CHARACTERISATION OF HYDRATION OF SUPPLEMENTARY CEMENTITIOUS MATERIALS WITH CALCIUM HYDROXIDE FOR USE IN BINARY AND TERNARY CEMENTS

ANUJ

DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

ANUJ

DEPARTMENT OF CIVIL ENGINEERING

Submitted

in fulfilment of the requirements of the degree of DOCTOR OF PHILOSOPHY

to the

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Dedicated to my Mother

CERTIFICATE

This is to certify that the thesis entitled "**CHARACTERISATION OF HYDRATION OF SUPPLEMENTARY CEMENTITIOUS MATERIALS WITH CALCIUM HYDROXIDE FOR USE IN BINARY AND TERNARY CEMENTS**", being submitted by Mr. Anuj, to the Indian Institute of Technology Delhi, for the award of 'Doctor of Philosophy' in Department of Civil Engineering is a record of the bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for submission of this thesis, which to the best of our knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.

(Dr. Shashank Bishnoi)
Associate Professor
Department of Civil Engineering
Indian Institute of Technology Delhi
New Delhi – 110016, India
Date:
New Delhi

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ABSTRACT

The utilisation of supplementary cementitious materials (SCMs) and blended SCMs is widely promoted for use in cement and concrete. Although it is important to characterise the reactivity of SCMs before adding them to cement and concrete, the methods for measuring their reactivity have not been focused upon. Most of the reactivity test methods assess the reactivity in the presence of calcium hydroxide (CH), but the hydration behaviour of SCMs with CH and the effect of the factors that influence the hydration are not well understood. A better understanding of the test methods that measure reactivity of SCMs and their blends will help in improving their reliability and usability.

This thesis focuses upon understanding the hydration behaviour of SCMs and their blends for characterising their reactivity. While several test methods that quantify the reactivity of individual SCMs are available, the advent of ternary cements necessitates the testing of not just the individual SCMs, but also their blends. The hydration and reactivity of SCMs and their blends was studied in blends with CH and the optimum conditions, in terms of the availability and quantities of CH, sulphates, alkalis and their combinations, for the hydration of one each of calcined clay, fly ash and slag were studied. The kinetics of hydration, phase formation, CH consumption and strength development of selected SCMs and their blends were studied using isothermal calorimetry, X-ray diffractometry, thermogravimetry and mortar compressive strengths. The hydration results indicate that the presence of silica, alumina, calcium and magnesium influences the rate of hydration, and formation of hydration products. SCMs like calcined clay and slag react faster due to the presence of alumina and their hydration behaviour varies depending upon the presence of sulphates, alkalis and the temperature. Metastable hydroxy-AFm type phases were found to be unstable at high temperature and a reduction in compressive strength and bound water was observed due to their conversion to hydrogarnet (C_3AH_6).

Further, the reactivity of SCMs and their blends were measured with the help of 4 different methods: modified Chapelle's test for calcium consumption, chemical shrinkage test based on bound water, heat of hydration in the presence of CH, sulphates and alkalis and lime reactivity test based on strength development. The reactivity of SCMs and blends using the cement mortar compressive strength was tested for comparing the results from reactivity test methods with 28 days and 90 days compressive strength. The hydration and development of

hydrates in selected SCMs and blends were analysed under all the reactivity tests so as to understand the influence of the test conditions on the hydration reactions.

The results show that although various problems are associated with carrying out the reactivity tests both at ambient and increased temperatures, useful information can be obtained from these tests. While at ambient conditions, the rate of reaction of most SCMs is too slow to follow and characterise using standard techniques, at higher temperatures, the nature of the reactions and the products is seen to be influenced. In some cases, even phases that are usually inert, e.g. quartz, are seen to react when the temperature is increased. In some of the systems, phases such as hydrogarnet, that are usually not observed in cementitious systems at normal temperatures, were also found to be formed in the test methods. The test methods were still seen to provide important information like that capacity to react to portlandite, the relative reactivity and information about the kinetics of reactions.

This thesis presents the test methods used, the materials studied, the results obtained and the key conclusions derived from these test methods.

सारांश

सीमेंट और कंक्रीट में उपयोग के लिए पूरक सीमेंट सामग्री (सप्लमेंटरी सिमेंटीशीयस मटीरीयल्ज़ - एस.सी.एम.) और मिश्रित एस.सी.एम. का उपयोग व्यापक रूप से किया जाता है। हालांकि एस.सी.एम. को सीमेंट और कंक्रीट में उपयोग करने से पहले उनकी अभिक्रियाशीलता को चिह्नित करना महत्वपूर्ण है, लेकिन उनकी अभिक्रियाशीलता को मापने के तरीकों पर ध्यान केंद्रित नहीं किया गया है। अधिकांश अभिक्रियाशीलता परीक्षण विधियों में कैल्शियम हाइड्रॉक्साइड (सी.एच.) की उपस्थिति में अभिक्रियाशीलता का आकलन किया जाता है, लेकिन सी.एच. के साथ एस.सी.एम. का जलयोजन व्यवहार और जलयोजन को प्रभावित करने वाले कारकों के प्रभाव को अच्छी तरह से नहीं समझा गया है। एससीएम और उनके मिश्रणों की अभिक्रियाशीलता को मापने वाले परीक्षण तरीकों की बेहतर समझ उनकी विश्वसनीयता और प्रयोज्य में सुधार करने में मदद करेगी।

यह थीसिस एस.सी.एम. और मिश्रित एस.सी.एम. के जलयोजन व्यवहार को समझने और उनकी अभिक्रियाशीलता को चित्रित करने पर केंद्रित है। जबकि कई परीक्षण विधियां जो विशिष्ट एस.सी.एम. की अभिक्रियाशीलता को निर्धारित करती हैं, उपलब्ध हैं, त्रिमिश्रित सीमेंट्स के आगमन के लिए न केवल अमिश्रित एस.सी.एम. के परीक्षण की आवश्यकता होती है, बल्कि मिश्रित एस.सी.एम. के परीक्षण की भी आवश्यकता होती है। एस.सी.एम.और मिश्रित एस.सी.एम. के जलयोजन और अभिक्रियाशीलता का अध्ययन सी.एच. के साथ और इष्टतम अवस्था वाले मिश्रणों में, जैसेकि सी.एच., सल्फेट्स, क्षार और उनके संयोजनों की उपलब्धता और मात्रा के संदर्भ में किया गया था। प्रत्येक निस्तापित क्ले, फ्लाई ऐश और स्लैग में से एक-एक चयनित एस.सी.एम. का अध्ययन जलयोजन अभिक्रिया के लिए किया गया। चयनित एस.सी.एम.और मिश्रित एससीएम के जलयोजन गतिविज्ञान, अभिक्रिया उत्पाद, सी.एच. खपत और कम्प्रेसिव स्ट्रेंथ का अध्ययन समतापी कैलोरीमेट्री, एक्स रे डिफ्रेक्टोमेट्री, थर्मोग्रैवीमेट्री और मोर्टार कम्प्रेसिव स्ट्रेंथ का उपयोग करके किया गया था। जलयोजन परिणाम संकेत देते हैं कि सिलिका, एल्यूमिना, कैल्शियम और मैग्नीशियम की उपस्थिति जलयोजन की दर और अभिक्रिया उत्पादों के निर्माण को प्रभावित करती है। एल्यूमिना की उपस्थिति के कारण निस्तापित क्ले और स्लैग जैसे एस.सी.एम. तेजी से अभिक्रित होते हैं और सल्फेट, क्षार और तापमान की उपस्थिति के आधार पर उनका जलयोजन व्यवहार भिन्न होता है। मेटास्टेबल हाइड्रॉक्सी-एएफएम प्रकार के

उत्पादों को उच्च तापमान पर अस्थिर पाया गया और उनके हाइड्रैगनेट (C_3AH_6) में रूपांतरण के कारण कम्प्रेसिव स्ट्रेंथ और रासायनिक आबंध जल में घटौति देखी गई।

इसके अलावा, एस.सी.एम. और मिश्रित एस.सी.एम. की अभिक्रियाशीलता को ४ अलग-अलग तरीकों की मदद से मापा गया: कैल्शियम की खपत के लिए संशोधित चैपल परीक्षण, रासायनिक आबंध जल के आधार पर रासायनिक संकोचन परीक्षण, सी.एच. की उपस्थिति में जलयोजन की ताप, तथा सल्फेट्स, क्षार और सी.एच. की अभिक्रियाशीलता परीक्षण पर आधारित कम्प्रेसिव स्ट्रेंथ। एस.सी.एम. और मिश्रित एस.सी.एम. का उपयोग २८ दिनों और ९० दिनों की सीमेंट मोर्टार कंप्रेसिव स्ट्रेंथ के साथ अभिक्रियाशीलता परीक्षण के परिणामों से तुलना के लिए किया गया था। चयनित एस.सी.एम. और मिश्रित एस.सी.एम. में जलयोजन और जलयोजन उत्पादों के विकास का विश्लेषण सभी अभिक्रियात्मक परीक्षणों के तहत किया गया ताकि जलयोजन अभिक्रिया पर परीक्षण की स्थितियों के प्रभाव को समझा जा सके।

परिणाम बताते हैं कि हालांकि विभिन्न समस्याएं सामान्य और बढ़े हुए तापमान पर अभिक्रियाशीलता परीक्षण करने से जुड़ी हैं, इन परीक्षणों से उपयोगी जानकारी प्राप्त की जा सकती है। जबकि व्यापक परिस्थितियों में, अधिकांश एस.सी.एम. की अभिक्रिया की दर मानक तकनीकों का उपयोग करने और उनका अनुसरण करने के लिए बहुत धीमी है, उच्च तापमान पर, अभिक्रियाशीलता और उत्पादों की प्रकृति को प्रभावित किया जाता है। कुछ मामलों में, यहां तक कि रासायनिक यौगिक जो आमतौर पर निष्क्रिय होते हैं, जैसे क्वार्ट्ज, तापमान बढ़ने पर अभिक्रियाशील देखा गया। कुछ परिस्थितिओ में में, हाइड्रोगरनेट जैसे उत्पाद जो आमतौर पर सामान्य तापमान पर सीमेंटेड सिस्टम में नहीं देखे जाते हैं, अभिक्रियाशीलता परीक्षण विधियों में भी पाए गए थे। परीक्षण विधियों को पोर्टलैंडाइट से अभिक्रिया करने की क्षमता, सापेक्ष अभिक्रिया और अभिक्रियाशीलता के गतिविज्ञान जैसी महत्वपूर्ण जानकारी प्रदान करने के लिए देखा गया था।

यह थीसिस उपयोग किए गए परीक्षण विधियों, अध्ययन में इस्तेमाल की गई सामग्री, प्राप्त परिणामों और परीक्षण विधियों से प्राप्त मुख्य निष्कर्ष प्रस्तुत करती है।

TABLE OF CONTENT

CERTIFICATE i
ACKNOWLEDGEMENTS iii
ABSTRACT v
सारांश vii
TABLE OF CONTENT ix
LIST OF FIGURES xv
LIST OF TABLES xxiii
LIST OF ACRONYMS xxv
LIST OF ABBREVIATED FORMULAE xxvii
Chapter 1: Introduction 1
1.0 Background 1
1.1 Objectives of the thesis 2
1.2 Scope of the thesis 2
1.3 Outline of the thesis 3
Chapter 2: Literature review 5
2.0 Introduction 5
2.1 Ordinary Portland cement 5
2.2 Hydration of OPC 7
2.2.1 Measuring cement hydration kinetics 8
2.3 Supplementary cementitious materials 10
2.4 Reactive SCMs 12
2.4.1 Calcined clay or metakaolin 12
2.4.2 Fly ash 15
2.4.3 Slag 18
2.4.4 Other SCMs 21
2.5 Non reactive/fillers 22
2.5.1 Limestone 23
2.5.2 Quartz 24
2.6 How SCMs are used 25
2.6.1 Binary cements 26
2.6.2 Ternary cements 28

2.7 Testing of cements ... 31
2.8 How SCMs are tested ... 32
2.8.1 Testing physical and chemical properties ... 32
2.8.2 Testing performance of SCMs by measuring their reactivity ... 34
2.8.3 Direct testing ... 37
2.8.3.1 Modified Chapelle's test ... 37
2.8.3.2 Frattini test ... 39
2.8.3.3 Saturated lime test ... 41
2.8.3.4 CH consumption using XRD/TGA and bound water using TGA ... 42
2.8.4 Indirect testing ... 46
2.8.4.1 Strength activity index ... 46
2.8.4.2 Lime reactivity ... 49
2.8.4.3 Electrical conductivity ... 51
2.8.4.4 Heat of hydration ... 54
2.8.4.5 Chemical shrinkage ... 56
2.8.4.6 Soluble silica ... 57
2.8.4.7 Selective dissolution ... 60
2.8.5 Other methods ... 62
2.9 Research gap ... 63
Chapter 3: Test methods ... 65
3.0 Introduction ... 65
3.1 Characterisation techniques ... 65
3.1.1 Laser diffractometry for particle size distribution ... 66
3.1.2 Sieve analysis ... 67
3.1.3 Blaine fineness ... 68
3.1.4 Helium gas pycnometer ... 68
3.1.5 Le Chatelier's flask ... 69
3.1.6 Thermogravimetry analysis ... 69
3.1.7 Loss on Ignition using muffle furnace ... 71
3.1.8 X-ray florescence ... 72
3.1.9 X-ray diffraction ... 73
3.1.10 Inductively coupled plasma – optical emission spectroscopy ... 74
3.1.11 Scanning electron microscopy ... 75
3.1.12 Isothermal calorimetry ... 77

3.2 Test methods for reactivity study 78
3.2.1 Modified Chapelle's test 78
3.2.2 Chemical shrinkage test 79
3.2.3 Heat of hydration for reactivity study 80
3.2.4 Lime reactivity test 80
3.2.5 Cement mortar compressive strength 81
3.3 Summary 82
Chapter 4: Characterisation of materials 83
4.0 Introduction 83
4.1 Raw materials 83
4.1.1 Calcined clays 83
4.1.2 Fly ash 83
4.1.3 Carbonates 84
4.1.4 Slag 84
4.1.5 Quartz 84
4.1.6 Blending of SCMs 85
4.1.7 Ordinary Portland cement 86
4.1.8 Chemicals 86
4.2 Raw material characterisation 87
4.2.1 Physical testing 87
4.2.1.1 Fineness 87
4.2.1.2 Loss on Ignition 91
4.2.1.3 Specific gravity 94
4.2.1.4 Surface area 95
4.3 Chemical analysis 99
4.3.1.1 X-ray fluorescence 99
4.3.1.2 Crystalline phase composition using X-Ray Diffraction 100
4.3.1.3 Soluble silica 104
4.4 Morphology 107
4.5 Summary 110
Chapter 5: Sulphates and alkali optimisation for hydration of SCMs with CH 111
5.0 Introduction 111
5.1 Experimental protocols 112
5.1.1 Heat of hydration 112

5.1.2 Hydration products ... 112
5.1.3 Compressive strength ... 113
5.2 Finding the optimum alkali and sulphate content for Calcined clay K1 ... 113
5.2.1 Effect of CH content ... 113
5.2.2 Effect of sulphate content ... 116
5.2.3 Effect of alkali content ... 118
5.2.1 Combined effect of sulphate and alkali content ... 120
5.3 Finding the most suitable alkali and sulphate content for fly ash FA2 ... 122
5.3.1 Effect of CH content ... 122
5.3.2 Effect of sulphate content ... 124
5.3.3 Effect of alkali content ... 125
5.3.4 Combined effect of sulphate and alkali content ... 127
5.4 Finding the most suitable alkali and sulphate content for slag S1 ... 128
5.4.1 Effect of CH content ... 128
5.4.2 Effect of sulphate content ... 130
5.4.3 Effect of alkali content ... 132
5.4.4 Combined effect of sulphate and alkali content ... 134
5.5 Summary ... 136
Chapter 6: Hydration of SCMs and their blends ... 137
6.0 Introduction ... 137
6.1 SCM/blends selected for hydration study ... 137
6.2 Hydration of SCMs ... 140
6.2.1 Calcined clay ... 140
6.2.2 Fly ash ... 145
6.2.3 Slag ... 150
6.2.4 Limestone ... 154
6.2.5 Quartz ... 159
6.3 Hydration of blends ... 163
6.3.1 Calcined clay limestone blend-B1 ... 164
6.3.2 Fly ash slag blend-B13 ... 169
6.3.3 Slag limestone blend-B15 ... 173
6.4 Assessment of carboaluminates ... 178
6.5 Summary ... 179
Chapter 7: Reactivity of SCMs and their blends ... 181

7.0 Introduction 181
7.1 Reactivity study 181
7.1.1 Modified Chapelle's test 181
7.1.1.1 Hydration products characterisation using XRD and TGA 184
7.1.2 Chemical shrinkage 186
7.1.2.1 Hydration products characterisation using XRD 188
7.1.3 Heat of hydration 190
7.1.3.1 Hydration behaviour studied using XRD and TGA 195
7.1.4 Lime reactivity strength test 196
7.1.4.1 Rate of strength development 199
7.1.4.2 Hydration products study using XRD and TGA 199
7.1.4.3 C-S-H analysis using SEM-EDS 203
7.1.5 Cement mortar compressive strength 209
7.1.5.1 Binary cement blends 209
7.1.5.2 Ternary cement blends 211
7.2 Comparison of hydration products of SCMs/blends with CH and with cement 213
7.3 Comparison of reactivity of SCMs/blends vs. cement mortar strength 215
7.4 Summary 216
Chapter 8: Conclusions and further research 219
8.0 Conclusions 219
8.1 Novel contributions 221
8.2 Suggested further research 222
References 225
Annexure 1: DTG graphs 243
Annexure 2: Correlation of cement mortar strength vs. reactivity tests 253
Author's curriculum vitae 261

LIST OF FIGURES

Figure 2.1 : Typical Portland cement hydration during first 24hr [55]. 9
Figure 2.2 : Ternary phase diagram for showing chemical composition of SCMs [59]....... 10
Figure 2.3 : XRD plot for silica incorporating Hgt (left) and silica-free Hgt (right) [87]. ... 15
Figure 2.4 : Thermodynamic modelling of FA hydration at different replacement levels of OPC [59]. 17
Figure 2.5 : Thermodynamic modelling of slag hydration at different replacement levels of OPC [59]. 19
Figure 2.6 : Thermodynamic modelling of OPC hydration with 4% of LS [66]................. 24
Figure 2.7 : Thermodynamic modelling of hydrated OPC with quartz at different temperatures [134]. 25
Figure 2.8 : SEM image of 14 days hydrated sample of FA and LS blend [143]................ 29
Figure 2.9 : XRD results for 90 days hydrated cement containing two FA [158]............... 30
Figure 2.10 : Frattini test results in which red curve is the theoretical curve of Calcium ions solubility [175]. 40
Figure 2.11 : Comparision of (a) step method and (b) tangent method for CH quantification using TGA-DTG [52]. 43
Figure 2.12 : Electrical conductivity results for different kaolinitic clays [175]................. 52
Figure 2.13 : Cumulative chemical shrinkage plot for pastes with clays calcined at different temperatures and CH at 40 °C [203]. 56
Figure 2.14 : Quantification of unreated slag in blended cement using SEM-EDS [48]...... 63
Figure 3.1 : Laser diffractometry instrument at Advance Materials Characterisation laboratory, IIT Delhi. 66
Figure 3.2 : Helium gas pycnometer (left) and sample chamber with sample cell filled with powder (right) at Advance Materials Characterisation laboratory, IIT Delhi. 69
Figure 3.3 : Thermogravimetric instrument at laboratory of Development Alternatives, New Delhi 70
Figure 3.4 : Hydrated paste sample cast in cylindrical tubes (left), slicing of solid samples using saw (middle) and sliced discs of hydrated sample (right). 71
Figure 3.5 : XRF at Advance Materials Characterisation laboratory, IIT Delhi (left) and pressed pellet sample of calcined clay prepared for XRF analysis (right). 72
Figure 3.6 : XRD at Advance Materials Characterisation Laboratory, IIT Delhi 73

Figure 3.7 : Electron interaction with sample and signal generation [52] 76
Figure 3.8 : Calmetrix Ical 8000 at Materials Research Laboratory, IIT Delhi.................... 77
Figure 3.9 : Experimental setup for the Modifed Chapelle's test at Materials Research Laboratory, IIT Delhi. 79
Figure 3.10 : Sample preparation for the chemical shrinkage test (left) and temperature controlled water bath with one specimen mounted (right) at Materials Research Laboratory, IIT Delhi. 80
Figure 4.1 : 3D turbo mixer at Materials Research Laboratory, IIT Delhi. 85
Figure 4.2 : Cumulative particle size distribution of (a) Calcined clays, (b) fly ashes, (c) carbonates and quartz, (d) slags and (e) OPCs. 89
Figure 4.3 : Volume frequency distribution plot for, (a): calcined clays, (b): fly ashes, (c): carbonates and quartz, (d): slags and (e): OPCs. 90
Figure 4.4 : TGA and DTG plots for (a): calcined clays, (b:) fly ashes, (c): carbonates and quartz, (d): slags, (e): OPCs. 93
Figure 4.4 : XRD plots showing phases present in (a): Calcined clays, (b): fly ashes, (c): carbonates and quartz, (d): slags, (e): OPCs. 103
Figure 4.5 : XRD plots showing difference between slag diffraction plot using internal standard and external standard method with rutile. 104
Figure 4.6 : Morphology of slag particle after 28 days of alkaline solution, (a): slag S1 and (b): slag S2. 106
Figure 4.7 : Morphology of SCMs and cement particles (a): clay K1, (b): K2, (c): K3, (d): fly ash FA1, (e): FA2, (f): FA2, (g): carbonate LS1, (h): LS2, (i): LS3, (j): Q, (k): slag S1 (l): S2, (m): OPC 1, (n) OPC 2. 109
Figure 5.1 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of clay K1 in Mix 1 and Mix 2. 114
Figure 5.2 : Comparison of hydration products evolved at 3, 7 and 28 days in Mix 1 and Mix 2 of clay K1. 115
Figure 5.3 : Compressive strength results at 3, 7 and 28 days for different mixes of clay K1. 115
Figure 5.4 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of clay K1 in Mix 2 and Mix 3-5 containing $C\bar{S}$. 117
Figure 5.5 : Comparison of cumulative energy per g of clay K1 for first 24 hours in, Mix 2 and Mix 3-5 containing $C\bar{S}$ (left) and Mix 2 and Mix 6-8 containing NaOH (right). ... 117

Figure 5.6 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 3-5 of clay K1 containing C$\bar{S}$. 118
Figure 5.7 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of clay K1 in Mix 2 and Mix 6-8 containing NaOH. 119
Figure 5.8 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 6-8 of clay K1 containing NaOH. 120
Figure 5.9 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of clay K1 in Mix 4, Mix 7, Mix 9 and Mix 10 and, (c): energy evolved in first 24 hours for Mix 4, Mix7, and Mix 9 and Mix 10. 121
Figure 5.10 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 9 and Mix 10 of clay K1 containing C$\bar{S}$ and NaOH. 122
Figure 5.11 : Comparison of (a): heat flow and, (b): cumulative energy evolved per g of fly ash FA2 in Mix 1 and Mix 2. 123
Figure 5.12 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 1 and Mix 2 of fly ash FA2. 123
Figure 5.13 : Compressive strength results at 3, 7 and 28 days for different mixes of fly ash FA2. 124
Figure 5.14 : Comparison of cumulative energy emitted per g of fly ash FA2 in Mix 2 and Mix 3-5 containing C$\bar{S}$. 124
Figure 5.15 : Comparison of hydration products formed at 3, 7 and 28 days in Mix 3, 4 and Mix 5 of fly ash FA2 containing C$\bar{S}$. 125
Figure 5.16 : Cumulative energy evolved per g of fly ash FA2 for Mix 2, Mix6-8 containing NaOH. 126
Figure 5.17 : Hydration products evolution at 3, 7 and 28 days in Mix 6-8 of fly ash FA2 containing NaOH. 126
Figure 5.18 : Comparison of cumulative energy emitted per g of clay K1 in Mix 4, Mix 7, Mix 9 and Mix 10. 127
Figure 5.19 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 9 and Mix 10 of fly ash FA2 containing C$\bar{S}$ and NaOH. 128
Figure 5.20 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of slag S1 in Mix 1 and Mix 2. 129
Figure 5.21 : Comparison of (a): hydration products evolution at 3, 7 and 28 days in Mix 1 and Mix 2 (b): Hydrotalcite (Htal) peak in 28 days hydrated samples of Mix 1 and Mix 2 of slag S1 130

Figure 5.22 : Compressive strength results at 3, 7 and 28 days for different mixes of S1. 130
Figure 5.23 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of slag S1 in Mix 2 and Mix 3-5 containing C$\bar{S}$. 131
Figure 5.24 : Cumulative energy per g of slag S1 for first 24 hours in Mix 2 and Mix 3-5 containing C$\bar{S}$ (left) and Mix 2 and Mix 6-8 containing NaOH (right). 131
Figure 5.25 : Comparison of hydration products formed at 3, 7 and 28 days in Mix 3, 4 and Mix 5 of slag S1 containing C$\bar{S}$. 132
Figure 5.26 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of slag S1 in Mix 2 and Mix 6-8 containing NaOH. 133
Figure 5.27 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 6-8 of slag S1 containing NaOH........ 134
Figure 5.28 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of slag S1 in Mix 4, Mix 7, Mix 9 and Mix 10 and, (c) energy emitted in first 24 hours for Mix 4, Mix7, and Mix 9 and Mix 10. 135
Figure 5.29 : Comparison of hydration products evolution at 3, 7 and 28 days in Mix 9 and Mix 10 of slag S1 containing C$\bar{S}$ and NaOH. 136
Figure 6.1 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of clay K1 in Mix 2, Mix 4, Mix 9 and Mix 9-50. 141
Figure 6.2 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of clay K1........ 143
Figure 6.3 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of clay K1. 144
Figure 6.4 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of clay K1. 144
Figure 6.5 : DTG plot showing Hgt decomposition in Mix 9-50. 145
Figure 6.6 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of fly ash FA2 in Mix 2, Mix 4, Mix 9 and Mix 9-50. 146
Figure 6.7 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of fly ash FA2........ 148
Figure 6.8 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of fly ash FA2. 149
Figure 6.9 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of fly ash FA2. 149

Figure 6.10 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of slag S1 in Mix 2, Mix 4, Mix 9 and Mix 9-50. 151
Figure 6.11 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of slag S1. 153
Figure 6.12 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of slag S1. 153
Figure 6.13 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of slag S1. 154
Figure 6.14 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of LS in Mix 2, Mix 4, Mix 9 and Mix 9-50. 156
Figure 6.15 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of LS1. 157
Figure 6.16 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of LS1. 158
Figure 6.17 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of LS1. 158
Figure 6.18 : DTG plot showing C-S-H decomposition in Mix 9-50 (left) and appearance of needle like crystals on 90 days hydrated Mix 9-50 sample. 159
Figure 6.19 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of quartz in Mix 2, Mix 4, Mix 9 and Mix 9-50.. 160
Figure 6.20 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of quartz. 162
Figure 6.21 : Appearance of C-S-H hump in the 90 days hydrated XRD results of sample of Mix 9-50.. 162
Figure 6.22 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of quartz.. 163
Figure 6.23 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of quartz. 163
Figure 6.24 : (a) Comparison of (a): heat flow and, (b): cumulative energy emitted per g of blend B1 in Mix 2, Mix 4, Mix 9 and Mix 9-50. 165
Figure 6.25 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of blend B1... 167
Figure 6.26 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of blend B1. 167

Figure 6.27 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of blend B1. 168
Figure 6.28 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of blend B13 in Mix 2, Mix 4, Mix 9 and Mix 9-50. 170
Figure 6.29 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of blend B13. 172
Figure 6.30 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of blend B13. 172
Figure 6.31 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of blend B13. 173
Figure 6.32 : Comparison of (a): heat flow and, (b): cumulative energy emitted per g of blend B15 in Mix 2, Mix 4, Mix 9 and Mix 9-50. 175
Figure 6.33 : Comparison of hydration products evolution at 3, 7, 28 and 90 days in (a): Mix 2, (b): Mix 4, (c) Mix 9 and, (d): Mix 9-50 of blend B15. 176
Figure 6.34 : Comparison of (a): CH consumption and, (b): bound water in Mix 2, Mix 4, Mix 9 and Mix 9-50 of blend B15. 177
Figure 6.35 : Compressive strength results at 3, 7, 28 and 90 days for different mixes of blend B15. 177
Figure 6.36 : Comparison of hydration products evolution at 3, 7 and 28 for Mix 9 of clay K1 and slag S1 prepared with pure CaO. 179
Figure 7.1 : Calcium consumed by 1 g of SCM in modified Chapelle's test. 182
Figure 7.2 : Calcium consumed by 1 g blend of SCMs in modified Chapelle's test........ 182
Figure 7.3 :Hydration products formed in SCMs K1, S1 and FA2 during the modified Chapelle's test (* = Hydrogarnet, # = Si- hydrogarnet, Kalo = Kaolinite, Htal = Hydrotalcite, Mu = Mullite, C-S-H= Calcium silicate hydrate gel). 184
Figure 7.4 : Plot for different hydrogarnets formed in case of slag S1 and K1. 185
Figure 7.5 : Hydration products formed in blend B1, B13 and B15 during the modified Chapelle's test. 185
Figure 7.6 : Cumulative chemical shrinkage of SCMs upto 28 days. 187
Figure 7.7 : Cumulative chemical shrinkage of clays and carbonates blends upto 28 days. 187
Figure 7.8 : Cumulative chemical shrinkage of fly ash and slag blends (B10-B15). 188
Figure 7.9 : Hydration products formed in SCMs during the chemical shrinkage test at 7 and 28 days. 189

Figure 7.10 : Hydration products formed in SCMs during the chemical shrinkage test at 7 and 28 days. 190
Figure 7.11 : Comparison of (a): heat flow and, (b): cumulative energy emitted of clay. . 192
Figure 7.12 : Comparison of heat flow (left) and, cumulative energy emitted of FA (right). 192
Figure 7.13 : Comparison of heat flow (left) and, cumulative energy of carbonate (right).192
Figure 7.14 : Comparison of heat flow (left) and, cumulative energy emitted of slag (right). 193
Figure 7.15 : Comparison of heat flow (left) and, cumulative energy emitted of blend B1-B3 (right). 193
Figure 7.16 : Comparison of heat flow (left) and, cumulative energy emitted of blend B1, B4, B5 and B8 (right). 193
Figure 7.17 : Comparison of heat flow (left) and, cumulative energy emitted of blend B1, B6, B7 and B9 (right). 194
Figure 7.18 : Comparison of heat flow (left) and, cumulative energy emitted of blend B1, B4, B5 and B8 (right). 194
Figure 7.19 : Comparison of heat flow (left) and, cumulative energy emitted of blend B10, B13 and B14 (right). 194
Figure 7.20 : Heat flow and cumulative energy emitted per g of blend B15. 195
Figure 7.21 : Lime reactivity compressive strength of SCMs. 197
Figure 7.22 : Lime reactivity strength of blended SCMs. 198
Figure 7.23 : Rate of strength development in lime reactivity test at 7, 10, 14 and 28 days. 199
Figure 7.24 : XRD plot for (a): K1, (b): FA2, (c): S1, (d) blend B1, (e) B13 and (f): blend B15 hydrated as per lime reactivity test conditions at 7, 10, 14 and 28 days. 201
Figure 7.25 : CH consumed per g of SCM in LR hydrated paste samples. 203
Figure 7.26 : Bound water in LR hydrated paste samples. 203
Figure 7.27 : EDS data points collected on 90 days hydrated paste samples of FA2 OPC (left) and FA2-LR samples (right). 204
Figure 7.28 : SEM-EDS scatter plot of points collected on binary blended cement having 30% replacement and OPC. 205
Figure 7.29 : SEM-EDS scatter plot of points collected on ternary blended cement having 45% replacement and OPC. 205

Figure 7.30 : SEM-EDS scatter plot of points collected on 10 days LR hydrated paste samples of clay K1, fly ash FA2 and slag S1. 206
Figure 7.31 : SEM-EDS scatter plot of points collected on 10 days LR hydrated paste samples of blend B1, B13 and B15. 206
Figure 7.32 : Comparison of outer and inner products of cement and LR data scatter of clay K1. 207
Figure 7.33 : Comparison of outer and inner products of cement and LR data scatter of fly ash FA2.207
Figure 7.34 : Comparison of outer and inner products of cement and LR data scatter of slag S1. 208
Figure 7.35 : Comparison of outer and inner products of cement and LR data scatter of blend B1. 208
Figure 7.36 : Comparison of outer and inner products of cement and LR data scatter of blend B13. 208
Figure 7.37 : Comparison of outer and inner products of cement and LR data scatter of blend B13. 209
Figure 7.38 : Compressive strength development in binary blended cement having 30% replacement of OPC1 with SCMs. 210
Figure 7.39 : Compressive strength development in binary blended cement having 30% replacement of OPC2 with SCMs. 210
Figure 7.40 : Comparison of compressive strength at 1, 3, 7, 28 and 90 days for binary blended cements with SCMs by replacing OPC1 and OPC2. 211
Figure 7.41 : Compressive strength development in ternary blended cement having 45% replacement of OPC1 with blends. 211
Figure 7.42 : Compressive strength development in ternary blended cement having 45% replacement of OPC2 with blends. 212
Figure 7.43 : Compressive strength development in ternary blended cement having 30% replacement of OPC1 with blends. 212
Figure 7.44 : Development of hydration products in binary blended cement having 30% replacement of OPC1 with SCMs. 213
Figure 7.45 : Development of hydration products in ternary blended cement having 45% replacement of OPC1 with SCMs. 214

LIST OF TABLES

Table 2.1 : Major compounds forming in cement clinker. 6
Table 2.2 : Main hydration products in OPC. 7
Table 2.3 : Classification of FA as per ASTM C 618. 16
Table 2.4 : Classification of reactivity test methods on the basis of testing duration. 36
Table 2.5 : Comparison of the test conditions and procedures used for modified Chapelle's test in different studies. 38
Table 2.6 : Comparison of the test conditions and procedures used for Frattini test in different studies. 40
Table 2.7 : Comparison of the test conditions and procedures used for saturated lime test in different studies. 42
Table 2.8 : Comparison of the test conditions and procedures used for CH consumption in different studies. 44
Table 2.9 : Comparison of the test conditions and procedures used for SAI in different studies. 47
Table 2.10 : Comparison of the test conditions and procedures used for lime reactivity test in different studies. 50
Table 2.11 : Comparison of the test conditions and procedures used for electrical conductivity test in different studies. 53
Table 2.12 : Comparison of the test conditions and procedures used for heat of hydration test in different studies. 55
Table 2.13 : Comparison of the test conditions and procedures used for chemical shrinkage test in different studies. 57
Table 2.14 : Comparison of the test conditions and procedures used for soluble silica test in different studies. 58
Table 2.15 : Comparison of the test conditions and procedures used for selective dissolution test in different studies. 61
Table 3.1 : Value of refractive index and absorption index used for PSD measurement. 67
Table 3.2 : Decomposition temperature ranges for different phases. 71
Table 3.3 : XRD Scan parameters for hydrated paste and raw powdered samples. 74
Table 3.4 : Mix design for test methods used for reactivity study (in gram). 79
Table 3.5 : Mix design for cement mortar strength test (quantities are in g). 81

Table 4.1 : Raw materials and chemicals used in the study.. 84
Table 4.2 : Blends of SCMs and their mix proportions. 86
Table 4.3 Physical properties of raw materials. 97
Table 4.4 : Raw materials composition measured using XRD (first result is using External standard, second result is from Internal standard). 98
Table 4.5 : Oxides composition of raw materials measured using XRF. 100
Table 4.6 : Mass absorption coefficient of different oxides for X-rays. 101
Table 4.7 : The soluble silica and alumina measured using acid digestion, XRD-XRF and ICP-OES. 105
Table 5.1 : Mix design for optimising sulphate and alkali content.................................... 112
Table 7.1 : Bound water of samples hydrated in modified Chapelle's test 186
Table 7.2 : Quantity of powder and water used for the lime reactivity test....................... 196
Table 7.3 : Correlation of the reactivity with the cement mortar compressive strength..... 216

<u>**LIST OF ACRONYMS**</u>

AFm	Monosulphate
AFt	Ettringite
ASTM	American Standards for Testing and Materials
C-S-H	Calcium Silicate Hydrate
CC	Calcium Carbonate
CH	Calcium Hydroxide
$C\bar{S}$	Calcium Sulphates or Gypsum
DTG	Differential Thermogravimetry
EDS	Energy Dispersive Spectroscopy
EN	European Norm
FA	Fly Ash
Hc	Hemicarboaluminate
Htal	Hydrotalcite
IS	Indian Standard
LOI	Loss on Ignition
LS	Limestone
MAC	Mass Absorption Coefficient
Mc	Monocarboaluminate
MK	Metakaolin
NaOH	Sodium Hydroxide
OPC	Ordinary Portland Cement
PFA	Pulverised Fuel Ash
PPC	Portland Pozzolana Cement
PPC	Portland Pozzolana Cement
PSD	Particle Size Distribution
S	Slag
SCMs	Supplementary Cementitious Materials
SEM	Scanning Electron Microscopy
SF	Silica Fume
Si/Al	Ratio of Silica to Alumina
Si/Ca	Ratio of Silica to Calcium

SSA	Specific Surface Area
Str	Strätlingite
TGA	Thermogravimetry Analysis
w/c	Water to Cement Ratio
w/p	Water to Powder Ratio
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

LIST OF ABBREVIATED FORMULAE

A	Al_2O_3
AFm	$C_6A\bar{S}_3H_{18}$
AFt	$C_6A\bar{S}_3H_{32}$
C	CaO
CC	$CaCO_3$
CH	$Ca(OH_2)$
$C\bar{S}$	$CaSO_4$
H	H_20
h-AFm	C_4AH_{13}
Hc	$C_3A.0.5CC_2H_{12}$
Hgt	C_3AH_6
Htal	$Mg_6Al_2(OH)_{16}CO_34H_2O$
Mc	$C_3A.CC.H_{12}$
S	SiO_2
Str	C_2ASH_8