properties named as porosity, permeability, expansion and shrinkage, water absorption, carbonation, sulphate and chloride concentration level. The performances of HSC under different curing conditions are compared and discussed with those of specimens cured under standard curing condition.

Finally, conclusions of the research works and recommendations for future studies are presented in chapter seven.



## CHAPTER 2 LITERATURE REVIEW

### 2.1 INTRODUCTION

Concrete structures are generally designed for a service life of 60 years, but experience shows that in urban and coastal environments, many structures begin to deteriorate in 20 to 30 years or even less time after being constructed [Nawy, 2001]. This premature deterioration arising from lack of durability of concrete could have serious environmental and economic consequences. Increasing the service life of concrete in long-term is one of the solutions for preserving the earth's natural resources [Sampaio et al., 2000].

The world's yearly cement production of 1.6 billion tons accounts for about 7% of the global loading of carbon dioxide into the atmosphere. Portland cement, the principal hydraulic cement in used today, is not only one of the most energy-intensive construction materials but it is also responsible for a large amount of greenhouse gasses [Aitcin, 2003]. Production of a tonne of Portland cement requires about 4 GJ of energy, and Portland cement clinker manufacture releases approximately 1 ton of carbon dioxide into the atmosphere. Ordinary concrete typically contains about 12% cement and 80% aggregate by mass [Sampaio et al., 2000]. Hence, any effort on reducing the consumption of cement could somehow contribute to reduction in potential environmental problems, reduction in cost, as well as preservation of natural resources, which as a whole could contribute to sustainable development.

In the current and future construction scenario, the increasing demand for cement and concrete must be supplemented by the use of supplementary cementitious materials such as fly ash and rice husk ash. The use of such materials as

partial replacement for the more energy-intensive Portland cement could result in substantial energy and cost savings. According to Mehta (1994), the cement production rate of the world is expected to grow exponentially to about 3.5 billion tons/year by 2015. He presumed that most of the increase in cement demand could be supplemented by the use of mineral cement replacement materials. He also suggested that this approach is necessary to prevent the possible ecological disaster due to global warming.

The presence of mineral cement replacement materials in concrete is known to impart significant improvements towards concrete durability. In addition, some of the mineral admixtures such as fly ash and ground granulated blast-furnace slag could enhance the workability of concrete. A high performance concrete with adequate workability and superior durability can be produced by a proper selection of mineral cement replacement materials and concrete mix proportions. Some of these materials can be obtained from industrial and agricultural by-products. The use of by products is an environmental-friendly method of disposing large quantities of materials that would otherwise pollute the land, water bodies and air [Mehta, 1994]. The use of these artificial pozzolans could bring about not only economical and ecological benefits but technical benefits as well. It is generally agreed that with proper selection of materials, mixture proportioning and curing technique, minerals additives can greatly improve the durability performance of concrete.

In this chapter, the definition of High Performance Concrete (HPC) and its importance to the construction industry are discussed. The principal requirements of HPC in term of its production, applications and problems associated with the use of HPC are also discussed and reviewed.

This chapter also introduces the common pozzolanic materials being used in the production of HPC. As literature discussion, existing knowledge on the effect of pozzolanic materials used as mineral additives or partial cement replacement materials to produce binary blended cementitious system in HPC, which are related to this study, are reviewed. Properties and performance of Ordinary Portland cement and binary blended cementitious system containing pozzolans used to produce HPC are discussed. Finally, this chapter also discusses the role, potential and importance of using ternary blended cement (TBC) as an alternative binders to OPC in producing HPC.

## **2.2 HIGH PERFORMANCE CONCRETE (HPC)**

HPC has been widely used in the construction industry for the past few decades. This is due to the increasing demand for more durable concrete to extend the service life and at the same time to reduce maintenance cost of concrete structures.

There are several definitions of HPC. ACI 363R(1992) defined HPC as concrete meeting special combinations of performance and uniformity requirements that cannot always be achieved routinely using conventional constituents and normal mixing, placing and curing practices. In addition, ACI 363R(1992) also specified that compressive strength for design should be at least 41 MPa or greater.

HPC was also defined as a concrete with water/binder ratio of less than or equal to 0.35 and shall have a characteristic compressive strength of at least 35 MPa or greater after 24 hours and at least 70 MPa or greater after 28 days [Roszilah et al., 2002]. Furthermore, the concrete should meet special requirements such as, ease of placement and compaction, resistant to segregation, enhanced long-term mechanical

properties (high early-age strength, toughness and volume stability) and superior long-term durability performance in severe environments [Hashem et al., 2002].

To achieve an ideal HPC, Nawy (2001) stated down five principal parameters as the following:

High performance

Economy

Resistance to wear and deterioration

Resistance to weathering and chemicals

Appropriate cement type.

Amongst the parameters stated above, an appropriate cement type has been recognised as the major factor that can influence performance of concrete with regards to the other parameters. The use of inappropriate type of cement in producing HPC might cause disintegration of the concrete in the structure when exposed to certain aggressive environmental exposure. Malier (1992) introduced two approaches as means of obtaining HPC, which are, reducing the flocculation of cement grains and widening the range of grain size of the binder. These could be realized by using combination of both chemical admixture such as high range water reducer and mineral admixture such as silica fume. Here, the high range water reducer will mainly disperse the binder particles through the adsorption and electrostatic repulsion mechanisms, while the much finer silica fume will act as filler, filling the interstitial spaces between the coarser cement particles. The net effect will be a

denser cement paste matrix, which will contribute to enhanced mechanical properties as well as durability performance.

The major advantages of using mineral additives in concrete are mainly, the improved concrete properties in the fresh and hardened states, as well as the potential economical and ecological benefits. Since HPC requires relatively higher binder content than normal concrete, the utilization of mineral additives could offer greater potential benefits. However, the selection of the mineral additives may require more attention due to their varying properties and effects.

### **2.3 CEMENT FOR HPC**

In order to produce HPC, selecting an appropriate type of cement is important. In choosing the appropriate type of cement, parameters such as the type of structure, the weather and other conditions under which the structure is to be built and the probable exposure condition of the structure during its life span should be given due consideration [Nawy, 2001].

Concrete structures exposed to marine environment and seawater sprays may require the use of sulphate resisting cement type [Maher and Bader, 2003]. For construction that needs a concrete to harden and develop early strength quickly, rapid hardening Portland cement will be essential [Taylor, 2002]. According to Nawy (2001), concrete structure with bulkier and heavier in cross section needs cement with low heat evolution characteristic to prevent excessive temperature gradient and probable thermal cracking which are normally associated with mass concrete. For this case, blended pozzolanic cement was found to be necessary to reduce the temperature rise

during hydration process and at the same time to improve the durability performance of concrete [Sabir et al, 2001].

The chemical compositions of cement could have significant influence on its properties and performances. The variation in the chemical compositions of any type of cement in particular the aluminate is one of the factors that determine the rate of reaction of cement when in contact with water [Fabien and Kimberly, 2007]. In addition, the size of the cement particles or its fineness, which is normally indicated by its specific surface area also plays an important role in determining the reactivity of cement [Aitcin, 2003]. According to De Larnard (1992), ultra fine particles of cement would react in two levels which are physical and chemical levels. In physical level, the cement will react as filler between the voids in hydrated cement matrix at early age, and on the chemical level, the cement will accelerate the hydration process. For blended cement containing pozzolanic materials, the finer particles produce a better pozzolanic reaction but it is still depending on the quality of pozzolanic materials used. Mazloom et al., (2004) stated that besides utilizing appropriate binder, water/binder ratio must be reduced and binder content should be increased in order to produce HPC.

#### **2.4 ORDINARY PORTLAND CEMENT (OPC)**

In the new era of concrete industry, Ordinary Portland Cement (OPC) still remains as a major binder used to produce HPC. OPC is either used as the sole binder in concrete mixes or as a major proportion of binder in blended cements. OPC consists of four major compound compositions, namely the tricalcium silicate ( $C_3S$ ), dicalcium silicate ( $C_2S$ ), tricalcium aluminate ( $C_3A$ ) and tetracalcium aluminoferrite ( $C_4AF$ ) [Neville, 2002].

$C_3S$  comprises of angular crystals which constitutes about 52% of OPC volume. It is responsible for initial setting and early strength gain of cement, especially to give an early strength (e.g. 7 days).  $C_2S$  are more rounded crystals that represent about 19% of OPC volume and it is responsible for long-term strength development. It will harden slowly but contributes notably to strength at ages over a month [Ajiwe et al., 2000]. In the case of  $C_3A$  which is normally in rectangular amorphous crystals, it mainly influences the setting characteristics of cement, whereas the non-crystalline  $C_4AF$  is responsible for the grey colour of cement with little contribution to setting as well as strength. The  $C_3A$  and  $C_4AF$  constitute about 10 and 8% of OPC volume, respectively [Taylor, 2002]. It is worth mentioning that the reaction of  $C_3A$  with water is very violent and leads to immediate stiffening of the cement paste, known as flash set. To prevent the flash setting phenomenon, gypsum is normally added to cement clinker. The present of excessive  $C_3A$  with its rapid setting, high heat evolution and sulphate susceptibility, is undesirable in concrete.

The actual proportions of the different major compounds could vary considerably from cement to cement, and indeed different types of cement are obtained by suitable proportioning of the raw materials. The major compositions of OPC are lime, silica, alumina and iron oxide. With the presence of water these compounds interact with one another to produce hydrated product which is Calcium Silicate Hydrate (C-S-H) and Calcium Hydroxide,  $Ca(OH)_2$ .

The C-S-H takes the form of extremely small interlocking crystals, which grow out slowly from cement grains to occupy the previously water-filled spaces. The microcrystalline material is responsible for the strength of the hardened concrete [Regourd, 1992].

$\text{Ca(OH)}_2$  forms a much larger crystals which act as fillers in the hardened concrete but do not interlock to form strength. In the presence of moisture in the concrete matrix,  $\text{Ca(OH)}_2$  will partly dissolve to form an alkaline solution that is useful to protect the steel reinforcement within the reinforced concrete structure [Taylor, 2002]. The ratio of C-S-H to  $\text{Ca(OH)}_2$  is approximately 7:2 by mass of concrete [Neville, 2002].

At any stage of hydration, the hardened cement paste consists of very poorly crystallized hydrates of the various compounds, referred to collectively as gel, crystals of  $\text{Ca(OH)}_2$ , some minor components, unhydrated cement and the residue of water-filled spaces from the fresh paste [Neville, 2002]. The formation of  $\text{Ca(OH)}_2$  crystals creates a bridging effect between crystallized C-S-H and because of  $\text{Ca(OH)}_2$  is crystallised in massive superimposed hexagonal plates, it creates capillary pores in the cement paste matrix (Figure 2.1). The capillary pores, either induced by  $\text{Ca(OH)}_2$ , air bubbles or micro crack have become a factor that contributes to an inferior engineering properties and durability performance of concrete [Regourd, 1992].

The capillary pores represent part of the gross volume of hardened cement paste which has not been filled by the products of hydration. Commonly, the hydration products of OPC occupy twice the volume of the original solid phase, therefore the volume of capillary system is reduced with the progress of hydration [Neville, 2002]. The progress of hydration is governed by the water/cement ratio and the degree of hydration. Water/cement ratios of lower than 0.23 would promote self-desiccation problems and a water/cement ratio higher than 0.36 will induce the formation of the capillary pores since the volume of gel is not sufficient to fill all the space available [Taylor, 2002].



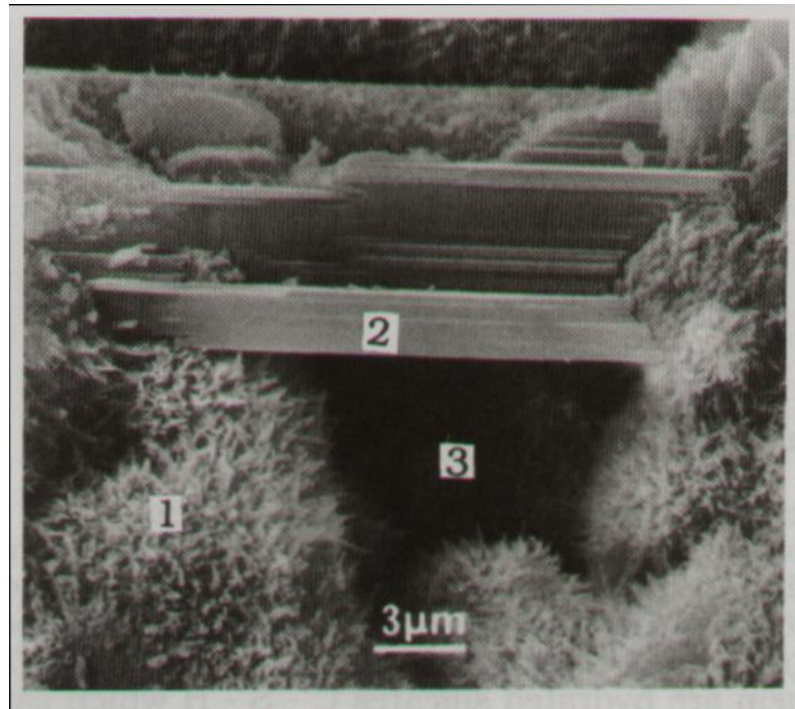


Figure 2.1: Hydrated OPC cement paste, w/c = 0.5, (1) Fibrous C-S-H, (2) Ca(OH)<sub>2</sub>, (3) capillary pore [Regourd,1992].

An improvement of capillary pore formations has been obtained by several processes, which reduce the porosity and the water/cement ratio problems. One of the processes introduced is by blending the OPC with pozzolanic materials either by using pre-blended pozzolanic cements or by mixer blending of cement with pozzolanic mineral admixtures. The small particles of pozzolans will act as fillers, filling the spaces between the coarser cement particles. In addition, the pozzolanic reactions between the amorphous silica of the mineral additive and Ca(OH)<sub>2</sub> produced by cement hydration reactions will occupy the pores which are not occupied by OPC hydration products. Hence, the hardened cement paste will be much more homogenous and denser, with finer pore size distribution.

## **2.5 POZZOLANIC MATERIALS**

Pozzolan is a material which, when combined with calcium hydroxide, exhibits cementitious properties. Pozzolans are commonly used as additives or as mineral replacements to Portland cement concrete mixtures to increase the long-term strength and other properties of Portland cement concrete. Pozzolans are primarily vitreous siliceous materials which react with calcium hydroxide to form calcium silicates; other cementitious materials may also be formed depending on the constituents of the pozzolans [Agarwal, 2006].

The specific definition of pozzolan according to ASTM C618-98 and accepted by almost by all scientists and researchers dealing with cementitious materials and concrete is a “siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious property but which will in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementing properties”. Other description for pozzolan includes any material, regardless of its geologic origin, which possesses hydraulic properties [Ramezaniapour, (1987)]. In addition, Neville (2002) described pozzolans as a natural or artificial material containing amorphous silica in a reactive form. The silica can combine with calcium hydroxide of OPC in the presence of water to form stable calcium silicates which have cementitious properties.

The first known pozzolan was pozzolana, a volcanic ash, for which the material was named. The most commonly-used pozzolan today is fly ash (FA), though silica fume (SF), high reactivity metakalolin (MK), ground granulated blast furnace slag (GGBS), rice husk ash (RHA) and other materials are also used as pozzolans. In Malaysia a waste from palm oil industry named as Palm Oil Fuel Ash or POFA has

been found to possess pozzolanic properties and has shown a promising potential to be used in concrete, however a careful design with an adequate amount of ash should be chosen to establish the potential benefit [Abdul and Warid.,1997]. Weerachart et al., (2007) recommended that the optimum replacement levels of OPC with POFA is between 20 to 30% while Chea et al., (2010) reported that POFA has a unburned carbon content and this unburned carbon reduced the workability of concrete and need more superplasticizer to be added in the concrete mix to maintain the fluidity level of concrete. However, the current study only focuses on silica fume (SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). These pozzolans are generally available in Malaysia. SF is commercially available, even though it originates from overseas. Sources of other pozzolans are rather abundant, nonetheless the utilization of these materials in the local concrete industry is very limited.

### **2.5.1 Silica fume (SF)**

SF is a by-product of the manufacturing process of silicon or various silicon alloys and silicon metal. ASTM C1240-04 defined SF as a very fine pozzolanic material, composed mostly of amorphous silica produced by electrical arc furnace as a by-product of the production of elemental silicon or ferro-silicon alloys. It is also known as condensed silica fume and microsilica.

The chemical compositions and properties of SF are influenced by the composition of the principal product being made by the furnace and furnace design [Malhotra and Mehta, 2004]. Usually, SF contains more than 80 to 85% of silica in non-crystalline form and has a spherical shape with average particles size of 0.1- 0.5  $\mu\text{m}$  and nitrogen BET surface area of 20,000  $\text{m}^2/\text{kg}$  [Yajun and Jong., 2003].

The use of SF as a mineral admixture or as partial cement replacement material in concrete industry was increasing in many mega projects all around the world. Many researchers reported and agreed that SF is a highly reactive pozzolan that could improve the properties and durability performance of concrete. Hence, SF has been highly regarded in the concrete industry especially in the production high strength and high performance concrete.

SF is normally used in dry and densified form as mineral admixture, proportioned to produce concrete with special performance qualities. It could generally improve the properties of hardened concrete through the filler effect and pozzolanic reaction with lime to increase the amount of calcium silicate hydrate gel formed, thus improving the strength and reducing the permeability of the concrete.

Although SF could impart significant contributions to strength and chemical resistance of concrete, it could also lead to increases in water demand, placing difficulties and plastic shrinkage problems in concrete (Thomas et al., 1999). Due to the high demand for this material in the concrete industry, SF has become significantly expensive. The increase of construction costs due to the increasing price of imported silica fume compared to other mineral admixtures has led researchers to turn their interest toward others supplementary cementitious materials and technique to obtain similar technical benefits as in the case of SF.

#### **2.5.1.1      *Chemical composition of SF***

SF as a by-product of the manufacturing process of silicon or various silicon alloys has a high content of SiO<sub>2</sub> in amorphous form. The chemical compositions of SF depend on the composition of the principal product being made by the furnace and furnace design [Mehta, 1986]. A furnace which is equipped with a heat recovery

system produces SF with lower value of loss on ignition (LOI) or carbon content. The LOI of SF is on the range of 2.41 to 2.75%.

According to Neville (2002), the SiO<sub>2</sub> content of SF could range from as low as 80 % to greater than 90 %. This variation is influenced by the silicon content in the alloy production. The higher the silicon content in the alloy used the higher the silica content in the resulting silica fume. Others compositions such as Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO and alkali contents are normally low. Even though MgO is usually found as part of SF composition, but it was reported not be deleterious to concrete.

The chemical compositions of SF have been reported to be consistent, i.e. not affected by time. This is due to the relatively high purity of the raw materials used in the production of silicon metal or ferrosilicon alloys [Mehta, 1986].

#### **2.5.1.2      *Physical characteristic of SF***

In term of mineralogy, SF consists essentially of an amorphous silica structure with a wide scattering peak. The amorphous silica structure and the fine particle are the main reasons for the excellent pozzolanic activity of SF [Sanchez et al., 1999]. The particle size of SF was reported to range from 0.1 to 0.5 µm and the nitrogen BET specific surface area is 20,000 m<sup>2</sup>/kg [Yajun et al., 2003].

SF has a low bulk density of around 2.0 to 3.0 kg/m<sup>3</sup>. The low bulk density of SF may cause difficulty in transporting and handling. In order to improve the handling and transport properties, SF is usually processed to increase its bulk density by densified, sluried or palletized process [Yajun and Jong., 2003].

Although SF could impart significant contributions to strength and chemical resistance of concrete, it could also lead to increases in water demand, placing

difficulties and plastic shrinkage problems in concrete [Thomas et al., 1999]. The agglomeration of SF particles in cement paste or mortar was also reported to decrease the chemical reaction of SF during hydration process. This agglomeration of SF can reduce its effectiveness by having a larger particle diameter, a smaller surface area (SSA) and a lower pozzolanic reactivity than the unitary grains [Boddy et al., 2000].

### **2.5.2 Fly ash (FA)**

FA is a finely divided residue that is a by-product of the combustion of ground or powdered coal exhaust fumes of coal-fired power stations. In certain place FA is also known as pulverized fuel ash (PFA) and it was found to possess pozzolanic properties due to the contents of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  [Xinghua et al., (2002)]. This material represents a substantial reserve of pozzolanic materials if it can be fully recovered. It is generally finer than cement and consists mainly of glassy-spherical particles.

Two major classes of fly ash are specified in ASTM C 618 on the basis of their chemical compositions resulting from the type of coal burned; the two classes are designated as Class F and Class C. Class F fly ash is normally produced from burning anthracite or bituminous coal, and Class C is normally produced from the burning of sub-bituminous coal and lignite (Halstead, 1986. Class C fly ash usually has cementitious properties in addition to pozzolanic properties due to free lime, whereas Class F is rarely cementitious when mixed with water alone (Halstead, 1986). Some Class C FA may contain lime content of higher than 10% and low sulphur content.

Even though the use of FA in concrete has increased in the last 20 years, less than 20% of the FA collected has been used in the cement and concrete industries (Helmuth, 1987).

#### **2.5.2.1      *Chemical compositions of FA***

Combustion of ground or powdered coal will produce a residue known as fly ash (FA). The chemical compositions of the FA may vary from one batch to another depending on the minerals associated with the coal and the burning condition during the combustion of the coal. In general, FA contains  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  and the amount of these three compositions constitutes as the main requirement of ASTM C 618-94 in determining the classification of FA. Swamy (1986) stated that the classification of FA through the amount of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  is confusing, since many class C FA was observed to comply with class F requirements. In addition, FA was also reported to contain more alumina and less silica in comparison with other pozzolans [(McCarthy et al., 2005)].

CaO is another oxide that normally presents in FA but its composition is governed by the type of coal used. The composition of CaO is usually lower than 10% for bituminous coal and greater than 10% for sub-bituminous coal [Neville, 2002]. The CaO composition will establish either the FA possesses a cementitious property or not. FA with high level of CaO will have cementitious properties as an additional to the pozzolanic property, while FA with low level of CaO only has a pozzolanic property [Ravindra,1986]. The amount of CaO is also used to identify the classifications of FA. FA with low CaO is classified as class F and that with high CaO content is classified as class C. ASTM C618 stated that, FA with CaO content

of less than 10 % is classified as Class F while FA with CaO content greater than 10% is classified as class C [Ravindra, 1986].

Other than the four oxide compositions discuss earlier, other compositions such as MgO, Fe<sub>2</sub>O<sub>3</sub>, alkalise and carbon are also present and normally determined. The carbon content is assumed to be equal to the LOI. Even though the amount of MgO of FA is in many cases higher than that observed in other pozzolans, but the MgO is not harmful because it exists in a non-reactive form [Neville, 2002].

#### **2.5.2.2      *Physical properties of FA***

FA consists of glassy spherical particles with some crystalline matter and carbon in the form of unburnt coal, which varies from plant to plant [Ramezaniapour, 1987]. The particle diameter of FA ranges between less than 1µm to 100µm with an average particle size of 20µm, while the specific surface area of FA is usually between 250 and 600 m<sup>2</sup>/kg and the overall value of specific gravity is 2.35 [Neville, 2002].

Mineralogy analysis of FA typically contains about 50 - 90% of glass. The reactivity of glass in FA is depending on the chemical compositions especially the CaO content. The typical crystalline minerals of low calcium FA are quartz, mullite, sillimanite, hematite and magnetite. These minerals do not posses any pozzolanic activity. High calcium FA contains minerals that may react with water, which are tricalcium aluminate, calcium aluminosulfate, anhydrite, free CaO, and alkali sulphates. High calcium FA also contains quartz and periclase but these two minerals do not give any effect on the reactions [Malhotra and Mehta, 2004].