EFFECT OF TEMPERATURE AND CEMENT CHARACTERISTICS ON CEMENT-SUPERPLASTICIZER INTERACTION

A THESIS

submitted by

ELSON JOHN

for the award of the degree

of

DOCTOR OF PHILOSOPHY

BUILDING TECHNOLOGY AND CONSTRUCTION MANAGEMENT DIVISION
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY MADRAS
CHENNAI 600 036

APRIL 2014

THESIS CERTIFICATE

This is to certify that the thesis entitled "**EFFECT OF TEMPERATURE AND CEMENT CHARACTERISTICS ON CEMENT-SUPERPLASTICIZER INTERACTION**" submitted by **Elson John** to the Indian Institute of Technology Madras for the award of the degree of **Doctor of Philosophy** is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Prof. Ravindra Gettu
(Research Guide)
Professor
Department of Civil Engineering
Indian Institute of Technology Madras

Chennai 600 036
Date:

ACKNOWLEDGEMENTS

The completion of my dissertation and subsequent Ph.D. has been a long journey. Much has happened and changed in the time I've been involved with this project. I am deeply appreciative of many individuals who have supported my work and continually encouraged me through the writing of this dissertation. Without their time, attention, encouragement, thoughtful feedback, and patience, I would not have been able to see it through the completion process.

My first debt of gratitude must go to my advisor, Prof. Ravindra Gettu, Department of Civil Engineering for his guidance, understanding, patience, and most importantly, his friendship during the time I shared with him. He patiently provided the vision, encouragement and advice necessary for me to proceed through the doctoral program and completion of my dissertation. I want to thank him for his unflagging encouragement and serving as a role model to me. He has always been patient when explaining the distinction of English words in writing and was very supportive and offered constructive criticisms while correcting the thesis. I owe my sincere and earnest thankfulness, for all I have learned from him, and for his continuous help and support in all stages of my work. I would also like to thank him for being an open person to ideas, and for encouraging and helping me to shape my interest and ideas. I could not have imagined having a better advisor and mentor for my Ph.D study. Prof. Gettu is a truly gifted technical writer, and I continue to strive to live up to his standards. The experience has been enriching and enlightening and I thank God almighty for giving me an opportunity to work as a research scholar with him at Indian Institute of Technology Madras.

I am truly obliged and thankful to Prof. Manu Santhanam for offering thorough and excellent feedback on this thesis. In addition, I thank him for giving guidelines and valuable suggestions on Chapters 6 and 7 of this thesis. His advice on research as well as on my career have been priceless. For this, I cannot thank him enough and I am forever grateful.

I owe sincere and earnest thankfulness to Dr. Radhakrishna G. Pillai for constant encouragement and motivation especially through the last phase of my work. The joy and enthusiasm he has for his research were contagious and motivational for

successful completion of my work. He's been motivating, encouraging, and enlightening me always, even during tough times in the Ph.D. pursuit.

I am deeply grateful to the present Head of Civil Engineering Department, Prof. A. Meher Prasad and the former head Prof. S. R. Gandhi for all the administrative support extended to me for carrying out this work.

I take this opportunity to extend my sincere gratitude to the members of my doctoral committee Prof. M. Subramaniam, Prof. Ganesh Babu, Prof. G. Appa Rao and Prof. Manu Santhanam for their input, valuable discussions and accessibility.

I would like to thank all Faculty members of Department of Building Technology and Construction Management Division, specially Prof. K. Ramamurthy, Prof. Koshy Varghese, Prof. M. S. Mathews, Prof. A. Ramachandraiah, Prof. K. N. Satyanarayana, Prof. K. Ananthanarayanan and Dr. Ashwin Mahalingam, Dr. Benny Raphael and Dr. Sivakumar Palaniappan for the guidance and support during the phase of my life as a research scholar in IIT Madras. The expectations and the goodwill they conferred in me has always been a constant source of inspiration to achieve higher goals.

I am pleased to record my gratitude to the Management of M. A. College of Engineering, Kothamangalam and Govt. of Kerala for sponsoring me for the Ph. D programme under Q.I.P. scheme. My special thanks to Prof. M. P. Varghese, Prof. Winny Varghese, Prof. M. G. Grasius, Prof. Paul. K. Mathew, Prof. George Issac, Prof. Lovely K. M, Prof. Mathews M Paul and other colleagues in the Department of Civil Engineering, M. A. College of Engineering for extending a helping hand at crucial times.

The staff of concrete lab will always deserve a special appreciation from my side for all the efforts they have put in towards the successful completion of my experimental work. I express my sincere thanks to all the lab staffs, in particular Ms. A. Malarrvizhi, Mssrs. Murali, M. Soundarapandian, Murthy, Krishnan, Subramaniam, Dhanasekaran, and Watson who has contributed their might for the smooth conducting of the experimental work.

I am also thankful to all the staff members of the Civil Engineering Department Office, Stores section and DCF for their excellent cooperation. I am also thankful to all people who have directly or indirectly helped me in carrying out this work.

It is a great pleasure to thank everyone from the organizations like BASF Construction Chemicals, Sika, Cera-Chem and Ultra tech limited for their hands-on work in completing my experimental studies. They also deserve my sincerest thanks, for their friendship and assistance which was meant more to me than I could ever express.

A good support system is important to surviving and staying sane during the time of research programme. I acknowledge the assistance and help of all my fellow research scholars and friends at IIT Madras. My time at IIT was made enjoyable in large part due to the many friends and groups that became a part of my life. My informal advisors and well wishers have been invaluable and I have greatly benefited from from their supports.

The list of the people I need to thank will not fit to a single acknowledgement section. I just mention some people whose contribution is obvious.

ELSON JOHN

ABSTRACT

Superplasticizers have become essential components of modern concrete due to beneficial effects in both the fresh and hardened state. There are many factors that can influence the interaction between cement and superplasticizer, such as the different characteristics of cement, the type and nature of superplasticizer, the ambiental conditions (especially temperature), etc. The inadequate knowledge of the behaviour of these admixtures and their effects, along with the use of high dosages, leads to significant problems in the construction industry. Therefore, it is essential to understand the influence of various factors on the cement-superplasticizer interaction to select an appropriate dosage of superplasticizer to make the concrete better. The main aim of this study is to understand the role of temperature and cement characteristics, such as fineness and SO_3 content of cement, in the cement-superplasticizer interaction, and their effect on the behaviour of cement paste, mortar and concrete.

The dependence of the relative fluidity of superplasticized cement paste on temperature has been evaluated with the help of the Marsh cone and mini-slump tests. In order to evaluate the influence of ambient temperature on the cement-superplasticizer interaction, studies are conducted with one superplasticizer from each of the four families of products used commonly in the construction sector. The saturation dosage of superplasticizer was determined from the Marsh cone test and it is observed that the saturation dosage increases with an increase in temperature. The loss in fluidity with time of cement paste is also studied with the Marsh cone test and it is seen that the loss in fluidity increases with an increase in temperature and decreases with an increase in dosage of superplasticizer. The water demand of cement paste increases with an increase in temperature, whereas the setting time decreases. The fluidity of cement mortar has been studied with the flow table test and it is observed that the initial spread decreases with an increase in temperature. The compressive and flexural strengths of mortar and concrete are also determined and it is observed that the early age strength increases with an increase in the exposure temperature whereas the long term strength decreases significantly.

The fluidity of cement paste decreases with an increase in fineness of cement, and the saturation dosage of superplasticizer (as determined from Marsh cone test) increases with an increase in the fineness of cement, indicating a higher superplasticizer demand at higher fineness. Also, the loss in fluidity increases with an increase in fineness of cement. The compressive and flexural strengths of mortar and concrete having cements of different fineness are also determined and it is observed that the initial strength increases with an increase in fineness of cement whereas the long term strengths are not significantly affected.

The influence of SO_3 content of cement on the cement-superplasticizer interaction is also studied. In general, the fluidity of cement paste increases with an increase in SO_3 content of cement and the loss in fluidity decreases; however, at lower SO_3 content, the cement paste shows an increase in superplasticizer demand. The mechanical properties of mortar and concrete are not significantly affected by the variation of SO_3 content of cement studied.

Another aspect studied in this work is the influence of the temperature on the hydration processes and on the development of microstructure of hydrated superplasticized cement paste. For this purpose, cement pastes are analyzed using several characterization techniques (X-ray diffraction, scanning electron microscopy, and thermal analysis). The results clearly indicate that the initial hydration is higher for the samples exposed to higher initial temperature and the later hydration decreases with increase in temperature. The addition of superplasticizer retards the hydration, especially at lower temperatures, and the microstructure seems to be more uniform in the presence of superplasticizer.

From the study, it is observed that the PCE based superplasticizer is least susceptible to changes in temperature and the LS based superplasticizer is the most. The saturation dosage is also the lowest for the PCE based superplasticizer compared to the other families of superplasticizers used. In general, the performance of PCE based superplasticizer is better compared to the other families of products in terms of initial workability and workability retention.

Keywords: Superplasticizer; Marsh cone; mini-slump; loss of fluidity; ambient temperature; Fineness of cement; SO_3 content.

TABLE OF CONTENTS

Title **Page No.**

ACKNOWLEDGEMENTS ..... **i**
ABSTRACT ..... **iv**
TABLE OF CONTENTS ..... **vi**
LIST OF TABLES ..... **xii**
LIST OF FIGURES ..... **xiv**

CHAPTER 1 INTRODUCTION
1.1 Background 1
1.2 Objectives and Scope 2
1.3 Structure of the Thesis 3

CHAPTER 2 LITERATURE SURVEY
2.1 Introduction 5
2.2 Cement Chemistry 6
2.2.1 Cement Composition 6
2.2.2 Hydration of Cement 7
2.2.3 Hydration of the Portland Cement Grain 8
2.3 Water Reducers and Superplasticizers 11
2.3.1 Characteristics and Chemistry of Superplasticizers 11
2.3.2 Mechanisms of Action of Superplasticizers 14
2.4 Cement-superplasticizer Interaction 19
2.4.1 Cement-superplasticizer Compatibility 19
2.4.2 Factors Affecting the Cement-Superplasticizer Interaction 20
2.4.2.1 Effect of the Chemical Structure of Superplasticizer 21
2.4.2.2 Effect of Calcium Sulphate 23
2.4.2.3 Effect of Soluble Alkalis 24
2.4.2.4 Effect of C_3A 25
2.4.2.5 Effect of Ambient Temperature 26
2.4.2.6 Effect of Fineness of Cement 28
2.5 Microstructure of Cement Paste 28

Table of Contents (Contd.)..... Page No.

2.5.1 Effect of Superplasticizer on the Microstructure of Hardened Cement Paste..... 28

2.5.2 Effect of Temperature on the Microstructure of Hardened Cement Paste..... 29

2.6 Effect of Superplasticizer on Properties of Concrete..... 30

2.7 Effect of Temperature on Properties of Concrete..... 31

2.8 Effect of Fineness of Cement on Properties of Concrete..... 32

2.9 Justification for the Present Study..... 33

CHAPTER 3 EXPERIMENTAL PROGRAMME

3.1 Introduction 34

3.2 Materials Used..... 35

3.2.1 Cement..... 35

3.2.2 Superplasticizers 36

3.2.3 Aggregates..... 37

3.3 Experimental Details..... 38

3.3.1 Testing Conditions 39

3.3.2 Tests on Cement Paste..... 39

3.3.2.1 Mixing Procedure for Cement Paste 40

3.3.2.2 Marsh Cone Test..... 40

3.3.2.3 Mini-slump Test 43

3.3.2.4 Water Demand (Standard Consistency) Test for Cement 44

3.3.2.5 Initial and Final Setting Time of Cement..... 45

3.3.3 Tests on Cement Mortar..... 45

3.3.3.1 Preparation of Cement Mortar 45

3.3.3.2 Determination of Flow Properties of Mortar 46

3.3.3.3 Determination of Mechanical Properties of Mortar 47

3.3.4 Tests on Concrete..... 48

3.3.4.1 Preparation of Concrete 49

3.3.4.2 Determination of the Flow Properties of Concrete (Slump Test)..... 49

3.3.4.3 Determination of the Mechanical Properties of Concrete..... 50

3.3.5 Microstructure Study..... 50

Table of Contents (Contd.) **Page No.**

3.3.5.1 Specimen Preparation 51
3.3.5.2 Scanning Electron Microscopy (SEM) 51
3.3.5.3 X-ray Diffraction (XRD) Techniques 53
3.3.5.4 Thermal (DTA/TG/ DTG) Analysis 54

CHAPTER 4 EFFECT OF TEMPERATURE ON THE PROPERTIES OF SUPERPLASTICIZED CEMENT PASTES

4.1 Introduction 56
4.2 Experimental Details 57
4.3 Test Results and Discussions 57
4.3.1 Effect of Temperature on the Fluidity of Cement Paste 57
4.3.2 Effect of Temperature on Evolution of Fluidity with Saturation Superplasticizer Dosage 65
4.3.2.1 Marsh Cone Test Results 65
4.3.2.2 Mini-slump Test Results 74
4.3.3 Effect of Temperature on Loss in Fluidity with Time for Superplasticizer Dosage Corresponding to the Saturation Dosage at 25°C 82
4.3.4 Effect of Temperature on Evolution of Fluidity with Superplasticizer Dosage Corresponding to the Minimum Flow at 25°C 87
4.3.5 Effect of Temperature on Water Demand of Cement without and with Superplasticizer 92
4.3.6 Effect of Temperature on Setting Time 98
4.4 Conclusions 103

CHAPTER 5 EFFECT OF INITIAL TEMPERATURE ON THE PROPERTIES OF CEMENT MORTAR AND CONCRETE

5.1 Introduction 105
5.2 Experimental Details 105
5.3 Test Results and Discussions 106
5.3.1 Effect of Temperature and Superplasticizer on the Fluidity of Mortar 106

Table of Contents (Contd.) **Page No.**

5.3.2 Effect of Temperature on the Evolution of Fluidity with Saturation Dosage of Superplasticizer at 25°C 110

5.3.3 Effect of Temperature on the Evolution of Fluidity with Dosage of Superplasticizer Corresponding to Minimum Flow at 25°C 118

5.3.4 Mechanical Properties of Cement Mortar with Temperature 126

5.3.4.1 Effect of Temperature on the Compressive Strength of Cement Mortar 126

5.3.4.2 The Effect of Temperature on the Flexural Strength of Cement Mortar 131

5.3.5 Effect of Temperature on Concrete Properties 135

5.3.5.1 Effect of Temperature on the Fluidity of Concrete 135

5.3.5.2 Effect of Temperature on the Mechanical Properties of Concrete 137

5.4 Correlation between Initial Fluidity of Cement Paste, Mortar and Concrete 141

5.5 Comparison between the Strength of Cement Mortar and Concrete 143

5.6 Conclusions 145

CHAPTER 6 EFFECTS OF THE FINENESS AND SO_3 CONTENT OF CEMENT

6.1 Introduction 148

6.2 Experimental Details 149

6.2.1 Materials Used 149

6.2.1.1 Cement 149

6.2.1.2 Superplasticizer 150

6.2.1.3 Water 150

6.2.2 Testing Conditions 151

6.3 Results and Discussions 151

6.3.1 Effect of Fineness of Cement on the Properties of Cement Paste, Mortar and Concrete 151

6.3.1.1 Effect on the Fluidity of Superplasticized Cement Paste..... 151

Table of Contents (Contd.) **Page No.**

6.3.1.2 Effect on Evolution of Fluidity of Superplasticized Cement Paste 155

6.3.1.3 Effect on the Setting Time of Cement Paste 158

6.3.1.4 Effect on the Fluidity of Superplasticized Cement Mortar .. 161

6.3.1.5 Effect on the Mechanical Properties of Mortar 162

6.3.1.6 Effect on the Superplasticizer Demand of Concrete..... 166

6.3.1.7 Effect on the Compressive Strength of Concrete 169

6.3.2 Effect of SO_3 Content of Cement on the Properties of Cement Paste, Mortar and Concrete 170

6.3.2.1 Influence on the Fluidity of Cement Paste..... 171

6.3.2.2 Influence on the Setting Time of Cement Paste 175

6.3.2.3 Influence on the Fluidity of Cement Mortar 177

6.3.2.4 Influence on Compressive Strength of Cement Mortar..... 179

6.3.2.5 Influence on Flexural Strength of Cement Mortar 180

6.3.2.6 Influence on Superplasticizer Demand of Concrete 181

6.3.2.7 Influence on Loss in Slump of Concrete..... 182

6.3.2.8 Influence on Compressive Strength of Concrete..... 183

6.4 Conclusions 185

CHAPTER 7 EFFECT OF CASTING TEMPERATURE ON THE MICROSTRUCTURE OF HARDENED CEMENT PASTE

7.1 Introduction 187

7.2 Scanning Electron Microscopy (SEM) 188

7.2.1 Background..... 188

7.2.2 Secondary Electron Imaging (SE)..... 188

7.2.2.1 Development of Microstructure at Half setting..... 189

7.2.2.2 Development of Microstructure at 1 day 193

7.2.2.3 Development of Microstructure at 3 days..... 195

7.2.2.4 Development of Microstructure at 7 days..... 198

7.2.2.5 Development of Microstructure at 28 days..... 200

7.2.3 Backscattered Electron Imaging (BSE)..... 203

7.3 Thermal analysis..... 209

Table of Contents (Contd.)..... Page No.

7.3.1 Background..... 209
7.3.2 Results and Discussions 209
7.4 XRD Analysis..... 213
7.4.1 Background..... 213
7.4.2 Results and Discussions 214
7.5 Conclusions 217

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

8.1 General Conclusions 218
8.2 Specific Conclusions..... 220
8.2.1 Influence of Temperature on the Properties of Cement Paste 221
8.2.2 Influence of Temperature on the Properties of Cement Mortar and Concrete 222
8.2.3 Influence of Fineness of Cement on the Properties of Cement Paste, Mortar and Concretes 223
8.2.4 Influence of SO3 Content of Cement on the Properties of Cement Paste, Mortar and Concrete..... 224
8.2.5 Influence of Temperature and Superplasticizer on Hardening and Hardened State Properties of Concrete 225
8.3 Recommendations for Further Research..... 226

REFERENCES..... 228

APPENDIX A 243

APPENDIX B 253

APPENDIX C 257

APPENDIX D 261

APPENDIX E 264

PUBLICATIONS BASED ON THE THESIS..... 276

LIST OF TABLES

Table No.	Title	Page No.
2.1	Typical portland cement composition	6
2.2	Chemical structure of superplasticizers (Rixom and Mailvaganam, 1999)	12
3.1	Chemical composition of cement used	36
3.2	Properties of superplasticizer	36
3.3	Summary of properties of aggregates	38
4.1	Saturation dosages of superplasticizer at different temperatures	61
5.1	Saturation dosages of superplasticizer at 25°C	107
5.2	Dosage of superplasticizer corresponding to minimum flow time at 25°C	108
5.3	Initial spread of mortar with dosage of superplasticizer corresponding to saturation point at 25°C and minimum flow at 25°C	109
5.4	Loss in spread of mortar with superplasticizer dosage corresponding to saturation point at 25°C	113
5.5	Comparison of spread of mortar at different ages with superplasticizer dosages at the saturation point at 25°C and minimum flow at 25°C	120
5.6	Mix proportions for concrete	136
5.7	Comparison between the compressive strengths of cement mortar and concrete	144
5.8	Comparison between the flexural strength of cement mortar and splitting tensile strength of concrete	145
6.1	Chemical composition of the cement samples used	150
6.2	Fineness and water demand of cement samples	150
6.3	Saturation dosages of superplasticizer with fineness	153
6.4	Setting time of cements with varying fineness	161
6.5	Mix proportions for concrete	167
6.6	Superplasticizer demand in concrete for a slump of 150 ± 20 mm	167
6.7	Loss in slump of concrete with fineness of cement	168
6.8	Setting times of cement with varying SO_3 content	177
6.9	Superplasticizer demand for concrete with cements of varying SO_3 content	182

List of Tables (cond.) **Page No.**

6.10 Loss of slump with time for concrete with varying SO_3 content of cement 183

7.1 Losses in mass corresponding to decomposition of CH 211

8.1 The major findings of the thesis in terms of the trends observed..... 220

LIST OF FIGURES

Figure	Title	Page No
2.1	Microstructure of hydrated portland cement (Taylor, 1997)	9
2.2	Physical action of superplasticizers (Aïtcin, 1998)	17
3.1	Particle size distribution of fine aggregates (0-4.75 mm)	37
3.2	Particle size distribution of coarse aggregates (4.75-20 mm)	38
3.3	Environmental chamber used for mixing and conducting the tests	39
3.4	Marsh cone test showing continuous and discontinuous flow	41
3.5	Geometry and dimensions (in millimetres) of the Marsh cone	42
3.6	Flow time curve showing the determination of saturation superplasticizer dosage (Gomes et al., 2001)	42
3.7	Mini-slump cone	43
3.8	Mini-slump test	44
3.9	Flow table test for mortar	47
3.10	Testing machine for mortar	48
3.11	Testing machine for concrete	50
3.12	Cutting machine	53
3.13	Epoxy impregnation setup	53
3.14	Polishing machine for cement paste	53
4.1	Curves of Marsh cone flow time versus superplasticizer dosage at different temperatures for the superplasticizers (a) PCE (b) SNF (c) SMF (d) LS	58-59
4.2	Curves of mini-slump spread versus superplasticizer dosage at different temperatures for the superplasticizers (a) PCE (b) SNF (c) SMF (d) LS	63-64
4.3	Evolution of Marsh cone flow time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS	66-67
4.4	Evolution of normalized Marsh cone flow time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS	70-71
4.5	Evolution of normalized Marsh cone flow time at different superplastiziser for different temperature (a) 5°C (b) 15°C (c) 25°C (d) 35°C (e) 40°C	72-74
4.6	Curves of mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS	75-76

List of Figures (Contd.) **Page No.**

4.7 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS 77-78

4.8 Curves of normalized mini-slump spread versus time at different superplasticizers for different temperature (a) 5°C (b) 15°C (c) 25°C (d) 35°C (e) 40°C..... 79-81

4.9 Curves of normalized Marsh cone flow time versus time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS for dosages corresponding to the saturation dosages at 25°C 82-84

4.10 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS for dosage corresponding to the saturation dosage at 25°C 85-86

4.11 Curves of normalized Marsh cone flow time versus time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS for dosage corresponding to the minimum flow at 25°C 88-89

4.12 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS for dosage corresponding to the minimum flow at 25°C 90-91

4.13 Water demand for different temperatures at varying sp/c dosage for superplasticizers based on (a) PCE (b) SNF (c) SMF (d) LS..... 92-94

4.14 Water demand of cement with superplasticizers at different temperatures (a) 5°C (b) 15°C (c) 25°C (d) 35°C (e) 40°C 95-97

4.15 Evolution of Vicat penetration values for cement pastes with and without superplasticizer at various temperatures for (a) Control (b) PCE (c) SNF (d) SMF (e) LS..... 99-101

4.16 Initial setting time for different temperatures with different superplasticizers..... 102

4.17 Final setting time for different temperatures with different superplasticizers..... 103

5.1 Initial spread of cement mortar in the flow table test for different temperatures 107

List of Figures (Contd.) **Page No.**

5.2 Initial spread of mortar in the flow table test for different temperatures (for superplasticizer dosage corresponding to the minimum flow at 25°C) 109

5.3 Spread of mortar with time at different temperature for superplasticizer dosage corresponding to the saturation dosage at 25°C for: (a) Control (b) PCE (c) SNF (d) SMF 111-112

5.4 Spread of mortar with temperature for different age with superplasticizer dosage corresponding to the saturation dosage at 25°C for (a) Control (b) PCE (c) SNF (d) SMF 114-115

5.5 Normalised spread loss with time at different temperatures for mortars with superplasticizer dosage corresponding to the saturation dosage at 25°C for: (a) Control (b) PCE (c) SNF (d) SMF 116-118

5.6 Spread of mortar with time and temperature for superplasticizer dosage corresponding to the minimum flow at 25°C for (a) PCE (b) SNF (c) SMF 119-120

5.7 Spread of mortar with temperature at different ages for the superplasticizer dosage corresponding to the minimum flow at 25°C for (a) Control (b) PCE (c) SNF (d) SMF 121-123

5.8 Normalised spread of mortar with time at different temperatures for superplasticizer dosage corresponding to the minimum flow at 25°C for (a) Control (b) PCE (c) SNF (d) SMF 124-125

5.9 Compressive strength of cement mortar for superplasticizer based on (a) Control (b) PCE (c) SNF (d) SMF 126-128

5.10 Compressive strength of mortar with temperature for specimen cured at (a) 3 days, (b) 7 days, and (c) 28 days 130-131

5.11 Flexural strengths of cement mortar for (a) Control (b) PCE (c) SNF (d) SMF 131-133

5.12 Flexural strength of mortars with temperature at (a) 3 days (b) 7 days and (c) 28 days 134-135

5.13 Change in slump of concrete with temperature 136

5.14 Compressive strength of concrete with temperature for superplasticizers based on (a) PCE and (b) SNF 138

List of Figures (Contd.) **Page No.**

5.15 Splitting tensile strength of concrete at different temperatures for superplasticizers based on (a) PCE (b) SNF..... 140-141

5.16 Correlation between fluidity of cement paste, mortar and concrete with temperature for superplasticizer based on (a) PCE (b) SNF 142

6.1 Marsh cone flow time versus superplasticizer dosage for cements with various fineness for the superplasticizers (a) PCE (b) SNF 152

6.2 Curves of mini-slump spread versus superplasticizer dosage for cements with various fineness for the superplasticizers (a) PCE and (b) SNF..... 155

6.3 Loss in fluidity in cement pastes with cements having varying fineness for (a) PCE and (b) SNF…… 156

6.4 Evolution of Vicat penetration values for pastes having (a) no superplasticizer, (b) having PCE, and (c) having SNF 159-160

6.5 Flow table spread of cement mortar..... 161

6.6 Compressive strength of mortars at (a) 1 day, (b) 7 days, and (c) 28 days. 163

6.7 Evolution of the compressive strength of mortar with cements having varying fineness with (a) no superplasticizer (control), (b) with PCE and (c) with SNF..... 164-165

6.8 Flexural strengths of mortars at (a) 7 days and (b) 28 days 166

6.9 Slump of concrete with cements of different fineness, having (a) PCE and (b) SNF 168

6.10 Compressive strengths of concrete with varying fineness at (a) 1 day, (b) 7 days, and (c) 28 Days 169-170

6.11 Marsh cone flow time with cements with varying SO_3 contents for (a) PCE and (b) SNF 172

6.12 Mini-slump spread with cement having varying SO_3 contents for (a) PCE and (b) SNF 173

6.13 Loss in fluidity of cement pastes with varying SO_3 content of cement for (a) PCE and (b) SNF 174

6.14 Evolution of Vicat penetration for cement pastes with cements of various SO_3 content for (a) Control, (b) PCE and (c) SNF 176-177

6.15 Flow table spread for mortar with varying SO_3 content..... 178

List of Figures (Contd.) **Page No.**

6.16 Compressive strengths of mortar with varying SO_3 contents at (a) 1 day (b) 7 days and (c) 28 days 179-180

6.17 Flexural strength of mortar with varying SO_3 contents at (a) 7 and (b) 28 days 181

6.18 Slump of concrete with SO_3 content (a) PCE (b) SNF..... 182-183

6.19 Compressive strength of concrete with varying SO_3 contents at (a) 1 day (b) 7 days and (c) 28 days 184

7.1 SE micrographs of cement paste at half setting for control paste 189-190

7.2 SE micrographs of cement paste at half setting for superplasticized cement paste 191-192

7.3 SE micrographs of cement paste after 1 day curing 194-195

7.4 SE micrographs of cement paste after 3 day curing 196-197

7.5 SE micrographs of cement paste after 7 day curing 198-199

7.6 SE micrographs of cement paste after 1 day curing 200-202

7.7 BSE images of cement paste after one day: (a) 5°C-Control (b) 5°C-PCE (c) 40°C-Control and (d) 40°C-PCE 204

7.8 BSE images of superplasticized cement paste after 3 days when exposed to initial temperatures of (a) 5°C, (b) 25°C and (c) 40°C..... 205-206

7.9 BSE images of superplasticized cement paste after 7 days, when exposed to various initial temperatures with and without superplasticizer 206-207

7.10 BSE images of superplasticized cement paste after 28 days exposed to various initial temperatures with and without superplasticizer……..208-209

7.11 DTA analysis of cement paste without superplasticizer after curing for 28 days and prepared at (a) 5°C (b) 25°C and (c) 40°C 210

7.12 TG curve of cement paste at the age of one day after exposure to 5°C..... 211

7.13 X-ray diffractogram of cement paste prepared at 25°C with age..... 214

7.14 X-ray diffractogram of cement pastes prepared at various temperatures and cured for (a) one day (b) 3 days (c) 7 days and (d) 28 days 215-216

A.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer at temperatures (a) 5°C (b) 15°C (c) 25°C (d) 35°C and (e) 40°C 241-243

List of Figures (Contd.) ..... Page No.

A.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer at temperatures (a) 5°C (b) 15°C (c) 25°C (d) 35°C and (e) 40°C 243-245

A.3 Marsh cone flow time curves of the two trials with SMF based superplasticizer at temperatures (a) 5°C (b) 15°C (c) 25°C (d) 35°C and (e) 40°C 246-248

A.4 Marsh cone flow time curves of the two trials with LS based superplasticizer at temperatures (a) 5°C (b) 15°C (c) 25°C (d) 35°C and (e) 40°C 248-250

B.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer for the cements having fineness of (a) F1-270 (b) F2-290 (c) F3-340 and (d) F4-360 kg/m^2 251-252

B.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer for the cements having fineness of (a) F1-270 (b) F2-290 (c) F3-340 and (d) F4-360 kg/m^2 253-254

C.1 Marsh cone flow time curves of two trials with PCE based superplasticizer for the cements having SO_3 content of (a) S1-1.7 (b) S2-1.88 (c) S3-2.19 and (d) S4-2.53% 255-256

C.2 Marsh cone flow time curves of two trials with SNF based superplasticizer for the cements having SO_3 content of (a) S1-1.7 (b) S2-1.88 (c) S3-2.19 and (d) S4-2.53% 257-258

D.1 TG curves of cement pates with and without superplasticizer at half setting, 1 and 28 days of curing and casted at (a) 5°C (b) 25°C and (c) 40°C 259-261

E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages 262-273

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Recent advancements in concrete technology, and the need for the better qualities and specialised applications of concrete have led to the wider production and use of high performance concretes. High performance of concrete normally refers to the improvement in workability, strength and durability, which can be achieved only by using admixtures, primarily superplasticizers that are necessary to ensure adequate workability at low water to cement ratios (w/c), leading to better mechanical integrity and lower permeability compared to conventional concrete. The multifunctional benefits of chemical admixtures, especially superplasticizers, make them essential components of modern high performance concrete. However, the improper use of these admixtures may lead to adverse effects such as slump loss, segregation of concrete, rapid set, entrainment of air, retardation, temperature evolution, etc. (Rixom and Mailvaganam 1999, Ramachandran 2002). Hence, one of the main challenges faced by the construction engineers today is to make high performance concrete with locally available materials for the varying and changing ambient conditions.

In addition to providing good workability immediately after mixing, the superplasticizer also influences the slump retention and setting process, which in turn can affect the strength and durability. The interaction between the cement and superplasticizer governs the flow behaviour of concrete. There are many factors that can influence the interaction, such as the characteristics of cement, the type and nature of superplasticizer, the ambiental conditions (especially temperature), etc. The inadequate knowledge of the behaviour of these admixtures and its effects, along with the use of high dosages, leads to significant problems in the construction industry.

The preparation and placing of superplasticized concrete in different environmental conditions, especially varying ambient temperatures, result in many problems caused by changes brought about in the cement-superplasticizer interaction and rate of hydration of cement. So, there is a necessity to adjust the composition of concrete to

incorporate these chemicals effectively to produce concrete with the desired performance.

There are different brands of cements available in the market, which have different characteristics within permissible ranges. Moreover, different families of superplasticizers are available, whose properties and actions are significantly different from each other. Hence, there is a distinct need for studying the influence of different characteristics of cement on the various families of commonly used superplasticizers.

The main aim of this study is to understand the influence of temperature and cement characteristics (i.e., fineness and SO_3 content of cement) on the cement-superplasticizer interaction and its effect on the properties of cement paste, mortar and concrete to give awareness to concrete users about the precautions to be taken care while using the concrete. The influence of ambient temperature, fineness of cement and SO_3 content of cement within the normal range is investigated with the aim of providing better cement superplasticizer combinations for the desired workability, slump retention, strength and durability.

1.2 OBJECTIVES AND SCOPE

The present thesis focuses on the study of some important factors that influence the cement-superplasticizer interaction, which in turn affect the fresh and hardened properties of the cement-based materials. The main objectives of the research are:

- To study the effect of temperature on the properties of fresh and hardened cement paste, mortar and concrete.
- To study the effect of fineness and SO_3 content of cement on the properties of cement paste, mortar and concrete.
- To understand the influence of temperature on the hydration process and microstructure development of superplasticized cement paste.

The scope of the study is limited to the following with respect to the main components and methods adopted:

- Study is limited to one brand of ordinary portland cement
- Study is limited to one commercial brand of superplasticizer from each of the families of superplasticizer available.
- The temperature range studied is from 5 to 40°C.

- The fineness of cement is varied from 270 to 360 m^2/kg.
- The SO_3 content of cement is varied from 1.70 to 2.53%.

1.3 STRUCTURE OF THE THESIS

The research strategy and the results obtained to achieve the objectives specified in the previous section are described in the following chapters of the thesis.

A review of the hydration of cement and the mechanism of action of superplasticizers is given in Chapter 2. The influence of superplasticizers on the hydration of cement is also discussed. The various factors affecting the cement-superplasticizer interaction are reviewed, and the need and motivation for conducting this study are emphasized in the same chapter.

Chapter 3 outlines the procedures for various tests conducted to study the influence of temperature, fineness of cement and SO_3 content of cement on various properties of cement paste, mortar and concrete. The sample preparation and procedure for various microstructure analyses are also presented.

The influence of temperature on the fluidity of cement paste is outlined in Chapter 4. The water demand and setting behaviour of cement paste with and without superplasticizers were studied using the Vicat apparatus. The influence of temperature on the setting time of superplasticized cement paste was also studied for various families of superplasticizers. The relative fluidity and loss in fluidity with time of cement paste were studied with the help of Marsh cone and mini-slump tests. In order to study the influence of superplasticizer dosage on the fluidity and loss in fluidity with time, various dosages (i.e., the dosages corresponding to the saturation point at each temperature, saturation point at 25°C for all temperatures and the dosage corresponding to the minimum flow at 25°C at all temperatures) were used. The saturation dosages of superplasticizer were determined from the Marsh cone test at various temperatures and compared for different superplasticizers.

Chapter 5 deals with the influence of temperature on the fresh and hardened properties of cement mortar and concrete. The fluidity of cement mortar was

evaluated using the flow table test, and the slump test was used for concrete. The compressive and flexural strengths were determined to assess the influence of temperature on the mechanical properties of superplasticized cement mortar, whereas the compressive and splitting tensile strengths were determined in concrete.

Chapter 6 deals with the influence of fineness and SO_3 content of cement on various properties of cement paste, mortar and concrete. The fresh properties of cement paste were characterised with the help of the Vicat penetration, Marsh cone and mini slump tests, whereas the fluidity of mortar was studied using the flow table test, and the slump test was employed for concrete. The superplasticizer demand for the concrete to produce 150 mm slump was determined to study the influence of fineness and SO_3 content of cement on the superplasticizer demand of concrete. The compressive strengths of mortar and concrete, and the flexural strength of mortar were also determined to study the influence of fineness and SO_3 content of cement on the mechanical properties.

The study of the effect of the temperature and superplasticizer on the hydration processes, as well as on the microstructure development, through characterization techniques like X-ray diffraction, scanning electron microscopy, and thermal methods are presented in Chapter 7. An attempt is made to provide an overall picture of the influence of temperature on the hydrated products, as well as their rate and amount of formation. The influence of superplasticizer on the microstructure development at various temperatures was studied using the PCE based superplasticizer.

The conclusions drawn from various tests conducted are summarised in Chapter 8. The scope for further research is also highlighted.

The five appendices at the end of the thesis give the individual test data for Marsh cone tests of pastes at different temperatures and for different cements, and the individual TGA and XRD data of hydrating cement paste made at different initial temperatures.

CHAPTER 2

LITERATURE SURVEY

2.1 INTRODUCTION

Modern concrete is not simply a mixture of cement, aggregate and water; it contains much more, often mineral admixtures, which give specific properties, and also chemical admixtures, which give even more specific effects. High performance concrete can be produced only by using admixtures, both mineral and chemical admixtures, which can affect the properties of concrete in the fresh and hardened state. According to ACI 116R (2000) an admixture is defined as 'a material other than water, aggregates, hydraulic cement and fibre reinforcement, used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing.

There are different types of chemical admixtures available in the market and their incorporation depends upon the application, for e.g., superplasticizers, air entraining admixtures, set accelerators, retarders, etc. Among the various chemical admixtures, superplasticizers have become essential components of high performance concrete due to their effectiveness and multifunctional use in concrete. They are added to concrete primarily to improve the workability at lower water to cement ratios, leading to better fluidity and compositional stability in the fresh stage. For the same workability, the water content can be reduced by the incorporation of the superplasticizer, which can result in an increase in strength. For the same workability and strength, the cement content of concrete can be reduced by the incorporation of the superplasticizer. Further, the lower water to cement ratio and better compaction of concrete with superplasticizer can lead to improved mechanical integrity and lower permeability of concrete in the hardened state. The performance of the superplasticizer in concrete depends on many factors like the nature and its chemical dosage, nature of cement and aggregates, amount and type of gypsum, water cement ratio and environmental conditions (Dodson and Hyden 1989; Chandra and Bjornstrom 2002). The interaction between the cement and admixtures is very complex and their compatibility decides the effectiveness of the admixtures in concrete. The properties of concrete, such as water demand, hydration kinetics, composition of the products, setting time, microstructure, strength, durability, etc. are influenced by the type and interaction between the cement and

admixture (Ramachandran 2002, Rixon and Mailvaganam 1999). Therefore, a proper understanding of the cement-superplasticizer interactions and the factors affecting those interactions are essential to make the concrete better.

In the present chapter, a review of the use of superplasticizers in concrete technology is reported, focussing on the mechanism of action and the various factors that influence the cement-superplasticizer interaction and its effect on the fresh, hardening and hardened states. A brief description of the cement chemistry and hydration reactions is incorporated in order to understand the interaction of superplasticizer and cement. A detailed review about the various families of superplasticizer, their mechanisms of action and the characteristics that influence the interactions is also given.

2.2 CEMENT CHEMISTRY

2.2.1 Cement Composition

Portland cements are multicomponent multiphase inorganic materials and consist of four major constituents whose amounts vary. The two silicate phases - tricalcium silicate (C_3S) and dicalcium silicate (C_2S) control the strength developments and the two aluminates - tricalcium aluminate (C_3A) and tetra calcium alumino ferrite (C_4AF) along with the sulphate phase (i.e., gypsum) influence the setting behaviour (Lea 1970, Hewlett 2004). In addition to the major compounds, there are minor compounds, such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O are also present in portland cement. The sodium and potassium oxides, generally known as alkalis, play an important role in the rheological behaviour and cement-superplasticizer interactions. Standards such as those of IS, ASTM, BIS and CEN give the acceptable ranges of components for various classes of cement. Typical composition of ordinary portland cement is given in Table 2.1.

Table 2.1 Typical portland cement composition

Type of compound	Composition (%)
C_3S and C_2S	70-80
C_3A	0-16
C_4AF	1-17
MgO	0.5 -6
Na_2SO_4, K_2SO_4	0.5-3
Free lime	0.2-4
Gypsum	4
Low alkali cement	< 0.6 $(Na_2O)_{eq}$

2.2.2 Hydration of Cement

All the cement compounds, viz., calcium silicates, calcium aluminates and calcium aluminoferrite undergo hydration; however, the rate of reaction and the heat of hydration vary and contribute to different characteristics of cement paste. For example, tricalcium silicate contributes to initial strength gain whereas dicalcium silicate contributes to the long term strength.

When water is added to cement, the tricalcium silicate reacts rapidly with water and the calcium (Ca^{2+}) and hydroxyl (OH^-) ions are released along with the liberation of large amount of heat. The pH of the aqueous solution rises to about 12 due to the dissolution of the hydroxyl ions. This initial hydrolysis slows down quickly resulting in a decrease in the heat evolved and then the reaction proceeds slowly with the production of calcium hydroxide until the system get saturated. Once this occurs, $Ca(OH)_2$ starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. The C-S-H crystals grow thicker on the surface, which makes it more difficult for the water molecules to reach the unhydrated tricalcium silicate, and the rate of hydration depends on the rate at which the water molecules diffuse through this coating. As the thickness of coating increases, the formation of C-S-H becomes slower and slower (Jolicoeur and Simard, 1998). The overall chemical reaction of the C_3S and the heat evolved (ΔH) are given in the following equation.

$$2C_3S+6H \Rightarrow C_3S_2H_3+ 3\,CH \quad (\Delta H = -\,520\ kJ/kg) \qquad (2.1)$$

The reaction of dicalcium silicate with water is similar to that of tricalcium silicate; however, the rate of hydration is much slower. The reaction and heat of hydration is as shown below:

$$2C_2S+4H \Rightarrow C_3S_2H_3+ CH \quad (\Delta H = -\,260\ kJ/kg) \qquad (2.2)$$

The tricalcium aluminate (C_3A) hydrates in the presence of gypsum and the reaction is as follows (Fernon 1997):

$$2\,C_3A+ H+ CS \Rightarrow C_6AS_3\,H_{32}+ 3CH \quad (\Delta H = -\,910\ kJ/kg) \qquad (2.3)$$

Ettringite (AFt) or calcium aluminate hydrates are needle like structures and covers the surface of the hydrating tricalcium acuminate particles and delay or prevent further hydration. The rate and extent of this reaction depend on the presence of sulphates in the system. If the supply of sulphate from gypsum is exhausted before the complete hydration of C_3A, instead of ettringite, calcium monosulphoaluminate (AFm) can be formed. If the availability of gypsum is less than that required for the rate of reaction of gypsum and sulphate ions, the formation of monosulphoaluminate can take place before the formation of ettringite. Again, if monosulphoaluminate is exposed subsequently to sulphate ions, this will lead to the formation of more ettringite.

Calcium aluminoferrite also reacts to form the same hydration products as that of C_3A. However, the rate of reaction is slower, which is further decreased by gypsum and higher iron oxide. The reaction is as given by the following equation:

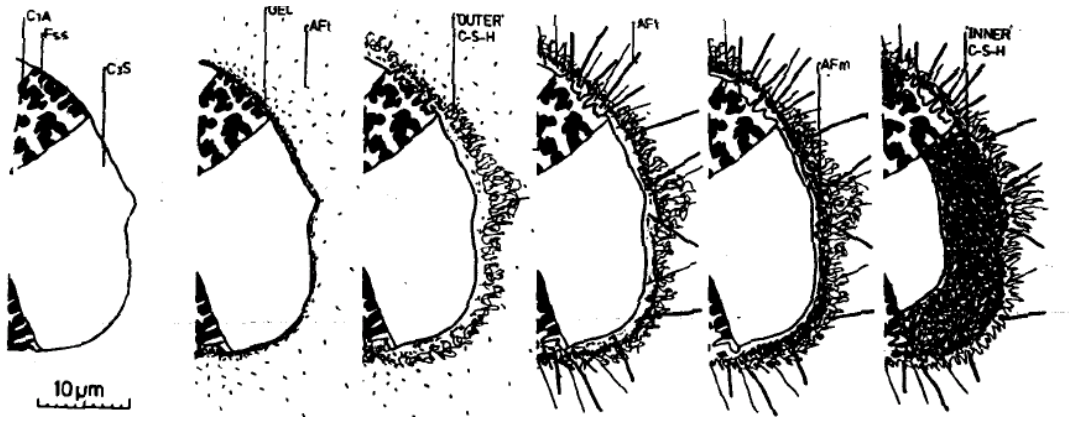
$$C_4AF + CS\,H_2 + 12H \Rightarrow C_4(A, F)\,CSH_{12} \quad (\Delta H = -420\ kJ/kg) \qquad (2.4)$$

The relative reactivity of different mineral phases with water can be given as $C_3A > C_3S > C_2S > C_4AF$. The aluminate phases and its hydration products play an important role in the early hydration processes and cement-admixture interactions.

2.2.3 Hydration of the Portland Cement Grain

Various reactions occur immediately after the first contact of water with the cement. The hydration process of cement can be divided into several stages corresponding to different chemical activities (Jolicoeur and Simard 1998). The microstructure development of a typical polymineralic cement grain is shown in Figure 2.1 from Taylor (1997). The unhydrated compounds are shown in Figure 2.1 (a). When the cement is in contact with water, the hydration reactions are initiated with a typical heat evolution pattern, which will vary with time. The heat evolution pattern can be divided into four different stages during the early hydration process: initial hydration period, dormant period, acceleration and deceleration period. The presence of admixtures will influence these mechanisms, especially those which occur during the early hydration period (Mehta and Monteiro, 2005; Jolicoeur and Simard, 1998; Taylor, 1997; Neville, 2000; Hewlett, 2004, Jayasree and Gettu 2010) as described below.

Initial hydration (0-15 minutes): During the initial hydration period, rapid heat generation takes place after addition of water to cement and is called the heat of wetting. Dissolution of the easily soluble components, like alkalis, calcium, sulphate phases and free lime, and the solubilization of variety of ionic species, like Na^+, K^+, Ca^{2+}, SO_4^{2-}, and OH^- ions, also take place during this stage. An amorphous gel layer of a colloidal product, rich in alumina and silica is formed over the cement grains during this stage due to the wetting and the subsequent dissolution of ions. Beyond the solubilization process, the nucleation process also starts at this stage, which leads to the formation of solid hydration product. The initial nucleation process involves the formation of calcium sulphoaluminate or ettringite from Ca^{2+}, $SO_4^{2-}$and $Al(OH)_4^-$ ions on the outer surface of layer of gel, as shown in Figure 2.1 (b). This initial nucleation is of great importance as far the rheology of the cement paste is concerned. The presence of more dissolved alkalis may increase the rate of initial dissolution of C_3A (Spiratos et al., 2003). On progressing, the cement grains are surrounded by a layer of hydration products. Due to this the rate of reaction reduces sharply, leading to lower heat of hydration. The presence of organic admixtures will affect the rate of crystallization and the growth leads to the change in hydration and hydration products. After the initial period, the chemical admixtures interact with these hydration products, instead of the hydrating compounds.



(a) (b) (c) (d) (e) (f)

Fig. 2.1 Microstructure of hydrated portland cement (Taylor, 1997)

Dormant period (2-4 hours): The reactions become slow and as a consequence the heat generation is also decreased. During this stage, the mix remains plastic and is called the dormant stage. The main mechanisms behind this are the formation of a diffusion barrier due

to the gel formation around the cement particle and the formation of the SiO_2 rich electrical double layer around C_3S. Again, the supersaturation of Ca^{2+}, OH^- and SO_4^{2-} in solution prevents further dissolution of ions. As the thickness increases, penetration of water through the coating becomes difficult, which results in the decrease in reactions, and the process becomes diffusion controlled. The growth of ettringite crystals takes place if there is an adequate concentration of SO_4^{2-} ions. If the concentration of SO_4^{2-} ions is inadequate, it will lead to the formation of calcium aluminate hydrate (C-A-H), which will result in flash set. Simultaneously, the reaction of C_3S produces the 'outer product' C-S-H, leaving space between the grain and hydrated shell, as shown in Figure 2.1 (c). If the SO_4^{2-} concentration is too high, due to the presence of hemihydrates and alkali sulphates, massive nucleation and growth of gypsum crystals (false set) occurs.

Acceleration period (4-8 hrs): After some time, the dormant period ends and the acceleration period starts. The reasons could be the weakening of the double layer by further hydration, increased diffusion and weakening of ionic strength around the hydrating particle etc. These mechanisms result in the end of the dormant period and the beginning of a new stage of high chemical activity, called the acceleration period. At this stage the paste loses its plasticity. The AFt is produced at this stage as a result of the secondary hydration of C_3A, and the hydration of C_3S results in the formation of the 'inner product' C-S-H and precipitation of C-H, as shown in Figure 2.1 (d). Later, C_2S and C_4AF continue to hydrate.

Deceleration period (8-24 hours): The reactions are slow after the acceleration period. They become diffusion dependent at this stage and hardening of the paste also takes place. Hexagonal plates of monosulphate (AFm) can be formed at this stage due to the reaction of C_3A with the AFt in the presence of the sulphate ion in the pore solution, as shown in Figure 2.1 (e). More hydration products form with the decrease in pore volume and free water content as the hydration progress. Finally, a steady state will reach (12-24 hours) in which temperature has little influence on hydration. Later hydration results in the formation of sufficient 'inner' C-S-H to fill the space between grain and shell, as shown in Figure 2.1 (f). The outer C-S-H becomes more fibrous during this period and the ettringite is completely converted to monosulphoaluminate within 1 to 3 days.

2.3 WATER REDUCERS AND SUPERPLASTICIZERS

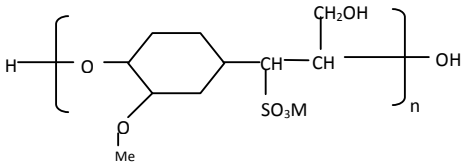
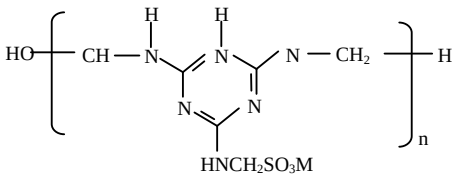
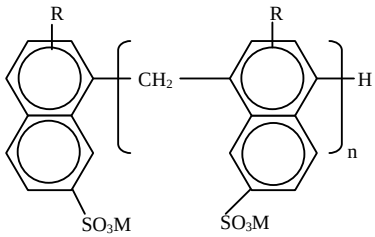
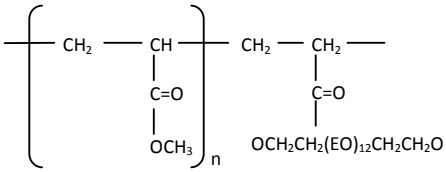
Water reducers or plasticizers are added to concrete to increase the workability with same water content or to decrease the water content for the same workability, so that better integrity and mechanical properties can be achieved. After the introduction of the first generation of superplasticizers in 1960s, these admixtures have become essential components of modern concrete.

Water reducers are classified as normal, medium and high range depending upon their ability to decrease the water content. Water reducers belong to the dispersant family; dispersants are long chain organic molecules having a polar hydrophilic end and non-polar hydrophobic groups that are adsorbed on the cement particles. These admixtures are synthetic high molecular weight water-soluble polymers that are effective in dispersing flocculated cement grains. Solubility is achieved by the presence of adequate hydroxyl, sulphonate or carboxylate groups attached to the main organic unit, which is usually anionic (Rixom and Mailvaganam, 1999; Ramachandran, 2002; Bentur, 2002).

2.3.1 Characteristics and Chemistry of Superplasticizers

Superplasticizers are high range water reducers. There are mainly four different families of superplasticizer available in the market: modified lignosulphonates (LS), sulphonated naphthalene formaldehyde (SNF), sulphonated melamine formaldehyde condensates (SMF), and the new generation of superplasticizers, which is made up of copolymers that include polycarboxylates (PCE), polyphosphonates, polyacrylates and monovinyl alcohols (Rixom and Mailvaganam, 1999; Ramachandran, 2002). The different families are based on the type of chemical and the origin and structures are presented in Table 2.3.

Table 2.2 Chemical structure of superplasticizers (Rixom and Mailvaganam, 1999)

Class	Origin	Structure (typical repeated unit)
Lignosulphonates (LS)	Derived from neutralization, precipitation, and fermentation processes of the waste liquor obtained during production of paper-making pulp from wood	 Me =CH_3 , M =Na
Sulphonated melamine formaldehyde (SMF)	Manufactured by normal resinification of melamine - formaldehyde	 M = Na
Sulphonated naphthalene formaldehyde (SNF)	Produced from naphthalene by oleum or SO_3 sulphonation; subsequent reaction with formaldehyde leads to polymerization	 R =H,CH_3, M
Polycarboxylic ether (PCE)	Free radical mechanism using peroxide initiators is used for polymerization process in these systems	 EO: Ethylene oxide

The lignosulphonate based admixtures are called normal range water reducers. At higher dosages, these admixtures can cause excessive retardation of setting and entrainment of air, which limits their dosage in practice (Ramachandran, 2002). In modified lignosulphonates, the sugar content is reduced, and hence the retardation is reduced (Aïtcin, 1998). Again, at

higher molecular weights, these admixtures can be considered as superplasticizers, though some retardation of the initial set will be there (Ramachandran, 2002). Again, the solubility of the product also affects the plasticizing efficiency and the sodium lignosulphonate is considered as a better superplasticizer compared to calcium lignosulphonate as the solubility of former is higher.

Salts of SNF and SMF are considered as superplasticizers. The use of these admixtures result in a significant water reduction at low dosages. They are ionic organic polymers with sulphonated groups. The sulphonic acids are neutralised by sodium or calcium counter-ions (Aitcin 1998). The SNF based superplasticizers appear to yield the best fluidizing effect in the molecular weight range of 4000-40000 gm/mole, while at higher ranges the effect decreases (Ramachandran, 2002). Generally the SNF based superplasticizer has good slump retention compared to the SMF based superplasticizer. Due to the poor slump retention characteristics, the SMF based superplasticizers are not commonly used in site construction.

The developments in the areas of superplasticizer during the past few years has resulted in the introduction of several polymeric surfactants with carboxyl, hydroxyl and phosphonate functional groups in the market as third generation superplasticizers, and are generically known as polycarboxylates (PCE). These are comb polymers with long chains and side chains, having hydrophobic and hydrophilic groups. The hydrophobic groups attach to cement particles and hydrophilic groups are in contact with water (Tanaka et al., 1999; Sakai et al., 2003). Various functional groups can be grafted to the backbone main chains (Ramachandran et al. 1998). The efficiency of these superplasticizers depends on the length of the main chain, and the length and number of side chains. Generally the PCE based superplasticizer shows lower superplasticizer dosage compared to first and second generation of superplasticizers. Moreover, unlike SNF, SMF or LS, PCEs could be tailor-made according to applications by altering the structure (Winnefeld et al., 2007; Magarotto et al., 2003; Houst et al., 2005; Falikman et al., 2005). Nawa et al. (2000) observed that increasing the length of graft chains and/or adsorption enhances the steric repulsion, resulting in good fluidity of paste initially; however, the influence of temperature on paste flow and flow loss of cement paste decreases with increasing length of polyethylene oxide graft chains. It is important to know that the water reducer effect and workability retention are conflicting properties; a good water reducer is a poor slump retainer, and vice versa. This means that

PCEs for ready mixed concrete are designed to have a good balance between initial fluidity and workability retention. On the other hand, PCEs for the pre-cast industry are designed for their maximum water-reducer effect and, consequently, have poor workability retention.

For polycarboxylate based superplasticizers, Uchikawa et al. (1995) showed that the delay of setting by the addition of admixture is due to the inhibition of the dissolution of calcium because of the formation of adsorbed layer of admixture on the surface of cement particles, and the retardation of the hydration of alite because of the fixation of the calcium ions dissolved in aqueous solution as a chelate complex, which binds with the carboxyl and hydroxyl group of molecule of admixture, and thereby decreases the lime saturation ratio. Jolicoeur and Simard (1998), and Zhang et al. (2010) suggested, for the SNF based superplasticizer, that the retardation was mainly due to the adsorption of admixtures on nucleating hydrate particles and intercalation into hydrate phases already formed such as ettringite, which inhibit the development of hydration products. Jayasree and Gettu (2010) observed higher retardation of setting time for the PCE based superplasticizer and correlated that to the higher concentration of the ionic functional groups in the aqueous phase or due to shorter backbone chain length in the PCE, which delays the cement paste setting. It is also reported that with direct addition of superplasticizer to obtain highly workable concrete, initial and final setting times are invariably increased in the order SMF <SNF < polyacrylates (Rixom and Mailvaganam 1999).

2.3.2 Mechanisms of Action of Superplasticizers

The interaction of the cement-water-superplasticizer system is complicated and the introduction of new generation superplasticizers further makes the interpretation of the mechanisms more complex. The major forces that govern the rheology of the cement paste are the van der Waal's attractive forces between the cement particles and the electrostatic repulsion of the cement particles due to the surface charges. If the former force is larger than the other, the cement particles tend to agglomerate. The aim of addition of superplasticizer is to prevent this agglomeration and disperse the cement particles effectively within the paste. The mechanism of action of superplasticizer with cement can be generally classified into two groups:

1) Physical interaction: the superplasticizer molecules adsorb on the cement particles and hinder the flocculation of cement particles due to electrostatic repulsion (i.e., lowering of the zeta potential) and/or through steric hindrance. As a result of this, the cement particles are more homogeneously distributed in the aqueous solution, minimising the requirement of mixing water and improving fluidity/workability of the concrete.

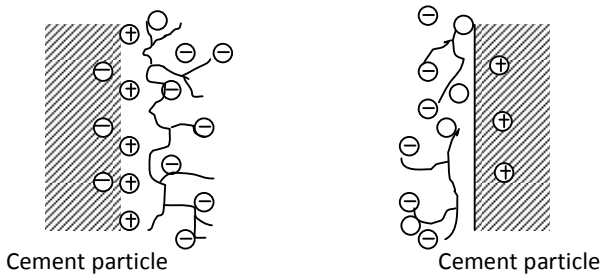
2) Chemical interaction: this includes the chemical absorption of the superplasticizer on the cement particles, its interaction with more reactive sites of the cement, formation of complex ions with Ca^{2+}, etc. This can affect the morphology of the hydrates.

The interaction of the superplasticizer in the cement paste can be of three components (Flatt and Houst, 2001; Banfill, 2003; Yamada et al. 2006; Jayasree et al. 2010). The first part is the absorption of superplasticizer by intercalation (incorporation of molecules of superplasticizer into the precipitates formed as the cement hydrates), co-precipitation (the process of precipitation of tiny solid nuclei of the superplasticizer along with the precipitation of the cement hydrates) or micellization (groups of polymer molecules are trapped within the hydrating cement making them unavailable for active dispersion), leading to the formation of an organo-mineral phase (Banfill, 2003). These phenomena that occur during the formation of ettringite and C-S-H decrease the amount of admixture available for dispersing the flocs of cement later on. A cement-admixture combination with a high degree of absorption will yield less fluidity for the same superplasticizer dosage. However, the consumption of the superplasticizer by absorption is generally small, especially if a delayed addition procedure is employed (Banfill, 2003).

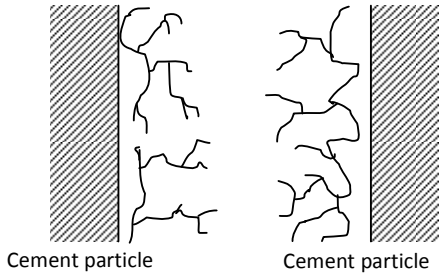
Another portion of the superplasticizer will be adsorbed on the surface of cement leading to the formation of an electrical double layer and that will lead to electrostatic repulsion (Uchikawa et al., 1997; Young, 2008). The term superplasticizer adsorption generally refers to the amount of superplasticizer by which the pore water is depleted. The superplasticizer molecules, having charged groups (SO_3^-, COO^-), adsorb on the surface of the cement particles and will give negative charges to the mineralogical phases of the cement (see Figure 2.2a), which results in the electrostatic repulsive forces (Aïtcin, 1998; Rixom and Mailvaganam, 1999; Yoshioka et al., 2002). This theory is further modified by Mollah et al. (1995), who observed that cement particles are covered by a layer of Ca^{2+} ions resulting in a trilayer of a

“diffuse ion swarm”, which delays the hydration reactions. This repulsion leads to the release of the water trapped in between the flocs to be available for the fluidity. This mechanism of action is observed in the cases of lignosulphonates, melamines and naphthalenes. The electrostatic repulsion depends on the composition of the solution and the adsorption of the superplasticizer, i.e., the greater the adsorption, the better the fluidity (Nakajima and Yamada, 2004). Flocculation of the cement particles occurs as the electrostatic potential diminishes, leading to the loss in fluidity of the paste. The zeta potential represents the measure of the electrostatic repulsion between the cement particles. The ionic nature of the superplasticizer leads to a higher zeta potential and results in strong adsorption (Houst et al., 1999). The zeta potential of the various phases of the cement are different and that will lead to preferential adsorption of the superplasticizers on some phases such as C_3A (Yoshioka et al., 2002). When the water is added to the cement, the initial hydration products form, and the zeta potentials of these early hydration products can be different and can influence the superplasticizer adsorption (Plank and Hirsch, 2007). It is found that the zeta potential of ettringite is more positive than that of calcium monosulphate (Plank and Hirsch, 2007), which leads to the increased adsorption of superplasticizer on the ettringite. However, in addition to the zeta potential, the adsorption of superplasticizer depends upon the type and morphology of the hydration products. It is also reported that the amount of superplasticizer adsorbed on monosulphate is higher than that of the ettringite (though the zeta potential of the latter is higher), may be due to the higher surface area of the former (Jolicoeur and Simard 1998; Ramachandran 2002).

In polycarboxylates, in addition to the electrostatic repulsive forces, the side chain molecules cause steric hindrance between the cement particles, which leads to deflocculation and dispersion (Rixom and Mailvaganam, 1999; Corradi et al., 2005; Collepardi, 2005) (see Figure 2.2b). The steric hindrance offered by the comb-like nature of the side chains and the efficiency of steric repulsion depends on the length of the main chain, and the length and number of side chains (Yamada et al., 2001; Sugiyama et al., 2003). The steric hindrance mechanism lasts for longer time compared to electrostatic repulsion and hence gives better performance.



(a) Electrostatic repulsion



(b) Steric hindrance

Fig. 2.2 Physical action of superplasticizers (Aïtcin, 1998)

The fluidity of cement paste depends on the amount of superplasticizer adsorbed on the cement grains. The optimal fluidity will be reached when the adsorption of the superplasticizer on the surface of the cement grains is maximum (Houst et al., 1999a; Roncero, 2000; Griesser, 2002) and depends on the composition and properties of the cement, and the type and nature of the superplasticizer. It should be noted that the fluidity will be better initially if the adsorption of superplasticizer is higher; however, it may not be possible to maintain the fluidity for sufficient time (Nkinamubanzi et al., 2000; Li et al., 2003; Corradi et al., 2005). Hence in such cases, a higher dosage of superplasticizer will be required to maintain the fluidity for the required time. The remaining superplasticizer, which is non-adsorbed, may be adsorbed subsequently on the cement particles and the newly formed hydrates, and maintains the dispersion of cement particles for more time, leading to better fluidity retention. The unadsorbed superplasticizer molecules also help the dispersion of cement particles by reducing the surface tension of mixing water, aiding in the decrease of the frictional resistance owing to the lining-up of linear polymers along the flow direction, and the lubrication produced by the low molecular weight polymers between the particles (Uchikawa et al., 1995; Tanaka et al., 1999).

In addition to the physical effects of adsorption, the superplasticizer can chemically react with cement grains, especially at the most reactive sites of cement particle surface (Jolicoeur and Simard, 1998). For example, polynaphthalene sulphonate reacts with C_3A in competition with SO_4^{2-} ions. It was also found that many organic admixtures delay the precipitation of the hydrated products as they solubilise the ionic species and associate or form a complex with them. Again, the crystal nucleation is inhibited by the presence of the organic admixture and leads to the slower formation of the hydration products, which change its morphology. The strong adsorption of the superplasticizer on the cement grain affects the surface charge, leading to an immediate deactivating effect on the C_3A, which results in fluidifying the cement paste (Gaidis and Gartner 1991).

For the PCE based superplasticizer, the ingress of non-adsorbed low molecular weight superplasticizer molecules between the cement grains causes additional dispersion due to volume repulsion (depletion effect) whereas the higher molecular weight polymers that cannot ingress between the cement particles coagulate (depletion coagulating effect) to improve the segregation resistance (Tanaka et al. 1999). Even the higher molecular weight fractions may not be completely adsorbed on the cement surface beyond a certain critical concentration (called as the critical micelle concentration for surfactants; Porter, 1994) giving rise to the effects given above.

The superplasticizer may incorporate air bubbles in concrete, which can also contribute to the fluidification; however, the strength and durability can reduce if the air content is high. The amount of air entrainment depends upon the type of the admixture used (Rixom and Mailvaganam, 1999; Ramachandran, 2002). Lignosulphonates incorporate significant amounts of air, which limits their dosage in concrete, in addition to other reasons already discussed earlier. The SNF and polycarboxylates can also incorporate air in the concrete due to which deairing agents are sometimes added to the commercial product. The SMF based superplasticizer usually does not incorporate significant amount of air. The entrained air can be removed while vibrating if the workability is high.

2.4 CEMENT-SUPERPLASTICIZER INTERACTION

Superplasticizers are introduced to cementitious system to improve the rheological properties. In addition to provide good workability initially, the superplasticizer has a strong influence on the kinetics and setting characteristics of the hydrating cement systems. However, if the dosages are beyond a critical superplasticizer concentration, the solid particles start to sediment due to the absence of yield stress (Flatt and Houst, 2001). Again the flow properties of cement paste can change significantly with time (Jayasree and Gettu, 2008), which can be attributed to the hydration, intercalation of superplasticizer, chemical degradation of the superplasticizer at high pH of the aqueous solution and the physical relaxation or change in molecular structure due to adsorption. It is observed that the rheological parameters change with time, and the increase in the yield stress is more pronounced than that of plastic viscosity (Jayasree and Gettu, 2008). It is also observed that the rate of increase is more significant at superplasticizer dosages less than the saturation dosage. Petit et al. (2010) attributed the change in changein rheological properties with time of cement based materials to the restructuring of microstructure, cement hydration, variation in free water content with temperature, water evapouration, and interaction between binder and admixture. The fluidity of cement paste is governed by many factors such as the dispersion characteristics between particles due to the mixing technique, type and dosage of superplasticizer, type and amount of hydration products, particle size distribution, etc. Hence, it is complicated and difficult to predict the major factors and interactions existing between the different components in a superplasticized cement paste. The cement superplasticizer interactions can be divided into two - the physical and chemical effects (Jolicoeur and Simard, 1998; Jolicoeur et al., 1994). The physical effects occur immediately after adding water to the cement and include superplasticizer adsorption through the electrostatic and van der walls forces, surface charging, induction of electrostatic repulsive forces and the repulsive forces. The chemical effects are due to the cement hydration and comprise surface binding to reactive sites, alteration of early hydration and hydration products.

2.4.1 Cement-superplasticizer Compatibility

A cement and superplasticizer combination that has a high degree of workability without any sign of segregation and bleeding is said to be compatible and this property of the cement-superplasticizer combination can be referred as compatibility. The term incompatibility refers to the adverse effect on the performance when a specific combination of cement and

superplasticizer is used. The incompatibility issues in turn can affect the hardened properties of concrete, primarily strength and durability. Even though there are lots of studies on the cement-superplasticizer interaction, still there exist problems between cement and chemical admixtures or these interactions are still not clear. Some superplasticizers will work with some cements and may not work with some other cements. Again, some cement-superplasticizer combinations show good compatibility at some climatic conditions and show problems in some other environmental conditions. The incompatibility problems like rapid set, retardation, rapid slump loss, segregation of concrete, entrainment of air, temperature evolution, improper strength gain, etc., can affect the fresh and hardened properties of concrete. The type and extent of interaction between cement and superplasticizer may influence the physio-chemical and mechanical properties of concrete, such as water demand, hydration kinetics, composition of the products, setting times, microstructure, strength, and durability.

2.4.2 Factors Affecting the Cement-Superplasticizer Interaction

The cement-superplasticizer interaction involves a complex blend of physical and chemical interactions and which makes it complicate to develop simple solutions to field oriented issues (Jayasree et al., 2011a). The cement-superplasticizer interactions have many dimensions. On one hand, there is the influence of the type of superplasticizer, and on the other end, the effects of the composition and relative proportioning of the ingredients of cement. In addition, the type and amount of gypsum incorporated in the cement (gypsum, hemihydrate or anhydrite) have an important role to play as sufficient amount of soluble sulphate and calcium ions should be available in the solution to form calcium aluminosulphate (ettringite). The physical properties of cement, like fineness, the environmental conditions, the rate and time of addition of superplasticizer, etc., can also influence the performance of the superplasticizer in the cementitious system. Again, the type and number of superplasticizers available in the market have been increasing day by day claiming different additional advantages. The high performance concretes, like self compacting concrete, use high dosages of superplasticizer, which makes the scenario more complicated. It is, therefore, necessary to understand the factors governing the interactions and the reasons for incompatibilities. The various factors that affect the cement-superplasticizer interactions are discussed in detail in the following sections.

2.4.2.1 Effect of Chemical Structure of Superplasticizer

For the lignosulphonates, excessive air entrainment can happen due to the presence of a low molecular fraction, which can lead to reduction in strength (Mollah et al., 1995; Rixom and Mailvaganam, 1999). In addition, excessive retardation can also happen due the presence of high sugar content, especially at high dosages. The type of salt can affect the performance of the superplasticizer, the sodium lignosulphonate is better compared to calcium lignosulphonate in terms of the plasticizing effect (Ramachandran, 2002). The lignosulphonates can form a complex with Ca^{2+}, which can cause a decrease in the Ca^{2+} concentration in the solution and lead to retardation by delaying the alite hydration. The lignosulphonates can be modified by removing the sugar by fermentation and removing the low molecular fraction by centrifuging to make them more effective.

The type and dosage of superplasticizer, degree of polymerization, degree of sulphonation, the position of functional group, the molecular weight distribution of the polymer, etc. can influence the interaction with cement, especially for the SNF and SMF based superplasticizer. It is seen that the superplasticizer with lowest molecular weight adsorbs more and the one which adsorbs least gives a higher zeta potential (Andersen et al., 1987). For SNF, the fluidity increases with a reduction in monomer content and with an increase in molecular weight; however, the increase in molecular weight leads to more retardation at an early age (Basile et al., 1989; Bonen and Sarkar, 1995). The alkali content also has a significant influence on the rheology and the influence of molecular weight of the SNF based superplasticizer (Rixom and Mailvaganam, 1999). For high alkali cement, SNF with higher molecular weight (e.g., 16000 g/mol) gives better fluidity in cement paste due to the higher surface charge provided by the larger molecules, leading to higher adsorption (Kim et al., 1999; Kim and Aïtcin, 2003; Page et al., 1999). In the case of low alkali cement, an SNF with lower molecular weight results in an increase in the induction period, probably due to lower adsorption, whereas the high molecular weight does not retard the setting significantly (Rixom and Mailvaganam, 1999). Again, the location of the sulphonate ($-HSO_3$) group in the naphthalene structure is also important in the effectiveness of SNF based superplasticizer; the β-position leads to better electrostatic repulsion (Aïtcin, 1998).

The action of SMF and SNF based superplasticizers are similar. However, the SMF based superplasticizer has more affinity to adsorb on C_3A than C_4AF and C_3S (Ramachandran et al.,

1998). The SMF based superplasticizers are more susceptible to temperature and the stability of SMF appears to vary with the temperature and could be the reason why it is not widely used, especially in countries with warmer climates. It is reported that the shelf life of SMF is 1.5 yrs if stored at 20°C, whereas only 5-7 months when it is stored at 40°C (Torresan and Khurana, 1998). This can be due to condensation at higher temperature and consequent increase in viscosity.

PCE based superplasticizers have a main chain and side chains are attached to them. The backbone chain consists of acrylic or methacrylic copolymers and various functional groups (polar or ionic, carboxyl or hydroxyl groups) can be grafted on the backbone chain as side chains. High molecular weight (1400-88000 gm/mole) can be obtained with sizes of upto 30-150 nm can be made for the PCE based superplasticizers (Uchikawa et al., 1997). The flexibility in the variations of the type and length of the main and side chains leads to the formation of wide range of products with very different properties with the PCE based superplasticizer (Yamada et al., 2000; Sakai et al., 2003; Sugiyama et al., 2003; Houst et al., 2005). The molecular structure will affect the adsorption of superplasticizer on the cement particles and consequently the fluidity as well as its retention (Uchikawa et al., 1997; Sugiyama et al., 2003; Yamada and Hanehara, 2003). Higher molecular weight and reduction in lower molecular weight fractions leads to better fluidity of cement paste (Magarotto et al., 2003). Winnefeld et al. (2007) suggested that higher fluidity can be achieved by lower side chain densities and shorter side chains, whereas the longer side chains will reduce the retardation. It was also suggested that higher the charge density, higher is the adsorption and the initial fluidity. For PCE-based superplasticizers, the charge density is higher when more free carboxylic groups are present (Winnefeld et al., 2007). The adsorption of PCE based superplasticizer on the cement particles depends on the dosage of superplasticizer and the amount of superplasticizer available in the solution. If the dosages are low all the fractions will be adsorbed, whereas beyond a certain dosage, the superplasticizer with larger molecular weight will be preferentially adsorbed (Flatt et al., 1998; Winnefeld et al., 2007). This leads to variation in the effectiveness of different products as they could have fractions with varying molecular weight (Flatt et al., 1998). The adsorption of the PCE based superplasticizer with short side chains is mainly instigated by the electrostatic attraction and a release of enthalpy, whereas PCEs with long side chains adsorb due to a huge gain in entropy (Plank et al., 2010). The molecular structure, the anionic charge density, molecular weight

and the type of anchor group present in a superplasticizer governs whether the enthalpy or entropy is the dominant force for the adsorption of the superplasticizer.

Compared to SMF and SNF, the adsorption of the PCE-based superplasticizer is less due to its lower charge density (Houst et al., 2005; Plank and Hirsch, 2007). This is attributed to the fact that the functional groups of the PCE type superplasticizers are weaker acids compared to sulphonate groups in SMF and SNF, and therefore, PCE type superplasticizers are weaker electrolytes and show a lower electronic activity. Corradi et al. (2005) have used the concept of combining different polymers with different rates of adsorption in the development of new PCE-based superplasticizers that are supposed to have both water reduction and flow retention properties. This is attributed to the addition of a new functional monomer that has a lower adsorption rate than the more conventional component.

2.4.2.2 Effect of Calcium Sulphate

Sufficient amount of soluble sulphate and calcium ions should be present in cement paste for normal set to occur and this is ensured by the addition of gypsum to the portland cement. Gypsum and anhydrite (i.e., anhydrous) calcium sulphate are available naturally or as a by-product of the acid based manufacture of fertilizers from phosphate ore. However, the use of synthetic gypsum in cement production can cause an increase in setting time due to the presence of water soluble fluorine and phosphates in the crystal lattice of gypsum (Hewlett, 2004). The SO_3 content of cement can vary by adding either gypsum or a mixture of gypsum and anhydrite; however, when the amount of anhydrite is high, the solubility of sulphate ions is drastically decreased in the presence of lignosulphonates (Aitcin 2000).

The amount and type of gypsum is important from the compatibility point of view. If the gypsum is replaced by natural anhydrite, problems like rapid set and accelerated slump loss can occur with superplasticizers having sulphonate functional groups and polycarboxylates, especially at low water to cement ratios (Dodson and Hayden, 1989; Jiang et al., 1999; Rixon and Mailvaganam, 1999; Nkinamubanzi and Aïtcin, 2004). This can be due to the slower rate of dissolution of natural anhydrite compared to gypsum and the adsorption of the superplasticizer on the surface of the anhydrite, thus reducing the availability of sulphates (Jolicoeur and Simard, 1998; Hanna et al., 2000; Ramachandran, 2002). If the availability of soluble sulphate ions in the aqueous solution is less than that needed by the C_3A, stiffening of

the cement paste can happen due to accelerated setting due to the formation of monosulphate, which can be converted to ettringite later (Jolicoeur and Simard, 1998). These incompatibility problems are not expected to occur when hemihydrate or soluble anhydrite or gypsum is used, as the solubility rates are not affected significantly by the superplasticizer (Dodson and Hayden, 1989). As adsorption of the superplasticizer on the C_3A and AFm is much more than on ettringite, in competition with the SO_4^{2-} ions, a good amount of superplasticizer will not be available in the solution for providing fluidity to the cement paste, which results in the loss of fluidity or an increase in the superplasticizer demand (Jolicoeur and Simard, 1998; Ramachandran, 2002). It was also reported that excess dissolved calcium sulphate can lead to rapid slump loss due to the alteration of hydration process, i.e., the formation of ettringite is inhibited (Fernon et al., 1997).

2.4.2.3 Effect of Soluble Alkalis

The alkali compounds have a significant role in the adsorption of superplasticizer on the cement particles and the interaction between cement and superplasticizer. It should be noted that the soluble alkali content may not be necessarily related with total alkali content. It is already been pointed out that the adsorption of SNF-based superplasticizer will be more for the cements with low soluble alkali content and will lead to more loss in fluidity as the available superplasticizer in the solution will be less (Dodson and Hayden, 1989; Nkinamubanzi et al., 2000). If the sulphate content is low, the superplasticizer will act as sulphite ion providers and interact with C_3A instead of dispersing it. Therefore, cements with high alkali content are expected to provide better workability retention and robustness, when used along with SNF-based superplasticizer (Nkinamubanzi and Aïtcin, 2004). It has been observed that the solubility of sulphate increases at higher alkali content in the aqueous solution, which decreases the loss in fluidity with SNF-based superplasticizer as the initial adsorption of superplasticizer is lower (Dodson and Hayden, 1989; Chandra and Bjornstrom, 2002). Soluble alkalis, such as Na_2SO_4, can be added to overcome the problem of poorer performance of the low alkali cement-SNF combinations (Jiang et al., 1999; Li et al., 2003; Spiratos et al., 2003). However, the addition of sodium sulphate can cause incompatibility problem with some polysulphonates, as it alters the formation of the ettringite (Li et al., 2003). For the PCE, the excess of alkali sulphates decreases the fluidity due to the shrinking of the side chains, which will affect the steric hindrance negatively (Hanehara and Yamada, 1999). The high alkali oxide content (Na_2O + K_2O >0.75%) of cement can lead to

efflorescence problems when used in conjunction with naphthalene and melamine based superplasticizers (Akman and Cavdar, 1999). According to Nkinamubanzi and Aïtcin (2004), the polycarboxylate based superplasticizer is less sensitive to the alkali and soluble sulphate contents of the cement than sulphonated superplasticizers, such as lignosulphonates and SNF.

2.4.2.4 Effect of C_3A

The C_3A phase of the cement has the most importance in the rheology of the cement paste as the zeta potential and reactivity of C_3A are high compared to other cement compounds of cement. The C_3A content or more specifically SO_3/C_3A ratio and the reactivity of C_3A can affect the early hydration and fluidity of cement paste as they can influence the adsorption of the superplasticizer on the surface of cement particles (Aïtcin et al., 2001). The availability of the sulphate ions in the solution is determined by the reactivity of calcium sulphate and its consumption is influenced by the reactivity of the C_3A. The amount of soluble sulphates and the reactivity of C_3A influences the hydration reactions of the aluminate phases and determines the setting behaviour, i.e., whether the setting of cement paste is normal, quick, flash or false set (Mehta and Monteiro, 2005; Spiratos, et al., 2003). The influence of superplasticizer on the C_3A hydration depends on the type and nature of superplasticizer. The adsorption of SNF and SMF based superplasticizers leads to the retardation of C_3A hydration and delays the conversion of ettringite to monosulphonate. Again, the morphology of the hydration products can also be affected as the SNF can form an organo-mineral compound with C_3A. The molecular weight of SNF will also affect the hydration; high molecular weight leads to lower retardation compared to a lower molecular weight. The form of C_3A will also affect the interaction of cement with PCE-based superplasticizer, the orthorhombic form being more reactive than cubic form. A high cubic C_3A content results in less flow retention as the PCE will be adsorbed first on the C_3A surface and the ettringite will be formed later, and will be covered by the hydration products later (Magarotto et al., 2003).

For low C_3A cement, the superplasticizer will be adsorbed more on the C_3S and C_2S, which will slow down its hydration and resulting in the reduction of early strength (Roberts, 1995). If the C_3A content is not enough for the consumption of dissolved suphate content, false set can occur (Ramachandran, 2002). The surface area of C_3A phase in cement is very high compared to its hydration product (i.e., ettringite) and adsorbs large amounts of admixture resulting in loss of fluidity. Therefore, the delayed addition of superplasticizer is

advantageous as the hydration of C_3A takes place and ettringite is formed before the superplasticizer is added (Roberts, 1995). Bonen and Sarkar (1995) investigated the effect of a polynaphthalene sulfonate superplasticizer on the fluidity of five types of cements with different constituents including ASTM Type I, II, III and V cements and found that the amount of C_3A in the cement affects the fluidity of cement pastes significantly; cements with lower C_3A content displayed higher fluidity.

2.4.2.5 Effect of Ambient Temperature

The ambient condition to which concrete is exposed can affect its properties and behaviour. The temperature is an important environmental factor that affects the cement-superplasticizer interaction. The responses of freshly prepared concrete like water demand, setting time, fluidity, loss in fluidity etc. are affected considerably by temperature (Soroka and Ravina, 1998; Nmai, 1998; Vydra et al., 2007). It has been reported that low temperatures decrease the fluidity and cannot be compensated with an increase in the superplasticizer dosage beyond the saturation dosage (Gettu et al., 1997; Roncero et al., 1999). At the same time, it was also observed that the higher temperatures increase the superplasticizer adsorption and the initial fluidity; however, it could increase the superplasticizer demand for maintaining the fluidity with time, over a range of temperature (Roncero et al., 1999; Greisser, 2002). The changes in rheological properties with time can be due to the restructuring of the microstructure, cement hydration, variation in free water content with temperature, mixture composition and interaction between binder and water (Petit, 2007). The increase in temperature leads to the increase in the reactivity of C_3S, more formation of ettringite and rapid loss in fluidity (Greisser, 2002; Spiratos et al., 2003). It is also reported that the increase in temperature can lead to the reduction in the free concentration of PCE in paste (i.e., the concentration reduced at extremely cold and hot temperatures (Ghafoori and Diawara, 2010).

Roncero et al. (1999), and Fernandez-Altable and Casanova (2006) concluded that though the fluidity increases with the temperature, it has no practical effect on the saturation dosage of superplasticizer, which is attributed to the dependence of saturation on the available surface area of the cement particles. Nehdi (2007) observed that the yield stress and shear modulus values for the various cement pastes increased nonlinearly with the increase of temperature. However, the shear modulus generally decreased with the increase of the superplasticizer dosage, and increased significantly with temperature increase. It was also observed that the

saturation dosage of PCE based superplasticizer increases with an increase in temperature. The effect of temperature on mixes with PCE based superplasticizers is dependent on the chemical structure (e.g., the carboxylates have the highest fluidity loss compared to other functional groups) (Felekoglu and Sarikahya, 2007; Grzeszczyk and Sudol, 2005). The increase in temperature leads to a lower increase of flow in the paste and lower flow loss in the case of longer polyethylene oxide graft chains (Nawa et al., 2000). This is attributed to the higher adsorption of the graft chains with an increase in temperature, as a result of which the steric repulsion of the longer graft chains is less affected.

Al-Martini and Nehdi (2007) suggest that the increase of yield stress versus temperature is not linear, which is in agreement with findings of Soroka and Ravina (1998) who observed that the rate of slump loss increase with temperature. It can also be observed that yield stress values generally decrease with the increase of the water reducer dosage, and increase significantly with temperature increase. The rate of increase in yield stress is much higher when temperatures exceed 40°C but this increase is less significant at high superplasticizer dosages. Generally, plastic viscosity decreases significantly with the increase of the water reducer dosage but reaches a threshold value beyond which no significant reduction in plastic viscosity can be achieved (Al-Martini and Nehdi, 2007)). In general, it is observed that at a low dosage of superplasticizer, thixotropy increases with the increase in temperature. This is due to the build up in the structure of cement paste due to the acceleration of hydration reactions. It has also been observed that there is a decrease in thixotropy when the dosages of admixtures increase. This is likely due to the delay in stiffening of cement paste induced by the action of chemical admixtures. Both yield stress and viscosity increase nonlinearly with temperature (Al-Martini and Nehdi, 2007).

The concentration of adsorbed and residual SNF can vary with paste temperature, resulting in direct implications on rheological properties of paste (Jolicoeur et al., 1997). The effect of temperature on mixes with PCE based superplasticizers is dependent on its chemical structure (e.g., the carboxylates have the highest fluidity loss compared to other functional groups) (Felekoglu and Sarikahya, 2007; Grzeszczyk and Sudol, 2005), with the increase in temperature leading to a lower increase of flow in the paste and lower flow loss for longer polyethylene oxide graft chains (Nawa et al., 2000). This is attributed to the higher adsorption of the graft chains with an increase in temperature, as a result of which the steric repulsion of

the longer graft chains is less affected. Roncero et al. (1999), Roncero (2000), and Fernandez-Altable and Casanova (2006) have observed that the saturation dosage is not affected with increase in temperature and concluded that the saturation dosage is dependent on the available surface area only.

2.4.2.6 Effect of Fineness of Cement

As the fineness increases, the surface area of cement also increases. The higher surface area of cement can lead to increase in the water demand, as well as the amount of superplasticizer for a given workability. Hence, the amount of superplasticizer adsorbed depends on the fineness, with finer cements leading to higher superplasticizer dosages (Aïtcin, 1998; Jolicoeur and Simard, 1998; Erdogdu, 2000; Vikan et al., 2007).

2.5 MICROSTRUCTURE OF CEMENT PASTE

In cementitious materials the microstructure develops during the hydration process; the anhydrous cement reacts with water to form hydration products and in the process the solid volume increases. In the case of portland cement, the hydration reaction is dominated by the hydration of tricalcium silicate, which produces calcium hydroxide (CH) and calcium silicate hydrate (C-S-H). The CH precipitates in the water filled pores and the C-S-H deposits around the hydrating cement grain (Scrivener 2004).

2.5.1 Effect of Superplasticizer on the Microstructure of Hardened Cement Paste

The microstructure of the hardened cement paste and the morphology of the hydration products can be altered by the presence of superplasticizers as it can affect the hydration reactions and interact with the early hydration products. It has been reported that the polysulphonate based superplasticizer can interact with the phases of cement and can form an organo-mineral composite that resembles ettringite (Aïtcin et al., 2001). The superplasticizer can modify the morphology of ettringite to small and thick crystals instead of the conventional needle-like geometry (Aïtcin et al., 1994; Hanna et al., 2000; Prince et al., 2002). The portlandite grains can decrease in size and may form thin plates instead of a block-like structure in the presence of a superplasticizer (Grabiec and Piasta, 2004). The superplasticizer can delay the dissolution of SO_4^{2-}, leading to the formation of monosulphoaluminate first and then the ettringite is formed (Prince et al., 2003). The lignosulphonate can reduce the solubility of anhydrite due to the reduction in the rate of

diffusion of ions at the solid-liquid interphase, and further promote this phase transformation (Prince et al., 2003). The incorporation of superplasticizer can alter the distribution of pores also. Higher numbers of small pores are formed in the presence of superplasticizer (Khatib and Mangat, 1999; Roncero, 2000) due to better silicate polymerisation and consequent reduction in pores (Puertas et al., 2005).

The continued hydration of cement will lead to the gradual decrease in the fluidity with time. Loss in slump with time is a real issue in practical considerations and the superplasticized concrete with high workability generally exhibits more slump loss compared to normal concrete, which can be attributed to the loss of consistency due to the low w/c during the dormant stage and the increased adsorption of the superplasticizers by the aluminate phase (Ramachandran et al., 1998). The C_3S phase of cement contributes to the loss in slump as the hydrate coatings restore charge interactions between the C_3S grains, thereby restoring the tendencies for flocculation (Ramachandran, 2002).

2.5.2 Effect of Temperature on the Microstructure of Hardened Cement Paste

Change in ambient temperature alters various properties of concrete, which can be due to the change in the rate of hydration and the nature of the hydrated products (Jolicoeur and Simard, 1998; Agarwal et al., 2000; Prince et al., 2002; Nkinamubanzi and Aitcin, 2004; Bedard and Mailvaganam, 2005; Hanehara and Yamada, 2008). The morphology of the hydration products seems to be significantly different at higher temperatures compared to lower temperatures. Lothenbach et al. (2007) observed that the ettringite needles formed at higher temperatures are significantly smaller compared to those formed at lower temperatures. The slower formation of the ettringite at lower temperature leads to larger crystals. The presence of ettringite needles at higher temperatures seems to be less compared to that at lower temperatures, probably due to the burial of the ettringite needles in the newly formed hydration products as the amount of hydration products is more at higher temperature. Matschei and Glasser (2010) suggest from thermodynamic calculations that a significant change in the AFm and AFt phases, and amount of $Ca(OH)_2$ with change in temperature. The increase in temperature leads to the increase in the reactivity of C_3S, leading to more formation and change in the morphology of ettringite (Greisser, 2002; Spiratos et al., 2003). Lothenbach et al. (2007) observed a decrease in coarser pores at lower temperatures compared to higher temperature, whereas Cao and Detwiler (1995) observed a more scattered

distribution of hydration products and an extremely porous microstructure for specimens cured at higher temperature. It was observed earlier that specimens cured at higher temperatures show an increase in porosity for the same degree of hydration (Kjellsen et al., 1990; Mouret et al., 1999). It is also observed that the hydration and the polymerization of C-S-H increase with an increase in curing temperature (Kim et al., 2012). The characteristic size of pores in cement paste increases with an increase in curing temperature (Valenza and Thomas, 2012). They attributed the variation in microstructure with curing temperature to the changes in the pore structure of the C-S-H hydration product.

2.6 EFFECT OF SUPERPLASTICIZER ON PROPERTIES OF CONCRETE

The superplasticizers are added to concrete to increase the workability at lower water to cement ratios, leading to higher strength. In addition to strength, the properties of concrete such as slump, air content, bleeding, segregation and setting time in the fresh state, and properties like permeability, abrasion resistance and durability in the hardened state can also be affected by the incorporation of the superplasticizer. The improper use of the admixtures can lead to incompatibility between the cement and superplasticizer, and adverse effects like loss of fluidity, retardation in setting, air entrainment and reduction in strength gain, as explained in the previous sections.

The incorporation of superplasticizer results in the decrease in the w/c and better compaction due to increased workability. The 28-day compressive strength of superplasticized concrete is often equal to or greater than that of the reference concrete (Rixom and Mailvaganam, 1999; Ramachandran, 2002). It is also reported that the concrete with saturation dosage of superplasticizer exhibited a slightly higher strength and the superplasticizer dosages above the saturation dosage cause bleeding, stiffening and reduced strength (Jayasree and Gettu, 2010). Dhir and Yap (1983) also reported that even though there could be some initial retardation, superplasticizers produce compressive strengths of the same order as the normal concrete at 3, 7 and 28 days. However, there are also reports of reduction of strength with the use of SNF and SMF based superplasticizers, especially with cements having low C_3A content, and high C_3S and C_2S contents (Ramezanianpour et al., 1995). This can be attributed to the higher adsorption on the C_3S and C_2S phases or gypsum crystallization and consequent false set in the absence of adequate C_3A (Roberts, 1995; Ramachandran, 2002).

There are contradicting reports on the influence of creep and shrinkage of superplasticized concrete. Ramachandran (2002) reported that the shrinkage of superplasticized concrete is larger than that of reference concrete. The larger dispersion of cement and cement hydrates in the presence of superplasticizer could be the reason for the increased shrinkage. Gettu et al. (2002) have reported that for SNF based superplasticizers, drying shrinkage is higher for superplasticized concrete. This could be attributed to the refinement of pore structure with more number of fine pores (Roncero, 2000; Gettu et al., 2002; Roncero et al., 2002).

2.7 EFFECT OF TEMPERATURE ON PROPERTIES OF CONCRETE

Hot weather concreting causes severe problems in fresh concrete due to increased water evaporation and accelerated slump loss due to higher temperature. At higher temperatures, the fresh concrete stiffens fast, and therefore, will no longer be workable (Soroka and Ravina, 1998; Thomas et al., 2003). According to ACI Guidelines the upper limit of ambient temperature to produce good quality concrete is specified as 32°C (ACI 305R-77, 1998). Higher temperatures lead to many problems in cement paste and concrete, such as increased water demand, shorter setting time, rapid loss in fluidity with time, etc., whereas at cold temperatures, cement paste and concrete experience problems, like slow setting, lower early strength, etc. (Alshamsi et al., 1993; Soroka and Ravina, 1998; Nmai, 1998; Ahmadi, 2000; Mounanga et al., 2006). Vydra et al. (2007) also observed that the induction period decreases with an increase in temperature. Low curing temperature at the early ages of curing will prolong the induction period reasonably. Alshamsi ei al. (1993) observed that the setting time decreases with an increase in temperature due to increased rate of hydration. Ghafoori and Diawara (2010) observed an increase in the optimum dosage of superplasticizer for maintaining the slump flow at higher temperatures for self compacting concrete. The rate of heat development due to hydration reflects the rate and amount of hydration (Alshamsi, 1994). Even though the high initial temperature accelerates the initiation of the acceleratory period, it does not have a significant influence on the amount of reactions taking place after that. Increase in temperature promotes hydration in the early ages, which leads to higher initial strength; however, at later stages, the strength of cement hydrates at higher temperature is reduced compared to the cements hydrated at lower temperatures (Lothenbach et al. 2007). This is due to the initial fast hydration, which leads to more rapid precipitation of hydration products during the early ages. This faster hydration of cement leads to a more heterogeneous distribution of hydration products. However, at lower temperatures, the hydration starts

slowly, which allows the ions more time for diffusion before the hydrates precipitate and lead to less dense C-S-H, a more even distribution of hydration products and a lower coarse pores. It is also observed that the inital and final setting time is significantly reduced by elevated curing temperatures (Zhang et al., 2012)

The flow parameters of mortar and concrete, which are made with significant amount of superplasticizers, depend a great extent on the time and temperature of the material (Petit et al., 2009). Ortiz et al. (2009) observed that the mortar workability is a function of the temperature of the aggregates and of their physical properties, such as absorption and friction. The compressive and tensile strengths of concrete tested under different temperatures show that they decrease with an increase in temperature (Shoukry et al., 2010). Kim et al. (1998), Ortiz et al. (2005) and Lothenbach et al. (2007) observed the development of strength at various curing temperature, and found that the concrete subjected to higher temperature had a higher early age strength but eventually attained lower later-age strength. It was also concluded that the concrete subjected to low temperature, at early age, had lower early-age strength but almost the same later-age strength (Kim et al., 1998; Ortiz et al., 2005; Lothenbach et al., 2007). It may be due to the formation of products of a poorer physical structure due to rapid initial hydration, which is probably more porous. In addition to this, high temperature leads micro-cracking, which can also contribute to the lower long-term strengths (Ortiz et al., 2005). These observations may be attributed to the increased rate of hydration of the cement particles and evaporation of water at higher temperature. Again, lower temperature could lead to setting problems. Extreme low temperature leads to decrease in early strength and longer duration for formwork removal, which in turn affects the rate of the work (Nmai 1998). It is also observed that the elevated temperature improves the initial compressive and flexural strengths of cement mortar and the later age strengths are decreased (Abd-ElAziz, 2012). Similar observations were also made by Zhang et al. (2012) on cement paste.

2.8 EFFECT OF FINENESS OF CEMENT ON PROPERTIES OF CONCRETE

Modern cement contains more C_3S content and higher fineness, generally. It is well known that the compressive strength of cement increases with fineness or specific surface area, and that for equal surface area, cements with a narrow particle size distribution have a higher strength than those with a wide size distribution. Many results indicate that the early strength

of a hardened cement paste is directly proportional to the fineness of the cement, but fineness cannot contribute to later-age strength. Since hydration starts at the surface of the cement particles, it is the total surface area of cement that represents the material available for hydration. Thus, the rate of hydration depends on the fineness of cement particles, and for a rapid development of strength, a high fineness is necessary. Increasing the fineness of cement beyond an optimum limit increases the water requirement of concrete (Sajedi and Razak, 2011). When finer cement is used with high C_3S, a higher 28 day compressive strength can be achieved with higher water to cement ratio (Aitcin, 2000). However, it is observed that the long term durability is affected by the initial higher strength (Aitcin, 2000). The initial strength has an increase with an increase in fineness and at later ages, the strength is affected more by the amount of coarse particles rather than fines (Celik, 2009). In contrast, excessively high fineness may increase the water requirement and cause a reduction in later strength gain (Sajedi and Razak, 2011). It is also observed that, at any age, the reacted thickness of cement grain can be considered independent of the initial cement particle size (Termkhajornkit and Barbarulo, 2012).

2.9 JUSTIFICATION FOR THE PRESENT STUDY

The present level of knowledge worldwide about the various factors affecting the interaction between cement and superplasticizer has been reviewed in this chapter. Many of these factors lead to adverse effects on the fresh and hardened properties of concrete. The issues like workability, loss in workability, setting and hardening behaviour, rate of development of strength and change in microstructure with the incorporation of superplasticizer and change in temperature have been discussed. There are contradictions regarding the influence of some factors, especially the influence of temperatures, which have been brought out.

In India, the cement standards are not very stringent and enable the manufacturers to adjust the final product in different ways. For example, the minimum fineness of cement is specified for various grades; however, the maximum is not specified. Again the IS code accepts a wide range in chemical composition.

Studies on cement-superplasticizer interactions in India have been limited to the workability evaluation of concretes containing these chemicals. There have not been many investigations to understand the physico-chemical nature of this interaction. Further, the effects of temperature on the cement-superplasticizer interaction have to be established.

CHAPTER 3

EXPERIMENTAL PROGRAMME

3.1 INTRODUCTION

A brief description about the cement hydration reactions and the influence of superplasticizers and ambient temperature has been presented in the previous chapter. The various factors affecting the cement-superplasticizer interaction and the properties of superplasticized concrete have also been discussed. It is needless to say that the use of superplasticizers in concrete and their effect on the different properties have already been studied extensively. These investigations have established the benefits of incorporating the superplasticizer, especially in the fresh state properties of concrete, and the formulation of new superplasticizers, and their modes of action and effectiveness have been the main objective of many studies. On the other hand, the cement-superplasticizer compatibility has been analyzed to a lesser extent and the mechanisms involved are still far from being fully understood. Moreover, there are only few studies that combine these different aspects in order to establish micro-macro relations. The ambient conditions, especially temperature, to which the concrete is exposed can vary in time and can affect the cement-superplasticizer interaction. Hence, it is necessary to study the effectiveness of the superplasticizers and its interaction with cement along with the factors.

The discussions in this chapter deal with the specifications of the materials used for the study and the various experimental procedures employed to study the properties of cement paste, mortar and concrete. The test methodologies used in this study can be applied to other cementitious systems containing additives (like fly ash, GGBS, micro silica etc.) and for concretes with special types of aggregates like recycled aggregates. However, in such cases the tests have to be repeated with the materials considered. The initial part of the chapter focuses on the properties of the materials and their technical specifications. Further, the tests used for the evaluation of the fresh and hardened state properties of the cement paste, mortar and concrete have been described. The properties of cement paste in the fresh state are studied using simple

tests like Marsh cone, mini-slump, standard consistency and setting time. These tests give an idea about the influence of the different superplasticizers, cement characteristics and ambient temperature on fluidity, loss in fluidity with time, water demand and setting of cement paste. The fluidity and loss in fluidity with time of cement mortar is analyzed using flow table test. The compressive strength and flexural strength are determined to study the effect of different parameters on mechanical properties of cement mortar. The workability of concrete is studied using the slump test, and the compressive and splitting tensile strengths of concrete are also determined. Micro-structural studies based on SEM, XRD and thermal analysis are conducted to understand the effect of superplasticizer and temperature on hydration process.

3.2 MATERIALS USED

3.2.1 Cement

Ordinary 53 grade portland cement conforming to requirements of IS 12269 (2004) was used throughout the study, except for the tailor-made cements employed for the study of the influence of fineness and sulphate content of cement (see details of the tailor-made cement in Chapter 6). The chemical properties of cement used were determined by the National Test House, Chennai, and are given in Table 3.1.

The physical properties of cement were also determined. The water demand for a paste of standard consistency and setting time were determined as per the procedures described in Sections 3.3.2.4 and 3.3.2.5. The water demand was found to be 29%, and the initial and final setting times were 197 and 299 minutes, respectively. The fineness of cement has been determined by the Blaine air permeability method, as per IS 4031: Part 2 (2005) and ASTM C 204 (2007). The specific surface area obtained was 292 m^2/kg, which is within the limits given for the 53 grade ordinary portland cement.

Table 3.1: Chemical composition of cement used

Composition	Percentage (%)
Calcium oxide (CaO)	59.04
Silica (SiO_2)	20.61
Alumina (Al_2O_3)	6.17
Iron oxide (Fe_2O_3)	3.76
Magnesia (MgO)	2.36
Sulphuric anhydride (SO_3^{2-})	2.27
Insoluble residue	2.36
Total loss on ignition	2.65
Total chloride content (Cl^-)	0.03
Sodium oxide (Na_2O)	0.16
Potassium oxide (K_2O)	0.28
Total alkalis $(Na_2O)_{eq}$	0.34

3.2.2 Superplasticizers

One superplasticizer from each of the four families of products used commonly in the construction sector (i.e., polycarboxylate ether, sulphonated naphthalene formaldehyde, sulphonated melamine formaldehyde and lignosulphonate) was incorporated to obtain representative results that would help understand the effect of the different types. The solid content of superplasticizer was determined in the laboratory as per IS 9103 (2004), and cross-checked with data from the corresponding supplier. It can be seen that the active part of superplasticizer varies from 35% to 42% for the different superplasticizers. The details of the superplasticizers used are given in Table 3.2. The superplasticizer dosages are given in the thesis as the ratio of the solid content of the superplasticizer to cement (sp/c), by weight, and the liquid phase in the superplasticizer has been accounted as part of the w/c.

Table 3.2: Properties of superplasticizer

Designation	Chemical type	Density (kg/litre)	Solid content (%)	Appearance
PCE	Polycarboxylate ether	1.09	35	Light brown
SNF	Polynaphthalene sulphonate	1.21	42	Dark brown
SMF	Polymelamine sulphonate	1.20	40	Colourless
LS	Lignosulphonate	1.10	35	Dark brown

3.2.3 Aggregates

River sand (grain size range of 0-4.75 mm) was used as the fine aggregate for the mortar and concrete, except in the study of the effect of temperature on the mortar, where standard sand was used. For the study of the effect of temperature and superplasticizer on the cement mortar, standard Ennore sand conforming to IS 650 (1991) was used. Crushed granite coarse aggregates (of 4.75-10 mm and 10-20 mm grain size ranges) satisfying the requirements of IS 2386 (2007) were used for the preparation of concrete.

The sieve analysis was done according to IS 2386 (2007), and the test results of fine and coarse aggregates are given in Figures 3.1 and 3.2, respectively. The sand has a fineness modulus of 2.84 and generally conforms to zone II grading as per IS 383 (2002). The properties of aggregates used are given in Table 3.3. The specific gravity, bulk density and coefficient of water absorption were determined for each aggregate according to IS 2386 (2007).

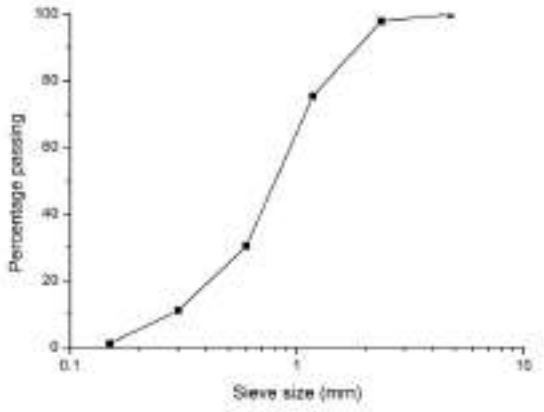


Figure 3.1 Particle size distribution of fine aggregates (0-4.75 mm)

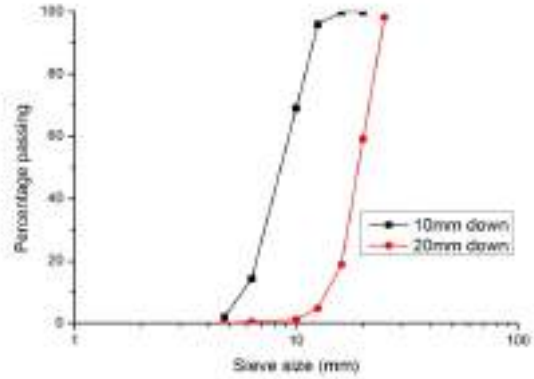


Figure 3.2 Particle size distribution of coarse aggregates (4.75-20 mm)

Table 3.3 Summary of the properties of aggregates

Properties	Sand	Coarse aggregates	
		4.75-10 mm	10-20 mm
Specific gravity	2.65	2.74	2.72
Water absorption (%)	0.53	0.32	0.23
Fineness modulus	2.84	3.20	5.03
Bulk density (kg/ m^3)	1660	1600	1610
Flakiness index (%)	-	-	17
Elongation index (%)	-	-	27
Angularity number	-	-	08
Crushing Value (%)	-	-	29
Impact Value (%)	-	-	30

3.3 EXPERIMENTAL DETAILS

To study the properties of cement paste, mortar and concrete, standard procedures were adopted. The following sections explain the details of the experimental techniques used in the characterization.

3.3.1 Testing Conditions

The properties of cement paste and mortar were studied on materials fabricated at the ambient temperatures of 5, 15, 25, 35 and 40°C, whereas the fresh and hardened state properties of concrete were studied on batches made at the ambient temperatures of 5, 25 and 40°C. For studying the effect of fineness and sulphate content of cement, the cement paste, mortar and concrete were fabricated at a temperature of 27°C. A walk-in environmental chamber (see Fig. 3.3) was used to maintain the temperature of the materials, mixing and measuring equipments, and for conducting the experiments. The chamber was set to have a relative humidity of 65%, which was maintained at all the temperatures, except in the case of 5°C, where the condensation of water raised the humidity slightly. All the material components were maintained at the prescribed temperature for at least 48 hours prior to the mixing, for preconditioning. The temperature of the materials was checked and found to be always within ±2°C of the prescribed temperature.

Figure 3.3 Environmental chamber used for mixing and conducting the tests

3.3.2 Tests on Cement Paste

The effects of the type of superplasticizer, fineness and sulphate content of cement, and ambient temperature on the fluidity and loss in fluidity of cement paste with time were studied using Marsh cone and mini-slump tests. The Vicat apparatus was used to study the effect of these parameters on the water demand and setting time. The

following sections outline the details of the preparation of cement paste and the methods used to characterize the properties.

3.3.2.1 Mixing Procedure for Cement Paste

The mixing time and procedure of mixing of cement paste are important as they can affect the fluidity of cement paste. The pastes were prepared using a 5-litre Hobart-type blender and a B type flat beater, with a mixing procedure that produce pastes comparable to those of concrete (Jayasree and Gettu, 2006). The mixing sequence adopted was as follows: the cement and 70% of mixing water were mixed at low speed (with a shaft speed of 139 rpm and planetary speed of 61 rpm) for one minute, and then the superplasticizer and remaining water were added and mixed for two minutes. The mixer was then stopped, and the sides of the bowl and blades were scraped (15-20 seconds). The paste was again mixed for two minutes at medium speed (with a shaft speed of 285 rpm and planetary speed of 125 rpm). The delayed addition of superplasticizer was adopted in this study because earlier studies have showed that the delayed addition of superplasticizer leads to better fluidity and fluidity retention (e.g., Uchikawa et al., 1995; Aiad et al., 2002). For the mixes without superplasticizer, the water is added entirely in the beginning, and the paste is mixed for 3 minutes at low speed as in the procedure for paste with superplasticizer.

3.3.2.2 Marsh Cone Test

The selection and dosage of superplasticizer becomes very important in determining the optimum composition of concrete. It is always better to make this choice at the construction site using the actual concrete under the local conditions. However, tests on concrete require significant labour, material and time. Therefore, several methods based on tests of paste and mortar have been developed for determining the optimum superplasticizer dosage in concrete. In this study, the Marsh cone test (Figure 3.4) is used to determine the saturation dosage of superplasticizer. This test has been used earlier to evaluate the relative fluidity and saturation dosage of superplasticizers in cement pastes and mortars by many researchers (de Larrard et al., 1998; Aitcin, 1998; Khayat and Yahia, 1998; Agullo et al., 1999; Roncero et al., 1999; Gomes et al., 2001; Roussel and Roy, 2005; Jayasree and Gettu, 2008). It has been shown (Jayasree and Gettu, 2008, Jayasree et al., 2011b) that the trend of the Marsh cone flow time curve is similar to that of the Bingham parameters, namely the yield stress and the

plastic viscosity, with respect to their variation with the superplasticizer dosage. It was observed that all three parameters decrease with an increase in superplasticizer dosage until the saturation dosage, after which it is practically constant (Jayasree and Gettu, 2008).

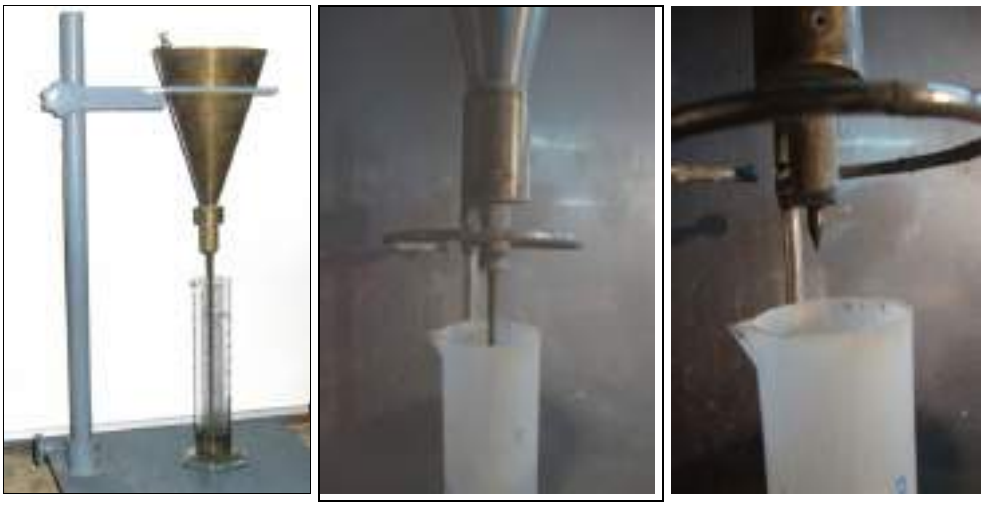
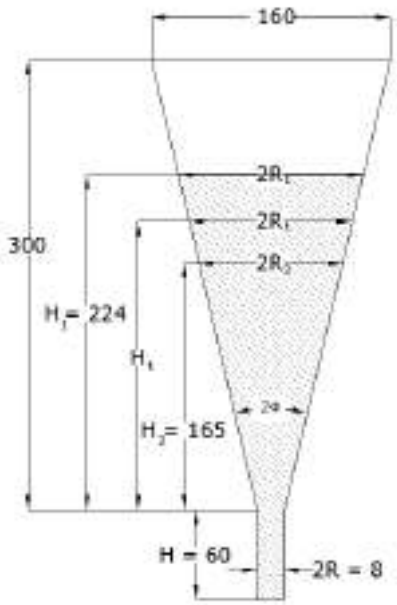


Figure 3.4 Marsh cone test showing continuous and discontinuous flow

The Marsh cone, consisting of a hollow metal cone (as per EN 445, which is similar to ASTM C 939 (1987)) with an opening of 8 mm diameter at the bottom, was used in this study. The dimensions of the Marsh cone are given in Figure 3.5. A reference volume of 1000 ml of cement paste is poured into the Marsh cone and the time taken for 500 ml of the paste to flow out is determined (Jayasree and Gettu, 2008). The fluidity of the paste is related to flow time; the longer the flow time, the lower is the fluidity. The logarithm of flow time is plotted against the sp/c dosage as the logarithm of flow time permits the use of a criterion that depends only on the intrinsic characteristics of the paste and not on the volume of the paste. The saturation point is the dosage of superplasticizer beyond which the further addition of superplasticizer does not increase the fluidity significantly (Agullo et al., 1999, Jayasree and Gettu, 2008).



R, H - Radius and length of nozzle

R_1, H_1 - Radius of the free surface and height of fluid in the cone at the initial moment

R_t, H_t - Radius of the free surface and height of fluid in the cone at any time t

R_2, H_2 - Radius of the free surface and height of fluid in the cone at the final moment

φ – Angle between the axis and the generator of the cone

Figure 3.5 Geometry and dimensions (in millimetres) of the Marsh cone

Gomes et al. (2001) proposed a method for the determination of the saturation dosage of superplasticizer based on the Marsh cone flow time curve of cement pastes, as illustrated in Figure 3.6. In this method, the internal angle corresponding to each data point is calculated and saturation dosage of superplasticizer is taken as the dosage corresponding to the point where the flow time verses sp/c dosage curve takes an angle of 140±10°, beyond which the fluidity does not increase considerably. Interpolation can be used to determine the dosage when there are no data points corresponding to this range of angles.

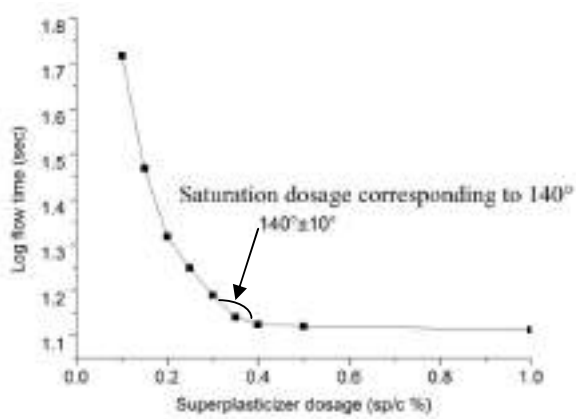


Figure 3.6 Flow time curve showing the determination of saturation superplasticizer dosage (Gomes et al., 2001)

The loss in fluidity of cement paste with time can also be studied with the help of Marsh cone test (Agullo et al., 1999; Roncero et al., 1999). In order to evaluate the loss in fluidity with time, the Marsh cone flow time was determined in this study up to one hour after mixing. In each case, after every measurement, the paste was kept covered (without agitation) and was mixed for 30 seconds at medium speed (with shaft speed of 285 rpm and planetary speed of 125 rpm) before the subsequent reading.

3.3.2.3 Mini-slump Test

The mini-slump test developed by Kantro (1980) has also been used to study the flow behavior of superplasticized cement paste, done by many researchers, was also employed here (Khayat and Yahia, 1998; Aitcin, 1998; Gomes et al., 2001; Jayasree and Gettu, 2008). The mini-slump mould has the shape of a truncated cone with dimensions proportional to the Abram's cone, as shown in Figure 3.7. In this test, the mould is filled with cement paste (prepared as explained in Section 3.3.2) and the spread diameter of the cement paste is measured in two directions orthogonally, after lifting the mould vertically upwards (see Figure 3.8); the average value is expressed as the spread of the cement paste. The bleeding and segregation of the paste can be examined visually.

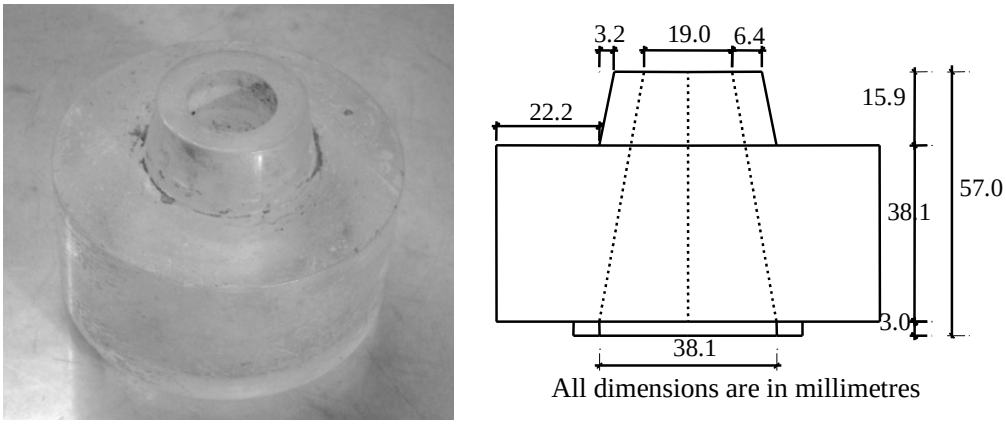


Figure 3.7 Mini-slump cone

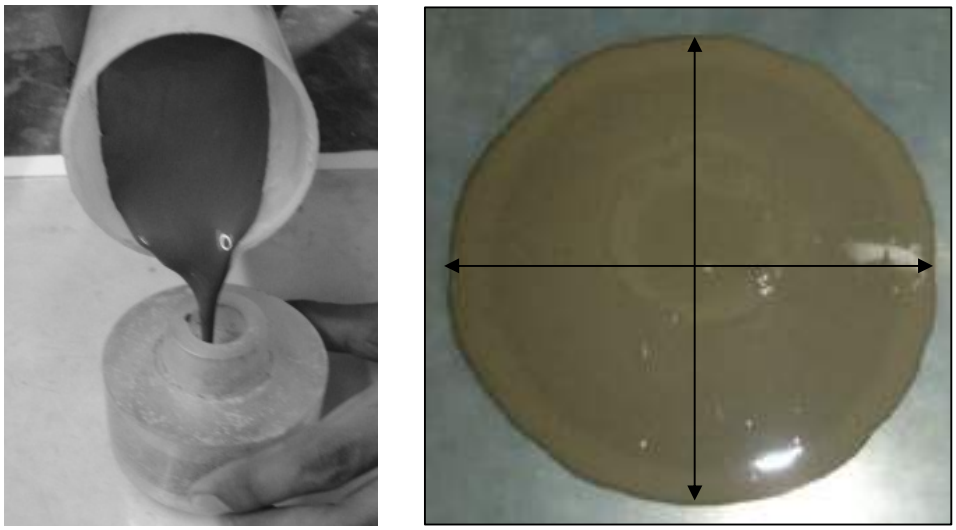


Figure 3.8 Mini-slump test

3.3.2.4 Water Demand (Standard Consistency) Test for Cement

The influence of varying dosages of superplasticizer, fineness and sulphate content of cement and ambient temperature on the water demand of cement was studied using the Vicat apparatus as per IS 4031: Part 4 (2005), which is similar to ASTM C 187-11 (2011). Cement pastes prepared as explained in Section 3.3.2, with varying amounts of water were used to fill the Vicat mould, and the penetration of the plunger was determined. Water demand of cement is the quantity of water that is required to produce a cement paste of standard consistency, defined as that which permits the Vicat plunger to penetrate up to 6 ± 1 mm (as per ASTM C 187, the penetration should be 10 ± 1 mm) from the bottom of the Vicat mould, and is expressed as a percentage by mass of dry cement.

To study the effect of type and dosage of superplasticizer on the water demand, various dosages of superplasticizer of different families were used, and the water demand was found out for each case. The effects of temperature on water demand were studied at different temperatures, including the standard conditions of temperature and humidity of 25°C and 65% respectively.

3.3.2.5 Initial and Final Setting Time of Cement

The initial and final setting times were determined as per IS 4031: Part 5 (2005). The procedure in this code is similar to that of ASTM C-191 (2001). The difference between the two procedures is that the cement paste used as per ASTM C-191 (2001) is of standard/normal consistency and the penetration of the needle for the initial setting time determination is 25 mm. In the present study, cement paste was prepared with a water content of 0.85 times of the water required for standard consistency. Initial setting time is determined as the period from the addition of water to the cement to the time at which the needle penetration corresponds to 35.0 ± 0.5 mm. The cement paste prepared as explained in Section 3.3.2.1 was filled in the Vicat mould and the needle penetration was observed at regular intervals to determine the setting time. The test was continued with a standard needle having an annular attachment. The final setting time corresponds to the time elapsed from the first addition of water to the cement to the time at which the needle makes an impression on the surface of the cement block and the annular ring fails to do so.

The setting time of superplasticized cement paste was determined and compared with the paste without superplasticizer to study the influence of the type of superplasticizer. To study the effect of superplasticizer and temperature, setting time was determined at different temperatures for cement pastes prepared with the saturation dosage of superplasticizer at 25°C (as determined by Marsh cone test) and with a water content of 0.85 times the normal consistency for the paste without superplasticizer at 25°C, for all the superplasticizers.

3.3.3 Tests on Cement Mortar

3.3.3.1 Preparation of Cement Mortar

The cement mortar was prepared using a 5-litre 1/6hp Hobart-type blender with a B flat beater. The cement to sand ratio of the mortar adopted was 1:1.6 with a water to cement ratio of 0.4 for the study of the effect of fineness and sulphate content of cement and 0.35 for the study of the effect of ambient temperature.

The mixing procedure for preparing the cement mortar for this study is as follows: The cement and sand were mixed for one minute to get a proper dispersion. Then,

70% of the mixing water is added to the mix and mixed with low speed (with a shaft speed of 139 rpm and planetary speed of 61 rpm) for one minute, and then the superplasticizer and remaining water are added and mixed for two minutes. The mixing is then stopped, and sides of the bowl and blades are scraped (15-20 seconds). The paste is again mixed for two minutes at medium speed (with a shaft speed of 285 rpm and planetary speed of 125 rpm). For the mixes without superplasticizer, the only difference is that the entire water is added in the beginning, and the paste is mixed for 3 minutes at low speed.

3.3.3.2 Determination of the Flow Properties of Mortar

The flow table test (see Figure 3.9), confirming to ASTM C-230C/C-230 M (2003) and C-1437 (2007), is used to study the fluidity of cement mortar. The mortar is prepared as explained earlier (Section 3.3.2.1) and is filled in the mould placed on the flow table in two layers. Each layer is tamped 20 times, with a rod of approximately 10 mm diameter and 100 mm length. The mould is a hollow truncated metallic cone with a base diameter of 100 mm, top diameter of 70 mm and a height of 50 mm. The excess mortar is removed and the top surface is leveled flush with the top of the mould, with a straight edge, by a sawing motion across the mould. The mould is removed vertically one minute after the mixing operation and the table is jolted for 25 times in 15 seconds. In order to account for the higher fluidity of superplasticized cement mortar, the standard flow table was modified by increasing its diameter using a polycarbonate plate, as seen in Figure 3.7. The spread of the cement mortar is measured in two directions, perpendicular to each other, and the average is expressed as the spread of mortar. In order to study the effect of time on the loss in fluidity of mortar, the spread was determined immediately after mixing, and subsequently at 30 and 60 minutes after the addition of water to cement. The mortar was kept in air tight containers at a constant temperature in between the measurements and mixed for 30 seconds at medium speed before each measurement.

Figure 3.9 Flow table test for mortar

In order to study the effect of temperature on the fluidity and loss in fluidity with time, the spread of mortar was determined at different temperatures. To study the effect of superplasticizer and temperature on the fluidity and loss in fluidity with time, mortar was prepared and tested with the saturation dosage of superplasticizer at 25°C, at different temperatures. In order to study the influence of superplasticizer dosage on the flow properties of mortar, a higher dosage corresponding to the minimum flow at 25°C was also used.

3.3.3.3 Determination of Mechanical Properties of Mortar

The mechanical properties, such as compressive and flexural strengths of mortar are important to evaluate the performance of both mortar and concrete. Specimens were prepared to study the effect of fineness, sulphate content of cement and ambient temperature on the compressive and flexural strength of cement mortar. A total of nine specimens of cubes and prisms were prepared from each mix.

All the materials (including the mould) were kept inside the environmental chamber for at least 48 hours for preconditioning, and the mixing and casting were done inside the chamber. Mortar cubes of 50×50×50mm were used to study the compressive strength of mortar. The mortar was prepared as explained above (Section 3.3.2.1) and filled in the mould in two layers. Each layer was tamped 32 strokes with a tamping rod. Mortar prisms of dimensions 160×40×40mm were used to determine the flexural strength. The moulds were filled with cement mortar prepared as explained above in two layers, and each layer was compacted with a jolting apparatus (confirming to IS: 10078 (2004)) with sixty jolts in 60 seconds. After casting, the specimens were kept

in the controlled condition for 24 hours, then demoulded, and placed in mist room for curing till the respective days of testing. The curing of the specimens could not be continued at the same temperature due to practical constraints (i.e., need to use the environmental chamber for one month at each temperature). Moreover, in practical situations, the concrete specimens will be at site conditions for the first 24 hours and then cured in a laboratory, where more controlled conditions can be expected. Three specimens were tested at surface dry condition for each prescribed age, and the average of the data from three specimens is taken as the strength of mortar.

The specimens were tested with a Controls Advantest 9 mortar testing machine (see Figure 3.10) for the determination of compressive strength and flexural strengths. The compression test was carried out as per ASTM C 109/109M with a loading rate of 900 N/s. The flexural strength of mortar was determined as per ASTM C348 (2002) with a loading rate of 40 N/s.

Figure 3.10 Testing machine for mortar

3.3.4 Tests on Concrete

Study of the influence of different parameters such as fineness and sulphate content of cement and the ambient temperature to which the concrete is exposed are important. To study the effect of fineness and sulphate content of cement on concrete, the ingredients were kept inside an environmental chamber for 48 hours at a temperature of 27°C and a relative humidity of 65% for preconditioning, and the mixing and casting were carried out at room temperature due to the practical considerations. Immediately after casting, the specimens were moved to the environmental chamber

maintained at 27°C and 65% relative humidity and the specimens were demoulded after 24 hours. Specimens for the 1 day strength were tested immediately after demoulding, and the rest of the specimens were cured in a mist room till the required age. For the study of the effect of temperature on the properties of concrete, the preconditioning of materials, mixing of concrete and casting of specimens was done inside the environmental chamber at 5, 25 and 40°C with a constant humidity of 65% except in the case of 5°C, where the condensation raised the humidity slightly. The compressive and splitting tensile strengths were determined after 3, 7 and 28 days.

3.3.4.1 Preparation of Concrete

The materials were batched and mixed in a pan type AIMIL mixer. In all the cases, the aggregates were assumed to be in saturated surface dry condition. The water needed for saturating them was added according to the absorption coefficients. The cement, fine aggregate and coarse aggregate were mixed for one minute to get a uniform dispersion of the materials. Then, 70% of the mixing water was added and mixed for a minute. The remaining water and superplasticizer were added to the above mixture and blended again for four more minutes.

3.3.4.2 Determination of the Flow Properties of Concrete (Slump Test)

Fluidity of concrete at its fresh state is one of the important properties of concrete when it is transported, placed, compacted and finished. This, in turn affects the long term performance of concrete to a large extent. The flow behavior of concrete has been characterised in this study using the slump test, as per IS 1199 (2004).

The slump test is an easy method and therefore is very commonly used in construction sites. To find the slump of concrete, the concrete prepared as explained above was filled in the slump cone immediately after mixing in three equal layers; each layer was successively tamped 25 times with a tamping rod of 16 mm diameter. The excess concrete was then removed and the top surface was leveled. The mould was removed and the settlement of the concrete was measured.

In addition to the slump of concrete, the loss in slump with time of concrete prepared with the saturation dosage of superplasticizer was also determined to study the influence of fineness and sulphate content of cement on the loss in slump of concrete.

The slump of concrete was determined immediately after mixing, and subsequently 30 and 60 minutes after the addition of water to cement. The mix was kept covered in between the measurements and blended for one minute before taking the measurements. For the study of the influence of temperature on the properties of concrete, concrete was prepared with the saturation dosage of superplasticizer at 25°C for all temperatures.

3.3.4.3 Determination of the Mechanical Properties of Concrete

The compressive strength of concrete were determined to find out the effect of fineness and sulphate content of cement, whereas compressive and splitting tensile strengths of concrete were determined to study the influence of ambient temperature. The tests were done with a Controls Advantest 9 testing machine (see Figure 3.11). The compressive strength was determined on concrete cube specimens of 150×150×150 mm, as per IS 516. The splitting tensile strength of concrete was determined on concrete cylinders of size 150×300 mm as per IS 5816. Two packing strips of hardboard of nominal thickness of 4 mm, conforming to IS 1658, and width approximately 15 mm and length greater than the length of the line of contact of the test specimen were employed. The loading rate used was 1.2 $N/mm^2/min$.

Figure 3.11 Testing machine for concrete

3.3.5 Microstructure Study

Microstructural studies were conducted to understand the influence of superplasticizer and temperature on the hydration behavior, as well as on the hardened properties of

concrete. These studies help understand the hydration behavior of cement paste with superplasticizer at different temperatures, with respect to the formation of new phases, the consumption of unhydrous phases as well as the formation of C-S-H and C-H. There are indirect as well as direct methods for this purpose. The average characteristics of the microstructure of cement paste can be analysed by indirect methods like differential thermal analysis/ thermogravimetric/ differential thermogravimetric analysis (DTA/TG/DTG) and X-ray diffraction (XRD). Morphology and arrangement of various phases of the microstructure are studied by direct methods like scanning electron microscopy (SEM). The degree of hydration at different stages, and the influence of superplasticizer and temperature on the hydration process are investigated in this study with the help of Scanning Electron Microscopy, X-Ray Diffraction and Thermal analysis.

3.3.5.1 Specimen Preparation

Cement paste, with and without superplasticizer, was prepared with a water to cement ratio of 0.35. The saturation dosages of superplasticizer at 25°C were taken as the dosage of superplasticizer for the pastes. To study the effect of temperature on the hydration process and the formation of hydration products, specimens were prepared at 5, 15, 25, 35 and 40°C. Cubes of 50 × 50 × 50 mm were moulded with cement paste, with and without superplasticizer, prepared as explained in Section 3.3.2.1. The specimens were cast and kept at the prescribed temperature for 24 hours, then demoulded and cured in a mist room for various periods. Specimens were tested at half-setting (corresponding to 20 mm Vicat penetration), and 1, 3, 7 and 28 days to study the effect of the evolution of the microstructure. After removing the specimen from the mist room at the prescribed age, it is placed in acetone for 4 days as acetone replaces the pore water and prevents further hydration (solvent exchange process), and dried in the laboratory environment for two days. The dried specimens were then placed in air tight containers for preventing contact with moisture. The required samples were cut from these cubes for the different microstructural analyses. The details of the techniques used are presented in the following subsections.

3.3.5.2 Scanning Electron Microscopy (SEM)

SEM studies were conducted to analyze the influence of temperature and superplasticizer on the microstructure and the composition of hydration products of

cement. SEM and Energy dispersive spectroscopy investigates the microstructure, while image analysis enables the determination of the degree of hydration of the cement. Effect of temperature on the hydration kinetics was also studied with the help of the above techniques. A comparative study of the microstructure of superplasticized cement pastes and reference pastes were done to aid the understanding of the influence of superplasticizer on the hydration process. The comparison of the microstructure of cement pastes at different temperatures gave an idea about the influence of the effect of temperature on the cement paste, with and without superplasticizer.

Sample preparation plays a very important (Scrivener, 1989) role during the microscopy study of cement paste samples especially in the case of backscattering electron imaging. The procedure of sample preparation include the preparation, curing for a predetermined period of time, cutting, grinding and polishing. The samples of approximately 2 square centimeters were cut from the cement paste cubes, prepared as explained in Section 3.3.5.1, using a Struers cutting machine (see Figure 3.12). In order to protect specimens against damage during grinding and polishing process, the specimens were impregnated in vacuum with a low viscosity epoxy resin and consequently allowed to harden at room temperature for 12-16 hours in a Struers epoxy impregnation machine (see Figure 3.13). The impregnated specimens were then carefully ground and polished. Coarse polishing with #500 and #1000 grit paper was done to remove the epoxy from the surface of the impregnated specimens. This surface was then subjected to fine polishing on an automated Struers polishing machine (see Figure 3.14) using a series of successively finer grades of diamond spray: 6, 3, and 1 µm. The sample was checked under an optical microscope to ensure the quality of polishing achieved; normally, 8-9 hours of polishing ensures a good surface. The next procedure involved the coating of specimen with a thin layer of gold-palladium to prevent charging during the analysis.

Figure 3.12 Cutting machine

Figure 3.13 Epoxy impregnation set up

Figure 3.14 Polishing machine for cement paste

The polished specimens were studied using backscattered electron images (BSE). Quantitative X-ray analysis was performed to obtain the elemental composition. BSE images were studied to obtain information about the phases present in the hydrated cement paste (C-S-H, calcium hydroxide, and sulphoaluminates) by analysing the compositional contrast offered by them. This technique was employed by Scrivener (1989) to distinguish the dense and porous phases in the microstructure of same paste. The unhydrated particles have higher molecular weight with higher back scattering intensity than hydrated particles (Zhao and Darwin, 1992; Puertas et al., 2005). In such studies it has been shown that C_4AF has the highest intensity, C-H is brighter than C-S-H and that the pores appear black.

Secondary electron (SE) images were also made to study the topography and morphology of hydrated cement paste. SE image analysis helps study the change in

morphology of different hydration products of cement paste with age. The effect of superplasticizer and temperature on the morphological changes of the cement paste are also studied using this technique.

3.3.5.3 X-ray Diffraction (XRD) Techniques

X-ray diffraction studies are used to analyze changes in the hydration process. XRD is used to identify the polycrystalline phases of hardened cement paste through the recognition of the X-ray patterns that are unique for each of the crystalline phases. So the technique allows the detection of ettringite (AF_t) and portlandite (C-H), along with the anhydrous phases of the cement (gypsum, C_3S, C_2S, C_3A, C_4AF, etc.).

The X-ray diffraction patterns of cement paste prepared at temperatures 5, 25 and 40°C, with and without addition of superplasticizer, at various periods of hydration (i.e., 1, 3, 7 and 28 days) were studied. These ages are selected as reference ages so as to assess the effects of superplasticizer and temperature on the rate of hydration. Samples of about 25 square mm and thickness of about 5 mm were cut from the specimen already prepared, as explained in Section 3.3.5.1. Just before each test, the surface undulations were removed by polishing the surface.

The XRD analysis was made with a Bruker D8 Discover powder diffractometer. In this apparatus, the Cu Kα (λ = 1.5418Å) radiation was produced in a Cu tube at 35kV, 25 mA. The tests were performed over a Bragg angle (2θ) range of 5-75° with a scan speed of one second per step on the samples.

3.3.5.4 Thermal (DTA/TG/ DTG) Analysis

Differential thermal analysis (DTA), as well as thermogravimetric (TG) analysis (DTG), were used to analyze the hydration reactions of superplasticized cement paste. In this technique the material was subjected to continuous heating at a uniform rate and the loss in mass of the sample at various temperatures was studied. The temperature difference, in DTA studies, between the sample and a reference material such as α-Al_2O_3, is analysed while both are subjected to the same heating program (Ramachandran and Beaudoin, 2001).

The loss in weight when the temperature of the substance is increased at a uniform rate was measured in the TGA. The reactions occurring during the heating process are responsible for the changes in the weight of the sample. The knowledge of the various reactions occurring in the cement paste at specific temperatures enables the identification of the constituents of the sample. In thermogravimetric analysis, the weight losses corresponding to thermal decomposition are studied whereas DTG analysis helps locate the temperature peak due to the decomposition of different phases in cement pastes.

The analyses were conducted with a NETZSCH STA 409 C/CD, in nitrogen atmosphere, within a temperature range of 20-1400 ºC, at a uniform rate of 10 K/min. The samples were prepared from the cement paste prepared and preserved as explained in Section 3.3.5.1. The cement paste samples were powdered and sieved through a 75 micron sieve, for the analysis.

CHAPTER 4

EFFECT OF TEMPERATURE ON THE PROPERTIES OF SUPERPLASTICIZED CEMENT PASTE

4.1 INTRODUCTION

A brief description about the cement hydration process and the factors influencing the hydration reactions has been presented in Chapter 2. The influence of superplasticizers and the ambient temperature on the hydration reactions, morphology of hydrated products and their effects on concrete have also been presented. Temperature can influence the fluidity, fluidity retention with time, water demand and setting of superplasticized cement paste and concrete, which in turn can affect the long term performance.

The specific objectives of the work on superplasticized cement pastes are to study the effect of temperature on:

- the fluidity and loss in fluidity with time of cement paste with different families of superplasticizer, using the Marsh cone and mini-slump tests.
- the changes in the water demand of cement and setting time in the presence of a superplasticizer.

In order to achieve the above mentioned objectives, different tests were conducted on cement paste. The various testing procedures adopted are explained in Chapter 3. The fluidity of cement paste was analysed using Marsh cone and mini-slump tests as explained in Sections 3.3.1.1 and 3.3.1.2. In order to study the influence of superplasticizer and temperature on the loss in fluidity, the flow of cement pastes were observed for an hour. The water demand and setting times were determined using the Vicat apparatus (Sections 3.3.1.3 and 3.3.1.4). The details of the experiments are given Section 4.2.

4.2 EXPERIMENTAL DETAILS

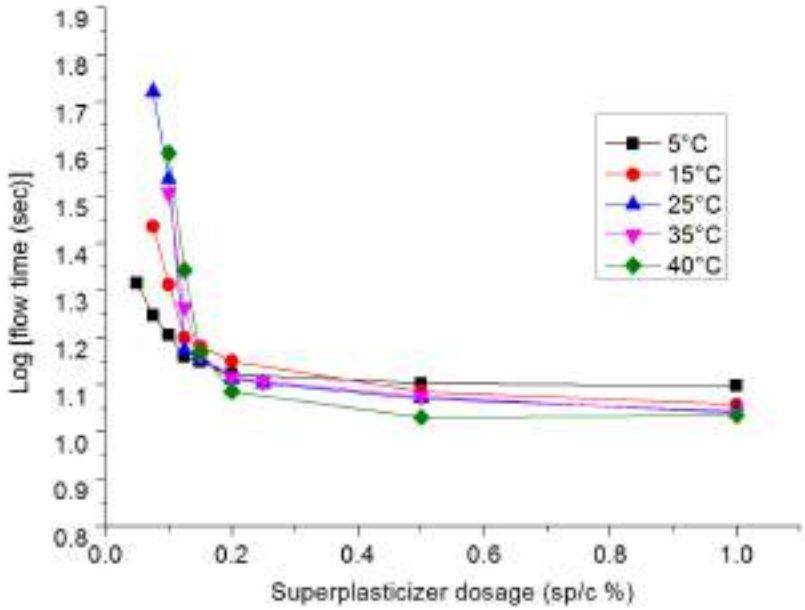
Ordinary 53 grade portland cement conforming to IS 12269 (2004) and de-ionized water were used for this study. The chemical composition of the cement is given in Table 3.1. One commercially available superplasticizer from each of the four families of products available (i.e., polycarboxylate ether (PCE), sulphonated naphthalene formaldehyde (SNF), sulphonated melamine formaldehyde (SMF) and lignosulphonate (LS)), was incorporated in this study. The properties of the superplasticizers used are given in Table 3.2. The superplasticizer dosages are given as the ratio of the solid content of the superplasticizer to cement (sp/c), by weight, and the liquid phase in the superplasticizer has been accounted as part of the water cement ratio (w/c). A constant w/c of 0.35 was used in the study, except in the case of determination of water demand and setting time.

The effect of temperature was studied at 5, 15, 25, 35 and 40°C. A walk-in environmental chamber was used to maintain the temperature of the materials, mixing and measuring equipments and for conducting the experiments. The chamber had a constant humidity of 65%, which was maintained at all the temperatures mentioned above except in the case of 5°C, where the condensation of water raised the humidity slightly. All the materials were maintained at the prescribed temperature for at least 48 hours prior to the test for preconditioning. The temperature of the materials was checked and found to be always within ±2°C of the prescribed temperature. The mixing and testing followed the procedures already explained in Chapter 3. The fabrication, as well as the Marsh cone, mini-slump, standard consistency and setting time tests were done within the chamber.

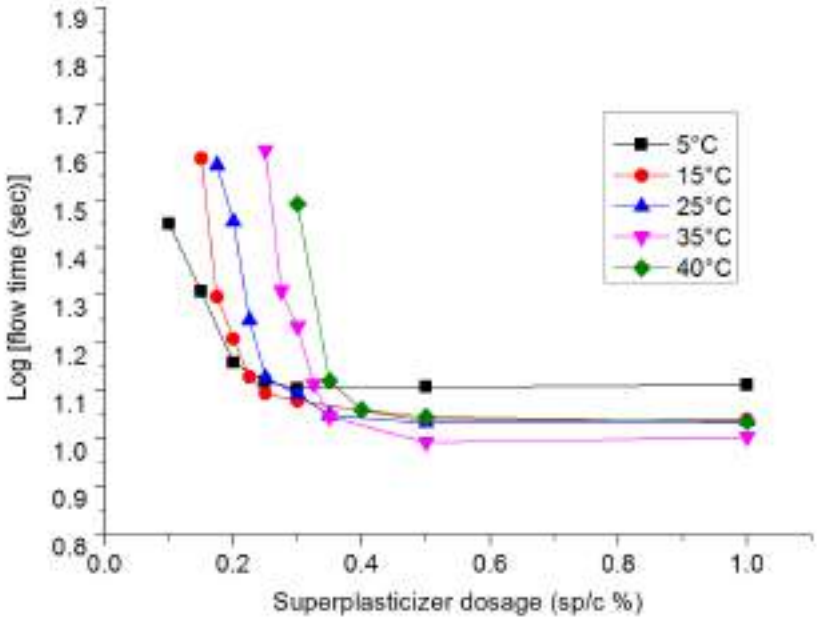
4.3 TEST RESULTS AND DISCUSSION

4.3.1 Effect of Temperature on the Fluidity of Cement Paste

The dependence of the relative fluidity of superplasticized cement paste with temperature is first evaluated here with the help of the Marsh cone tests. In each case, two trials were performed and it was seen that there was not much variation in the results. The results from all the trials are given in Appendix A. Typical results for different types and dosages of superplasticizers are shown in Figures 4.1(a-d).

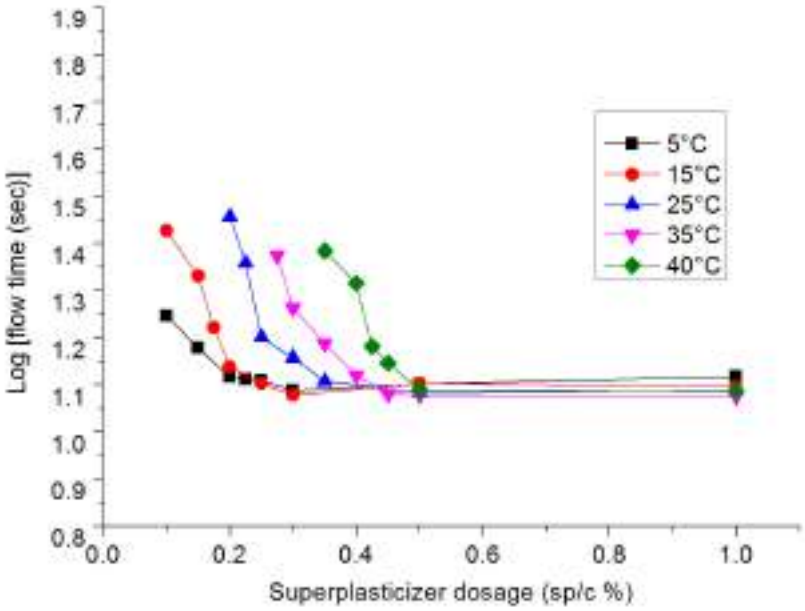


(a)

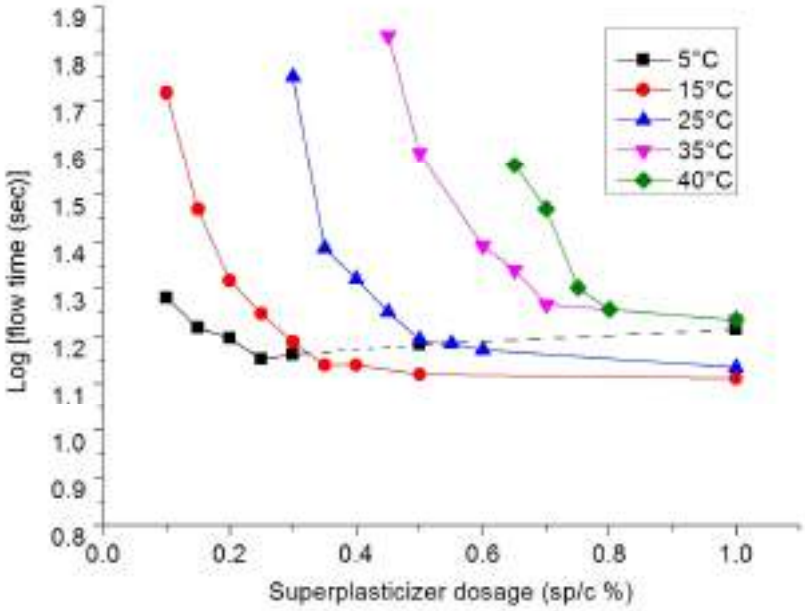


(b)

Figure 4.1 Curves of Marsh cone flow time versus superplasticizer dosage at different temperatures for the superplasticizers (a) PCE and (b) SNF



(c)



(d)

Figure 4.1 Curves of Marsh cone flow time versus superplasticizer dosage at different temperatures for the superplasticizers (c) SMF and (d) LS

All the superplasticized cement pastes (Figure 4.1) show a decrease in flow time with an increase in sp/c until a certain dosage beyond which the decrease in flow time becomes negligible or the flow time increases slightly. This trend corresponds to the expected increase in the fluidity with an increase in superplasticizer content up to the saturation dosage, for given w/c and temperature. The Marsh cone test has been used previously by many researchers to evaluate the relative fluidity and the saturation dosage of superplasticizer (Aitcin, 1998; Agullo et al., 1999; Roncero et al., 1999; Gomes et al. 2001; Jayasree and Gettu, 2008). It has been shown recently by Jayasree and Gettu (2008, 2011b) that the trend of the Marsh cone flow time is similar to that of the Bingham parameters, namely the yield shear stress and the plastic viscosity, with respect to the superplasticizer dosage. It was concluded that beyond the saturation dosage there is no further decrease in either of these two parameters. Moreover, it was found that the saturation superplasticizer dosage denotes the transition of the rheology of the cement paste from viscoelastic to linear viscous behaviour.

It is observed from Figure 4.1 that the fluidity is lower (i.e., the flow time is higher) at higher temperatures when the dosages of superplasticizer are low. The fluidity increases or remains almost constant at higher dosages of superplasticizer, except in the case of the LS based superplasticizer. The lower fluidity observed at higher temperatures and lower dosages of superplasticizer may be due to the higher water demand of cement at higher temperatures and the insufficient quantity of superplasticizer to disperse the cement particles efficiently. In terms of the Bingham parameters, the trend implies that, at lower superplasticizer dosages, the yield shear stress and the plastic viscosity are higher at higher temperatures. This supports the conclusions drawn from viscometer studies by Al-Martini and Nehdi (2007), and Nehdi and Al-Martini (2007). However, at higher dosages of superplasticizer, this effect is compensated and the fluidity increases, as also observed by Roncero et al. (1999). This has been attributed the response to the presence of two competing mechanisms coming to play due to the decrease in fluidity (or consistency) of the superplasticized cement paste caused by a higher water demand of the cement and the increase in fluidity probably due to a decrease in viscosity or an increase in the effectiveness of the superplasticizer at higher temperature (Roncero et al., 1999; Roncero, 2000).

Saturation dosages of different families of superplasticizers calculated from Marsh cone flow time curves at various temperatures (Figure 4.1 a-d) are given in Table 4.1. All the four families of superplasticizers show significant sensitivity to temperature, with the saturation dosage of superplasticizer increasing with an increase in temperature. This can be attributed in part to the higher rate of hydration at higher temperatures (Kjellsen and Detwiler 1992; Escalante-García and Sharp 1998; Mounanga et al. 2004). The PCE based superplasticizer shows the least temperature sensitivity whereas the LS based superplasticizer shows the maximum sensitivity. This confirms the better robustness of the PCE in comparison to the other admixtures

Table 4.1 Saturation dosages of superplasticizer at different temperatures

Temperature (ºC)	sp/c dosage (and corresponding flow time in seconds)			
	PCE	SNF	SMF	LS
5	0.13% (14s)	0.20% (14s)	0.20% (13s)	0.25% (14s)
15	0.13% (16s)	0.25% (12s)	0.25% (14s)	0.35% (14s)
25	0.13% (15s)	0.25% (13s)	0.25% (16s)	0.50% (16s)
35	0.15% (15s)	0.33% (15s)	0.40% (15s)	0.70% (19s)
40	0.20% (12s)	0.35% (13s)	0.45% (16s)	0.75% (18s)

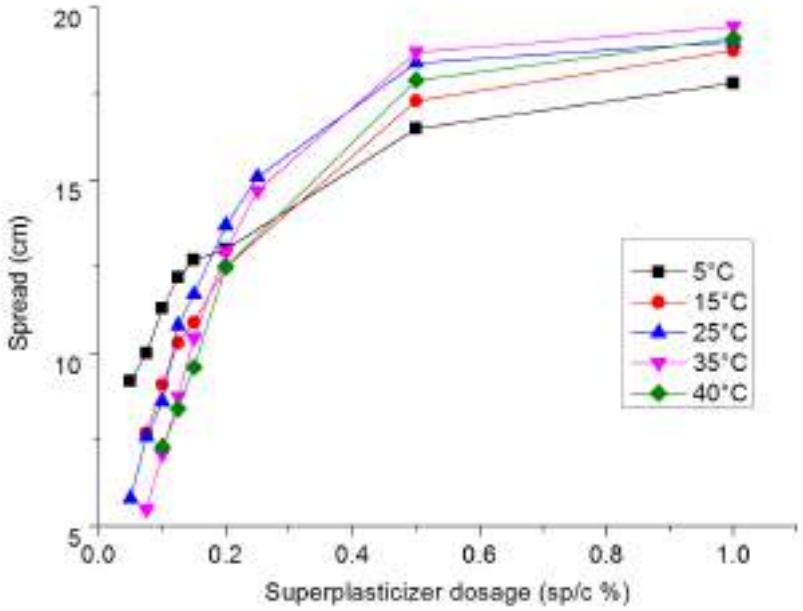
It can be seen in Table 4.1 that the flow times at the saturation dosage are all in the same range (i.e., 12 to 19 seconds), indicating a comparable level of fluidity, and possibly similar rheological behaviour, in all the pastes considered here, when the superplasticizer dosage corresponds to the saturation point.

In Figure 4.1a and Table 4.1, it is observed that the flow of cement paste with the PCE based superplasticizer decreases with an increase in temperature at lower dosages, and increases with temperature at higher dosages but the saturation dosage remains same over the range of 5-25ºC and increases only at higher temperatures. The trends shown by the SNF and SMF based superplasticizers (Figures 4.1b & c) are similar. At lower temperatures (5-25ºC), the saturation dosage remains the same for both superplasticizers. However, at higher temperatures, the SMF based superplasticizer requires a higher dosage compared to the SNF based superplasticizer. At 5°C, both

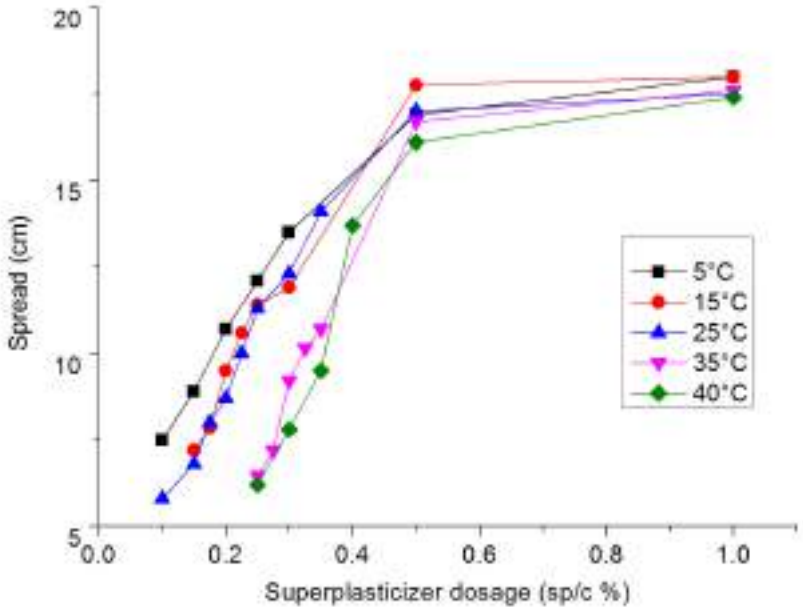
SNF and SMF based superplasticizer have a saturation dosage of 0.2%, which increases to 0.25% at 15° and 25°C. At 35°C and 40°C, the SNF based superplasticizer had lower saturation dosages than the SMF based superplasticizer. This indicates that the SNF based superplasticizers are more effective at higher temperatures compared to SMF based superplasticizer, even though at lower dosages both can have almost the same effect. The LS based superplasticizer shows more susceptibility to changes in temperature (Figure 4.1d); there is a reduction in the flow at all dosages with temperature, which may be due to the lower efficiency of the dispersing mechanism of LS based superplasticizer at higher temperatures. In contrast with the behaviour of the other superplasticizers, the LS gives higher flow times (i.e., lower fluidity) at higher temperatures. Note that at higher dosages (0.5 and 1%) of the LS based superplasticizer at 5ºC, segregation was observed, to indicate which the curve is plotted with dashed lines.

The increase in saturation dosage with temperature observed here is in accordance with the observations of Nehdi and Al-Martini (2007). On the contrary, Fernandez-Altable and Casanova (2006) did not observe any significant effect of temperature on the saturation dosage of a PCE based superplasticizer. This may be because the cement pastes were prepared by them at ambient temperature and then tested at different temperatures, whereas in the present study all the material components and the paste were always at the prescribed temperature.

Figures 4.2 a-d shows the graphs of mini-slump spread versus superplasticizer (sp/c) dosage. From the results, it is observed that the mini-slump spread generally increases with an increase in superplasticizer dosage for all superplasticizers, which reaffirms the trends observed in Marsh cone test. The mini-slump results also show that the spread is lower at higher temperatures and at lower dosages of superplasticizer, and the flow increases at the higher temperatures and at higher dosages of superplasticizer, which again supports the trends observed in the Marsh cone test results.

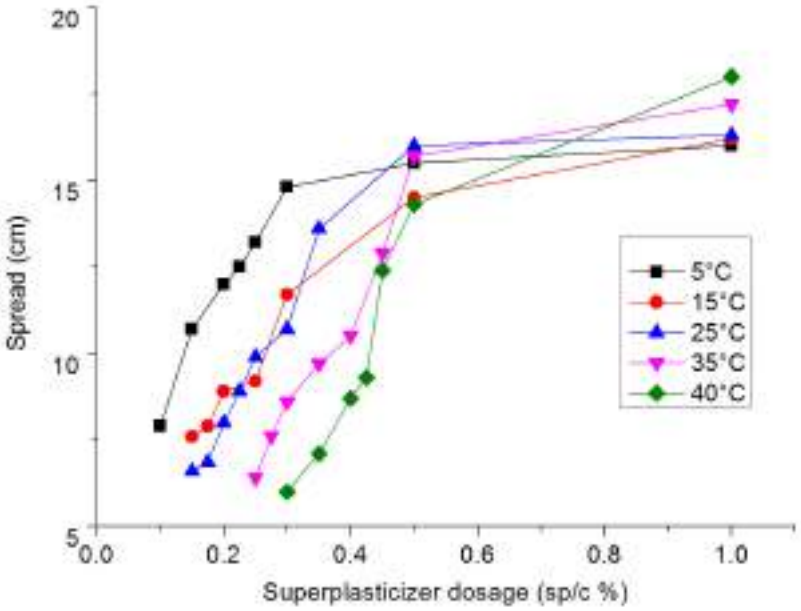


(a)

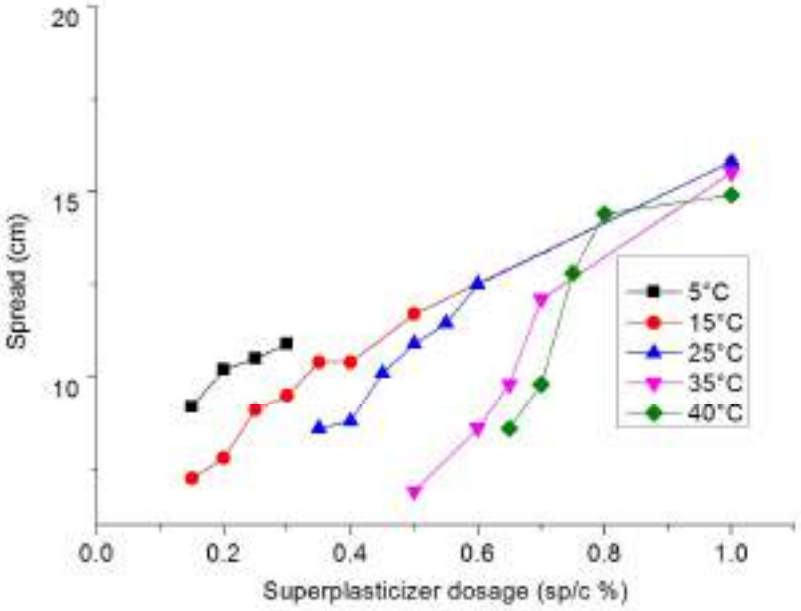


(b)

Figure 4.2 Curves of mini-slump spread versus superplasticizer dosage at different temperatures for the superplasticizers (a) PCE and (b) SNF



(c)



(d)

Figure 4.2 Curves of mini-slump spread versus superplasticizer dosage at different temperatures for the superplasticizers (c) SMF and (d) LS

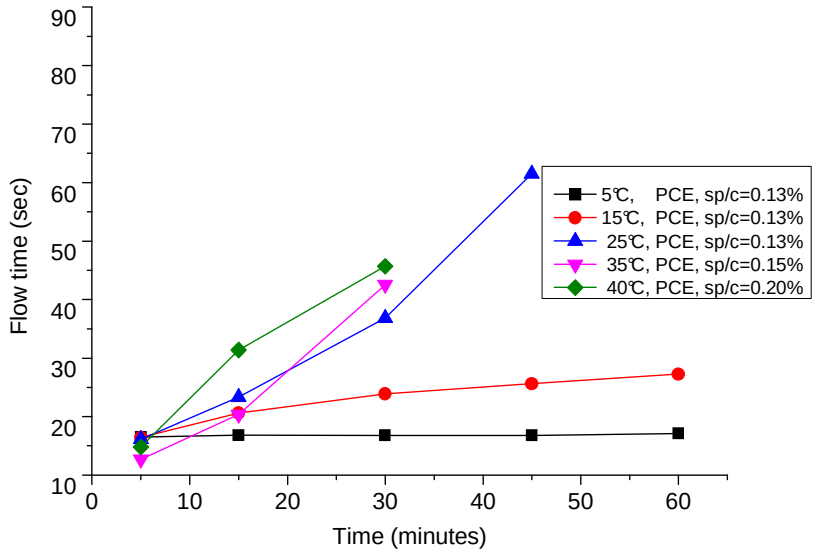
From Figure 4.2a, it is clear that the mini-slump spread of the PCE based superplasticized cement paste increases with an increase in superplasticizer dosage. The spread is lower at higher temperatures for lower superplasticizer dosages whereas it increases with temperature at higher dosages, which supports the results obtained from Marsh cone. A similar trend can be seen in Figures 4.2b and 4.2c showing the plots for SNF and SMF based superplasticized cement pastes, respectively. The LS based superplasticizer (see Figure 2.4d) shows a clear reduction in spread as temperature increases at all temperatures. Data pertaining to pastes with LS that exhibited segregation have been excluded from the plots, i.e., at 5ºC with 0.5% and 1.0% sp/c dosages.

4.3.2 Effect of Temperature on Evolution of Fluidity with Saturation Superplasticizer Dosage

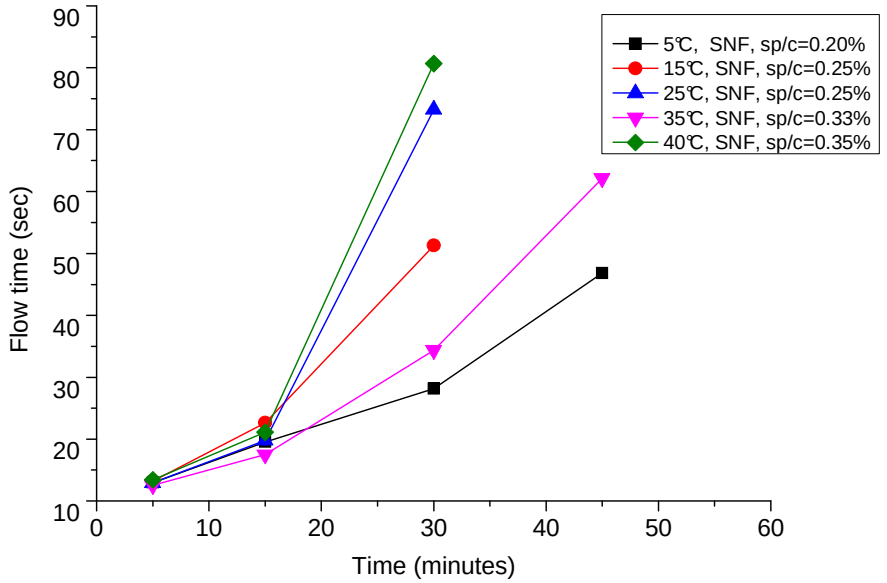
Marsh cone and mini-slump tests were performed immediately after mixing and subsequently 15, 30, 45 and 60 minutes after, on pastes with the saturation dosage of superplasticizer at each temperature. In each case, after every measurement, the paste was kept covered (without agitation) and was mixed for 30 seconds at medium speed (with shaft speed of 285 rpm and planetary speed of 125 rpm) before the subsequent reading. The saturation dosages of superplasticizer used at the different temperatures are those given in Table 4.1.

4.3.2.1 Marsh cone test results

The evolution of the Marsh cone flow time is plotted in Figures 4.3 a-d for pastes with saturation dosages corresponding to each temperature.

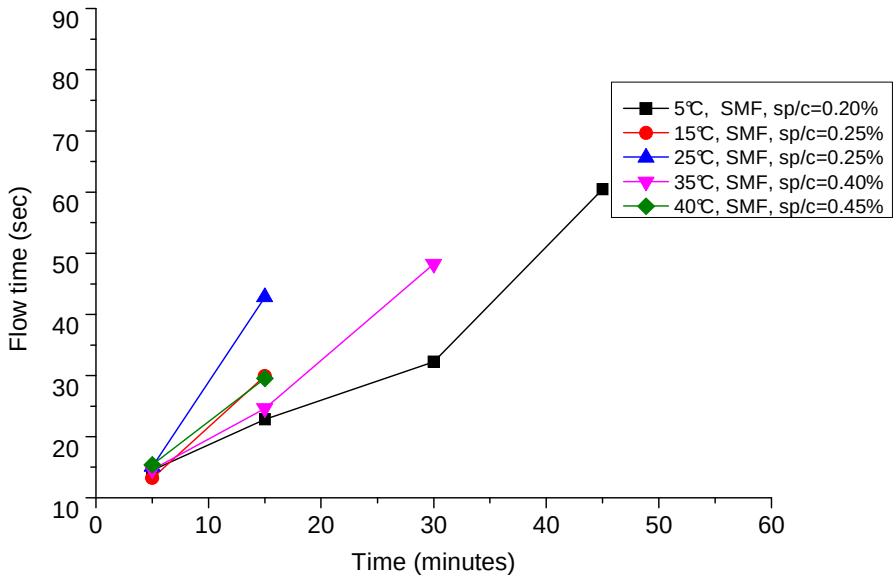


(a)

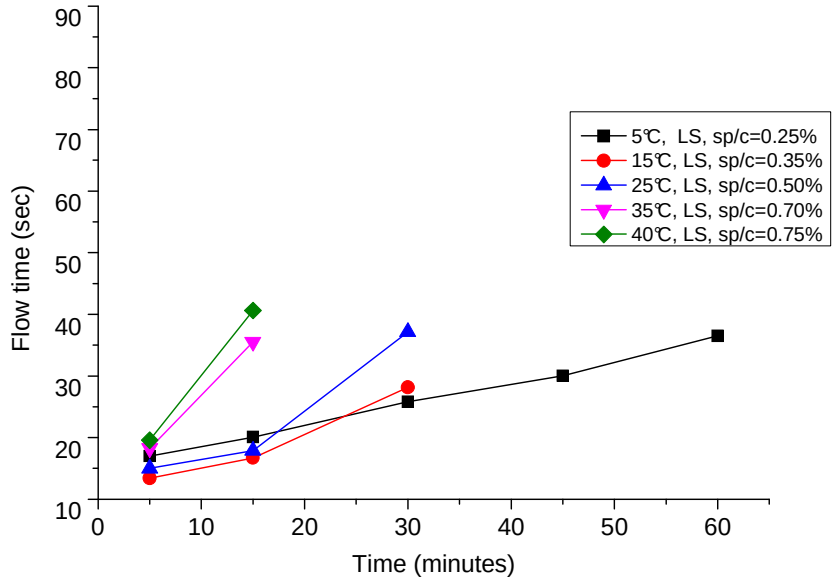


(b)

Figure 4.3 Evolution of Marsh cone flow time at different temperatures for superplasticizers based on (a) PCE and (b) SNF



(c)



(d)

Figure 4.3 Evolution of Marsh cone flow time at different temperatures for superplasticizers based on (c) SMF and (d) LS

From the test results (Figure 4.3a-d) it is observed that the fluidity of cement paste generally decreases with time. Similar increase in the Marsh cone flow time with time

has also been recorded by previous researchers (Agullo et al., 1999; Roncero et al., 1999; Jayasree and Gettu, 2008). This trend is also supported by the increase observed in the Bingham rheological parameters (i.e., yield shear stress and plastic viscosity) of the superplasticized cement paste with time in the studies of Roy and Asaga and Roy (1980), and Jayasree and Gettu (2008). The change in the rheological behaviour with time can be attributed to hydration reactions, intercalation of superplasticizers, chemical degradation of the polymer due to the high pH of the aqueous solution and physical relaxation or change in molecular structure due to adsorption (Tattersall and Banfill, 1983; Justnes et al., 2003; Jayasree et al., 2011a).

It is also observed from the present test results that the loss in fluidity with time generally increases with an increase in temperature, which may be due to higher rate of hydration due to the increase in temperature and the consumption of superplasticizer by the new hydrates. The increased rate of hydration results in the accelerated decrease in free water at higher temperatures. Ravina and Soroka (1994) state that the reduction in free water causes stiffening causing an increase in the rate of fluidity loss with the rise in temperature. Earlier researchers observed that the higher temperatures increase superplasticizer adsorption, which leads to better the initial fluidity and increases the superplasticizer demand for flow retention over a certain range of temperatures (Roncero et al., 1999; Griesser, 2002). The adsorption of the admixtures over the cement particles plays a key role in the workability retention. Some admixtures are designed to have a rapid adsorption and others are designed to have a delayed adsorption in order to better control the workability loss, having enough available molecules in the solution that will be adsorbed over time ensuring, in this way, good workability retention. Kim et al. (2000) observed an inverse relation between the superplasticizer adsorption and fluidity in the naphthalene based superplasticizer. It was concluded that the initial fluidity will be more with higher initial adsorption, which leads however to lower fluidity retention. Also, the temperature increase causes an increase in the reactivity of C_3A, which leads to more rapid loss of fluidity and formation of higher ettringite contents with finer morphology in the presence of superplasticizer (Ramachandran et al., 1998; Greisser, 2002; Spiratos et al., 2003).

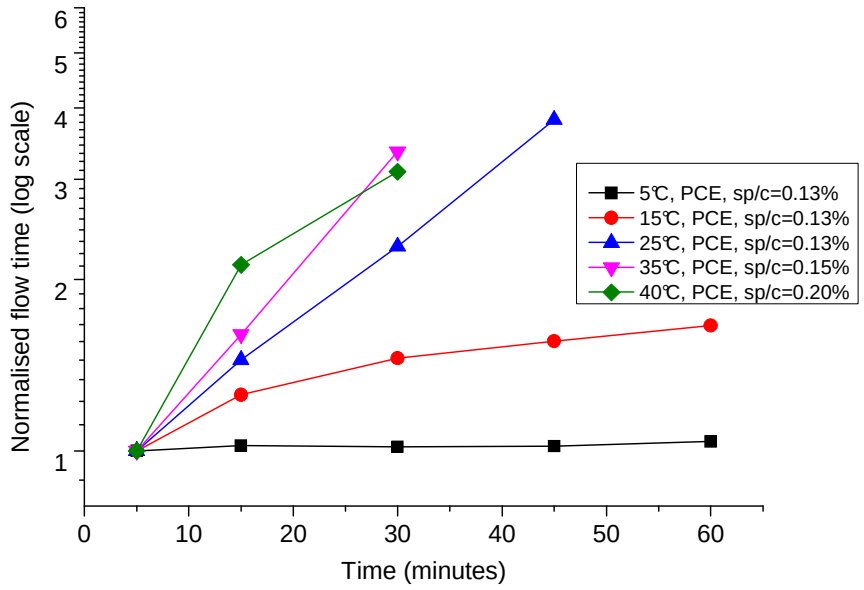
The flow trend of PCE based superplasticized cement pastes with time for different temperatures is shown in Figure 4.3a. It is observed that the loss in fluidity with time increases with an increase in temperature. At 5ºC and 15ºC, the pastes exhibit good flow even after an hour, whereas at 25ºC the paste does not exhibit continuous flow even beyond 45 minutes. Similarly, the pastes do flow freely through the cone after 30 minutes at 35ºC and 40ºC. (Note that data pertaining to discontinuous flow through the Marsh cone are not shown in the plots.)

In the case of the SNF based superplasticizer (Figure 4.3b), except at 35ºC, there is lower flow retention with an increase in temperature. At 35ºC, the cement paste with SNF based superplasticizer shows better flow retention compared to 15ºC and 25ºC, which may due to the slightly higher saturation dosage of superplasticizer at 35ºC, which may increase the superplasticizer available for adsorption a later stage.

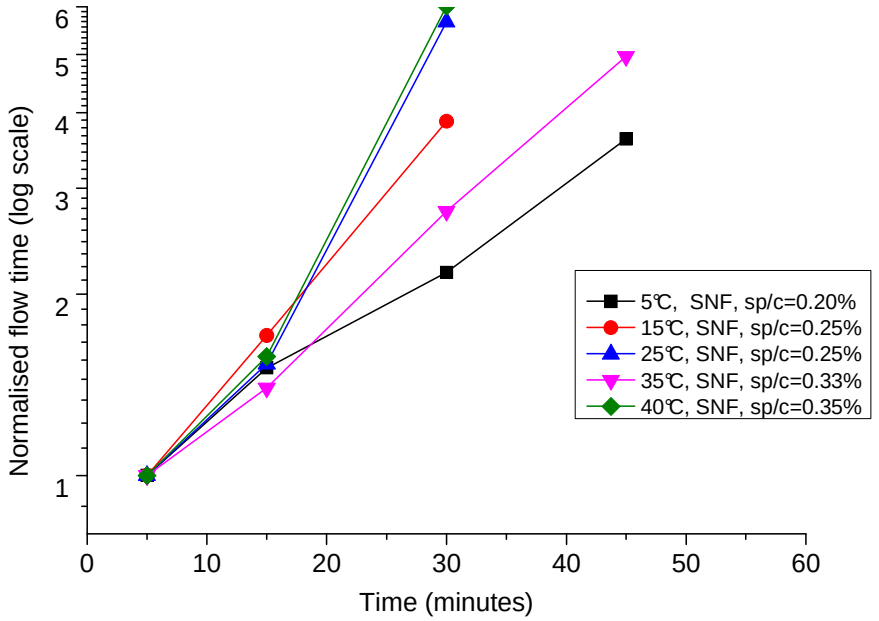
The SMF based superplasticizer (Figure 4.3c) also showed a reduction in flow retention with temperature. At 5ºC, the cement paste had good flow till 45 minutes, whereas at 15ºC, 25ºC and 40ºC, the paste does not show any continuous flow after 15 minutes and at 35ºC it showed a continuous flow till 30 minutes. The better flow retention at higher temperatures (i.e., at 35ºC and 40ºC) could be due to the higher saturation dosage of superplasticizer at higher temperature.

The LS based superplasticizer shows a clear reduction in flow retention with temperature (Figure 4.3d). At 5ºC, the LS based superplasticized cement paste shows good flow for one hour whereas at 15°C and 25ºC, it does not show any continuous flow after 30 minutes; and at 35°C and 40ºC, it does not exhibit continuous flow beyond 15 minutes.

In the test results, it can be observed that the initial flow time varies slightly from one temperature to another. In order to get a better comparison of the flow times, the values have been normalized by the initial flow time at that temperature. The semi-log plots of normalized flow time versus time after mixing are shown in Figures 4.4 (a-d), where the trends are the same as those identified in Figures 4.3 but the variations are more clear.

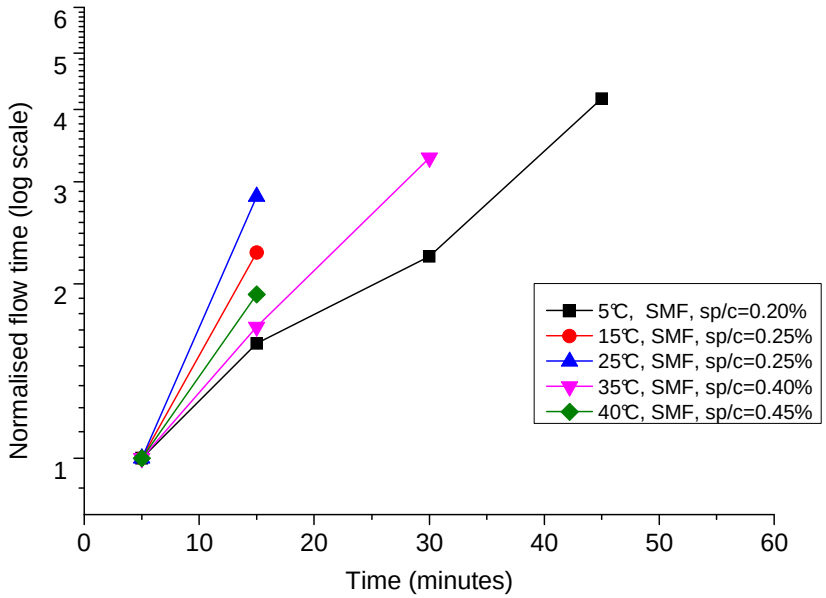


(a)

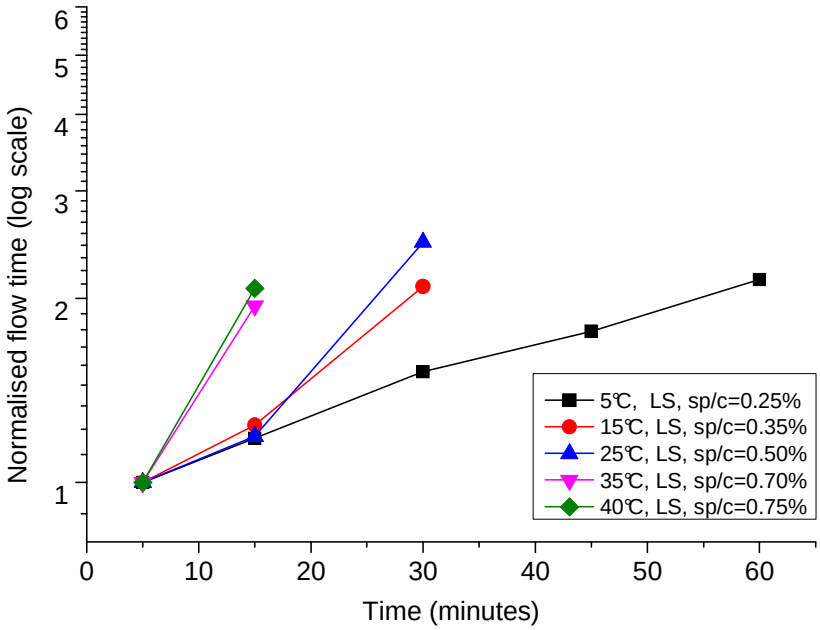


(b)

Figure 4.4 Evolution of normalized Marsh cone flow time at different temperatures for superplasticizers based on (a) PCE and (b) SNF



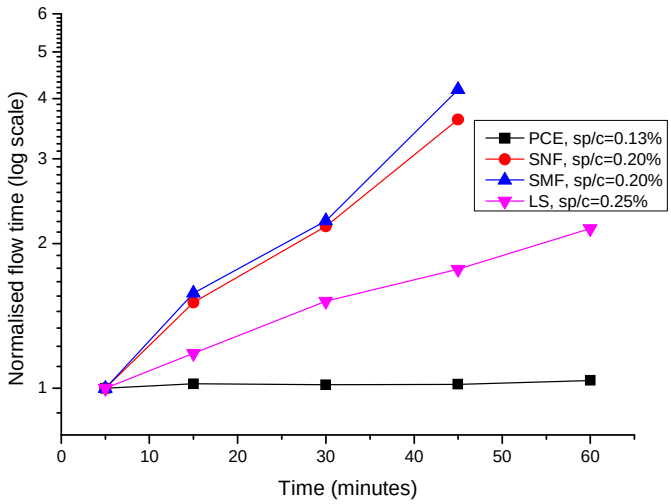
(c)



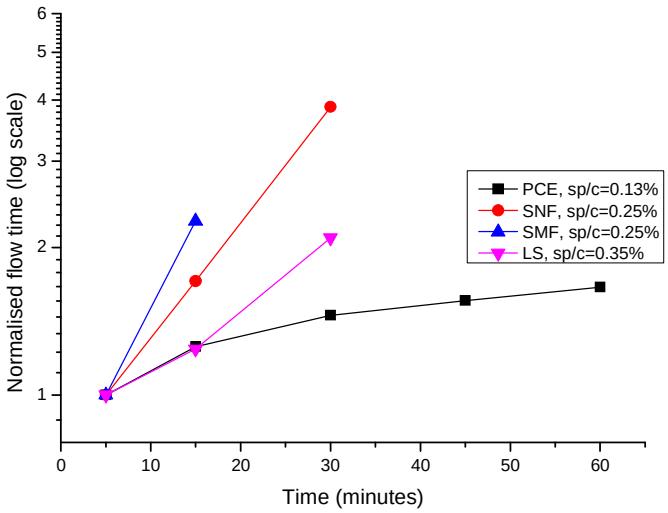
(d)

Figure 4.4 Evolution of normalized Marsh cone flow time at different temperatures for superplasticizers based on (c) SMF and (d) LS

In order to compare the evolution of fluidity of the different superplasticizers at a given temperature in the pastes with the saturation dosage of superplasticizer, the normalized Marsh cone flow time is plotted against time for each temperature in Figures 4.5 a-e.

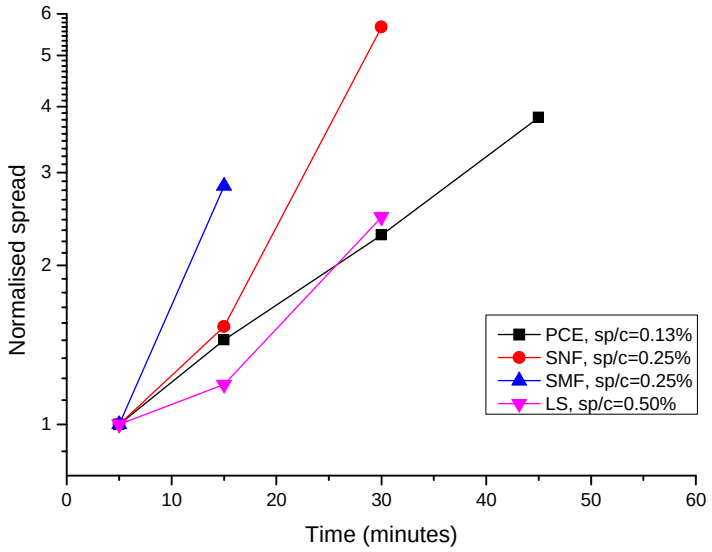


(a)

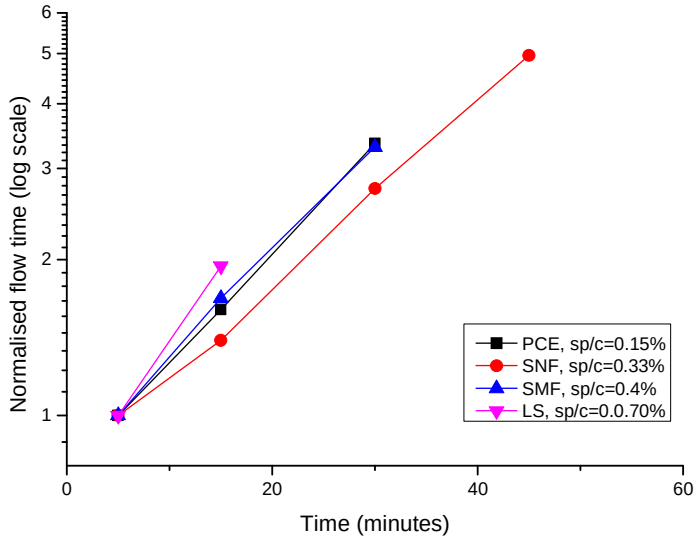


(b)

Figure 4.5 Evolution of normalized Marsh cone flow time for different superplasticizers at different temperature (a) 5°C and (b) 15°C

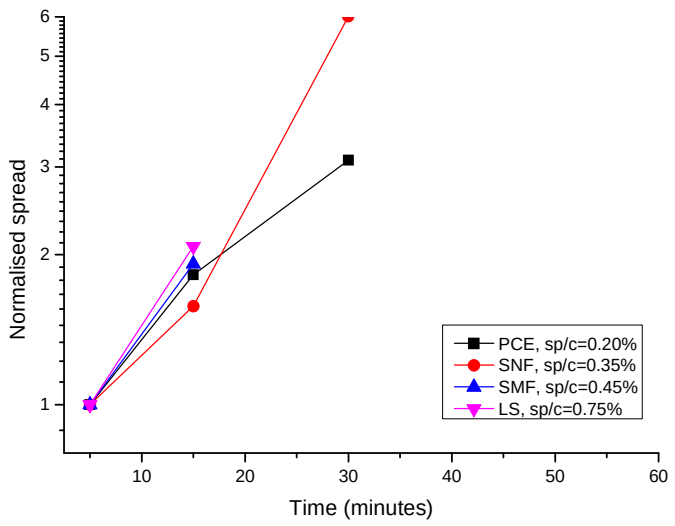


(c)



(d)

Figure 4.5 Evolution of normalized Marsh cone flow time for different superplasticizers at different temperature (c) 25°C and (d) 35°C



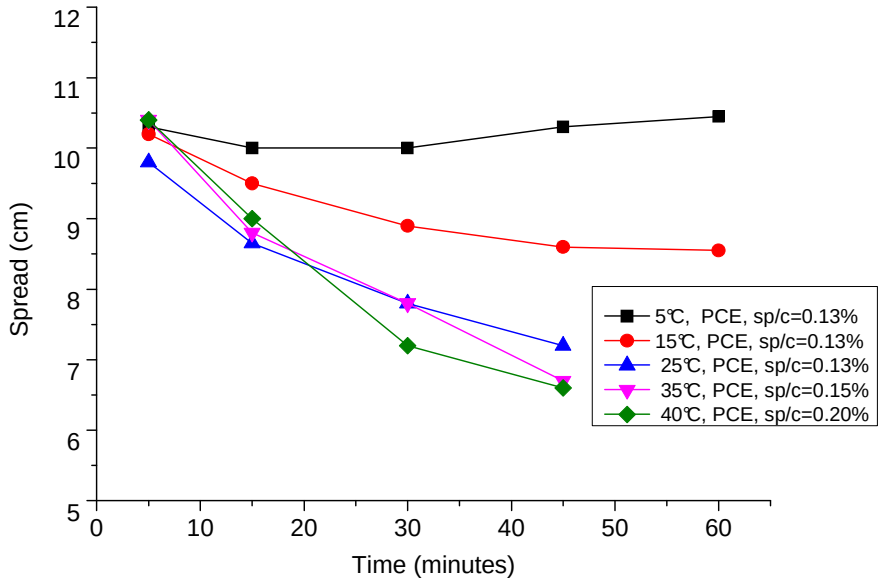
(e)

Figure 4.5 Evolution of normalized Marsh cone flow time for different temperature at different superplasticizers (e) 40°C

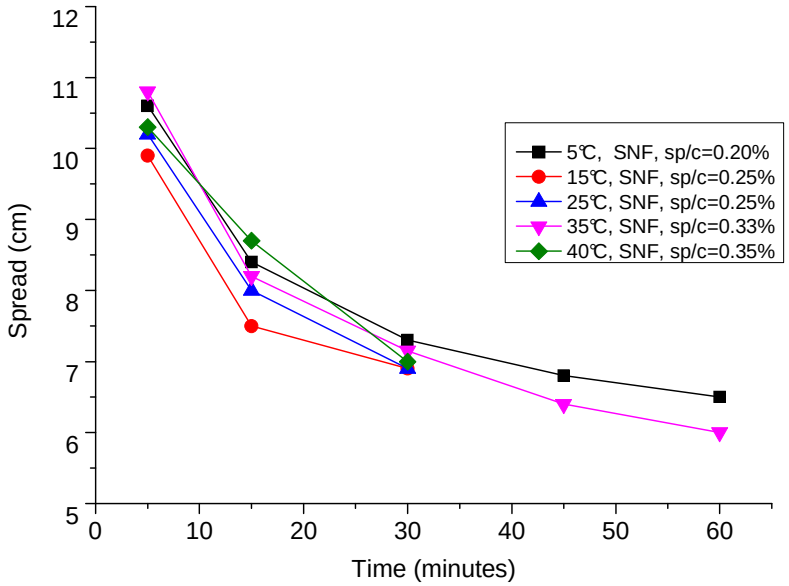
The PCE based superplasticizer shows the lowest loss in flow with time at all temperatures, except at 35°C, possibly because of the lower increment in the superplasticizer dosage at 35°C compared to the other superplasticizers. At lower temperatures (i.e., 5-25°C), the SMF based superplasticizer shows the maximum loss in fluidity with time. The LS based superplasticizer showed better flow retention compared to the SNF and SMF based superplasticizers at lower temperatures; however, at higher temperatures (35°C and 40°C), the yielded a higher loss in fluidity compared to other superplasticizers.

4.3.2.2 Mini-slump test results

The mini-slump spread was also measured for one hour for cement pastes with the saturation dosage of superplasticizer. The spread is plotted against time in Figures 4.6(a-d). The mini-slump spread generally decreases with an increase in time, as also observed by earlier researchers (Kantro, 1980; Lim et al., 1999). The trends indicate the decrease in fluidity with time, which reaffirm the Marsh cone test results.

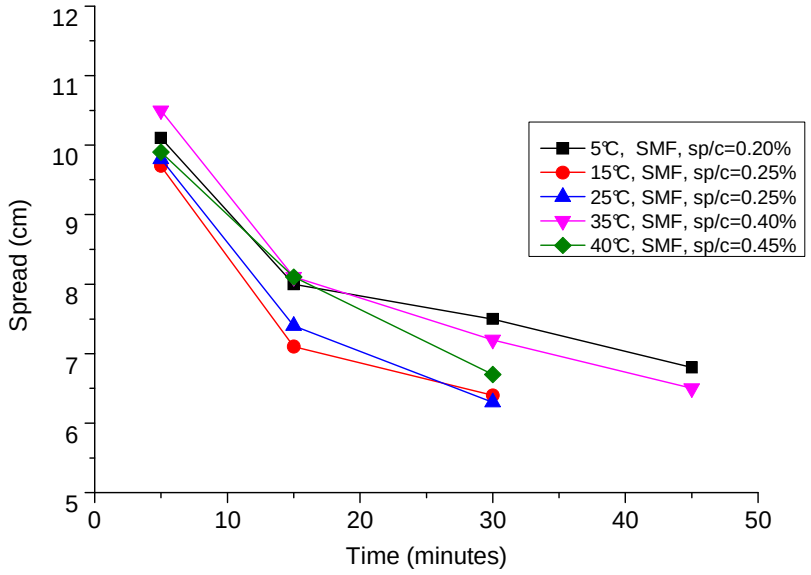


(a)

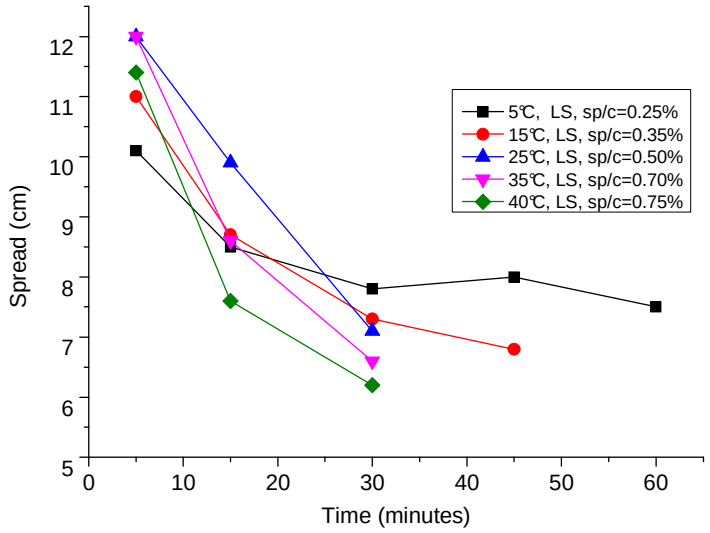


(b)

Figure 4.6 Curves of mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE and (b) SNF



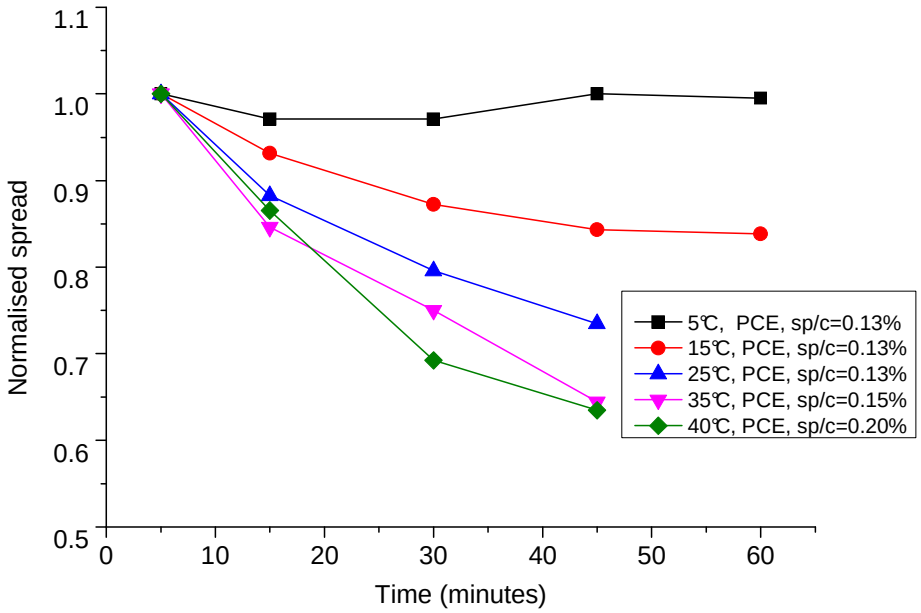
(c)



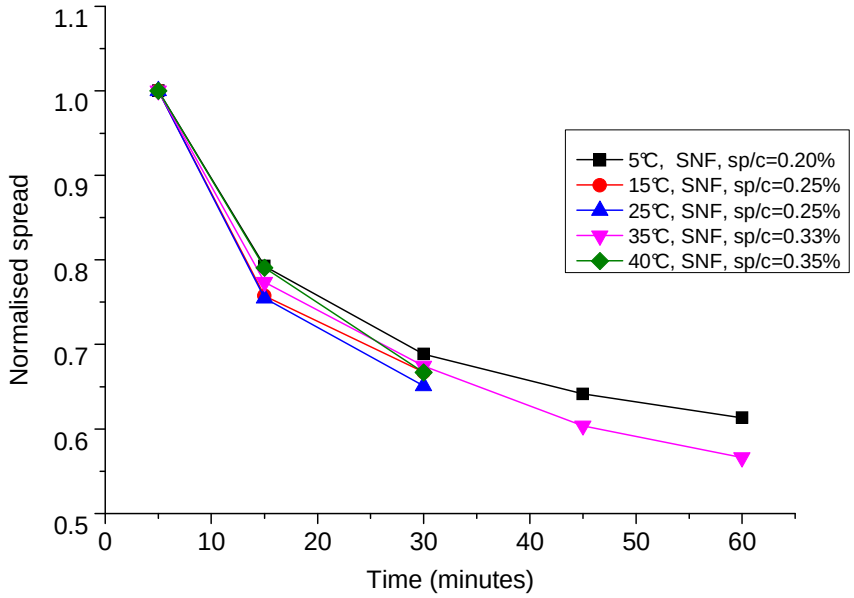
(d)

Figure 4.6 Curves of mini-slump spread versus time at different temperatures for superplasticizers based on (c) SMF and (d) LS

The mini-slump spread curves have also been normalized as there are differences in the initial spreads at different temperature. The normalized curves with reference to the initial flow are shown in Figures 4.7a-d.

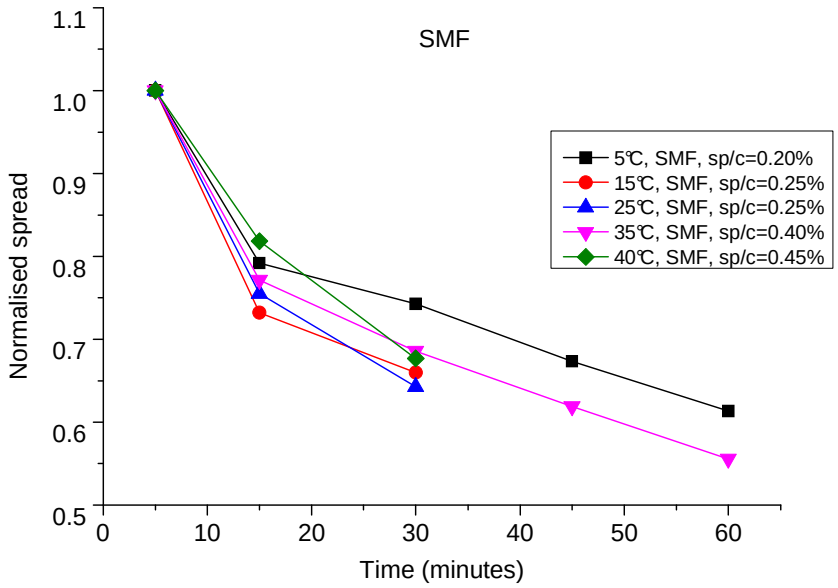


(a)

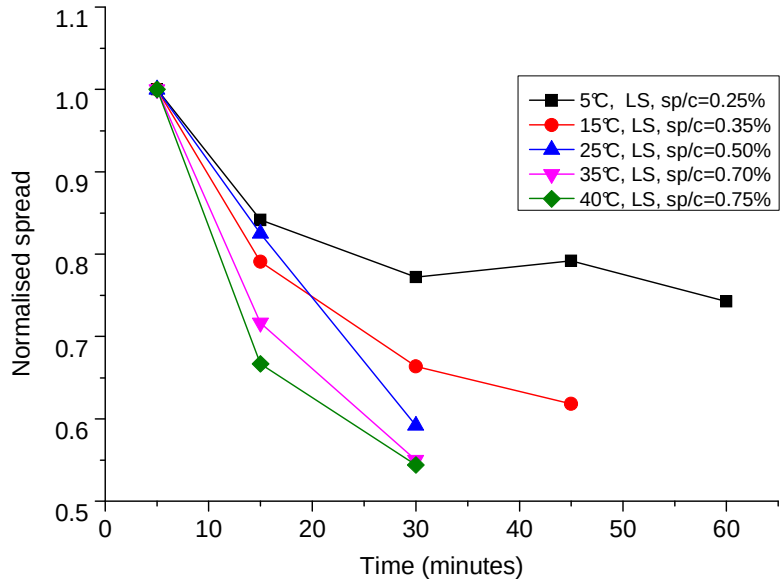


(b)

Figure 4.7 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE and (b) SNF



(c)

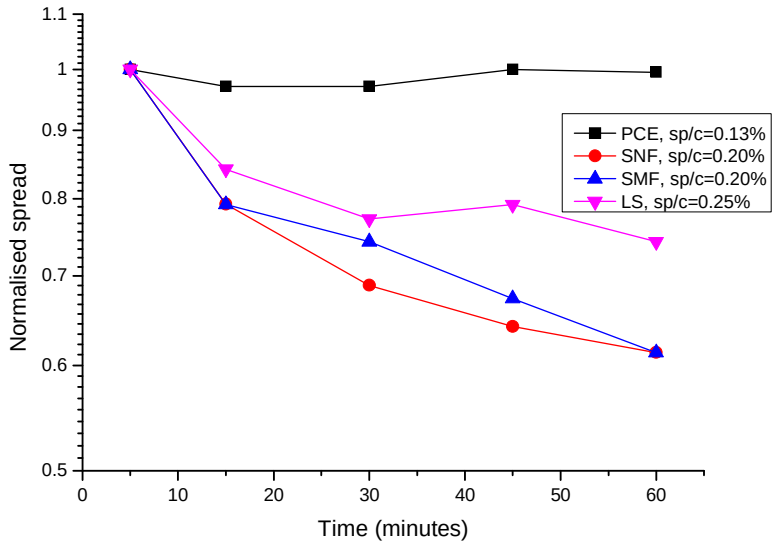


(d)

Figure 4.7 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (c) SMF and (d) LS

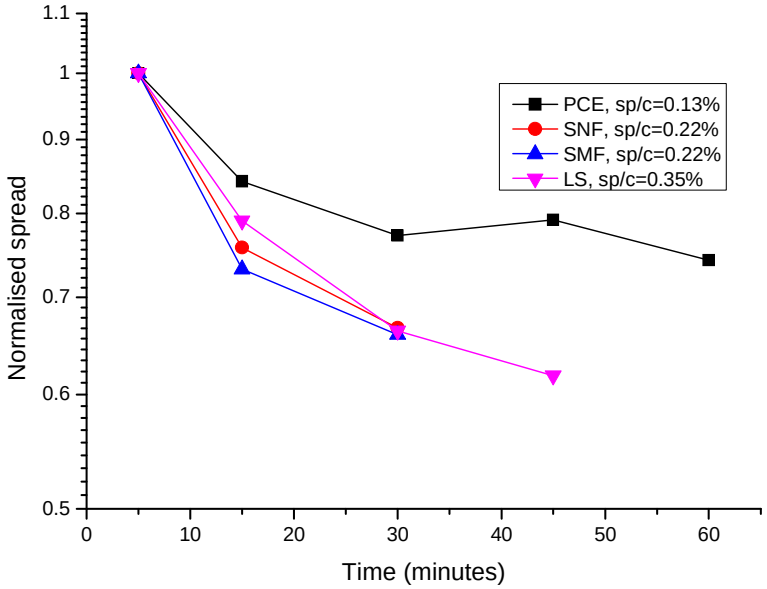
It is observed from the mini slump test results (Figures 4.7 a-d) that the loss in spread generally increases with an increase in temperature. At lower temperatures, the PCE based superplasticizer does not yield any significant loss in flow; however; at higher temperatures there is a higher loss in fluidity with time. The loss in spread with time is more predominant in the case of SNF and SMF based superplasticizers at all temperatures. The pastes with SNF and SMF show slightly lower loss in spread at higher temperatures (i.e., at 35°C and 40°C) compared to lower temperatures, possibly due to of the higher dosage of superplasticizer at higher temperatures, as also observed in the Marsh cone tests. The LS based superplasticizer yields a clear increase in the loss in spread at higher temperatures.

The normalised mini-slump spread is plotted against time in Figures 4.8 a-e for the different temperatures to compare the effect of type of superplasticizer on the loss in spread. It is observed that the PCE based superplasticizer gives a lower loss in spread with time compared to the other superplasticizers, the SMF based superplasticizer gives a higher loss in spread at the lower temperatures and LS based superplasticizer gives a higher loss in spread at higher temperatures.

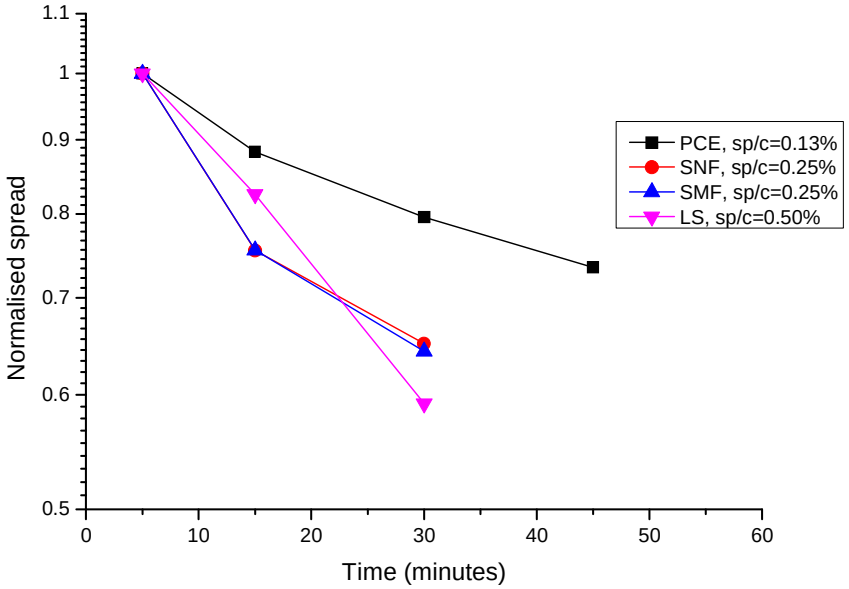


(a)

Figure 4.8 Curves of normalized mini-slump spread versus time at different superplasticizers for different temperature (a) 5°C

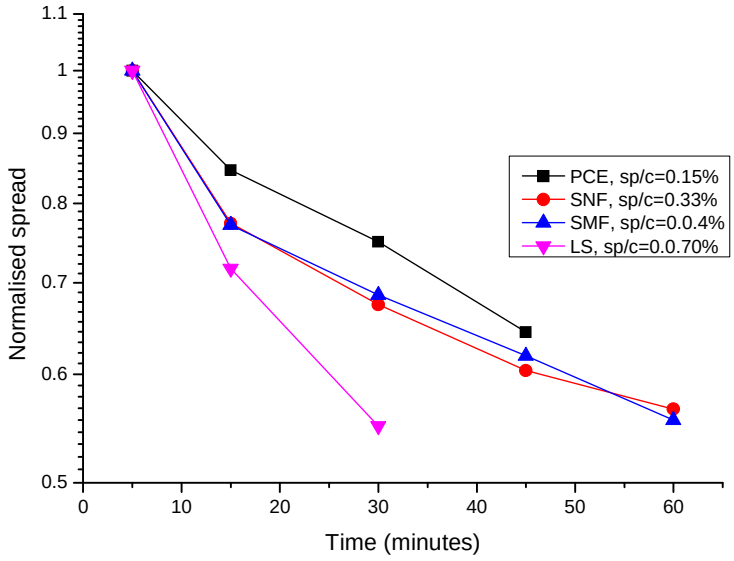


(b)

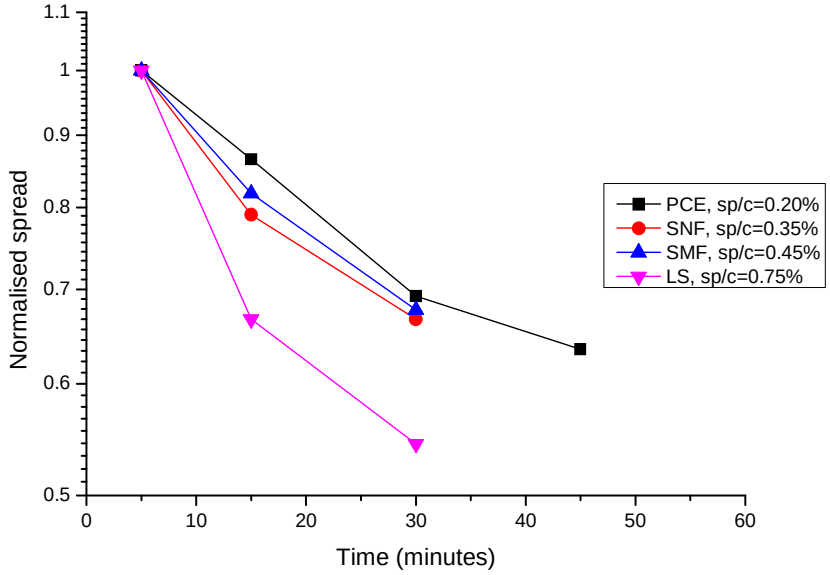


(c)

Figure 4.8 Curves of normalized mini-slump spread versus time at different superplasticizers for different temperature (b) 15°C and (c) 25°C



(d)



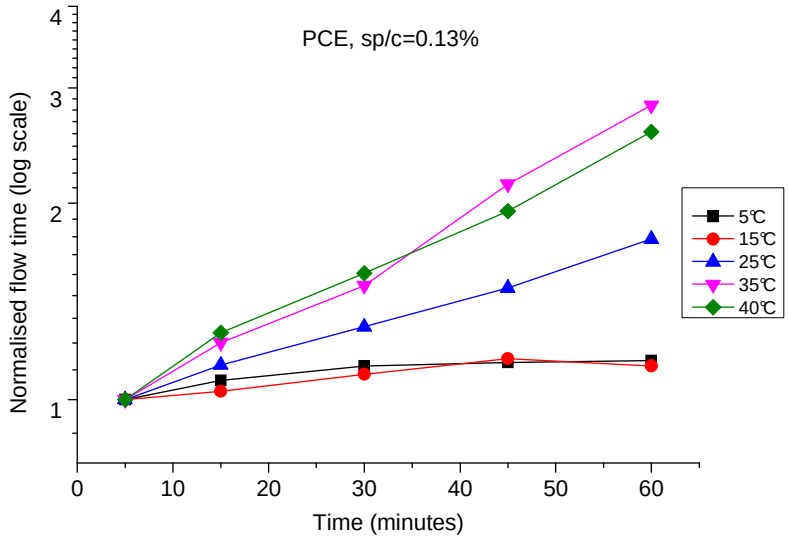
(e)

Figure 4.8 Curves of normalized mini-slump spread versus time at different superplasticizers for different temperature (d) 35°C and (e) 40°C

4.3.3 Effect of Temperature on the Loss in Fluidity with Time for Superplasticizer Dosages Corresponding to the Saturation Dosages at 25°C

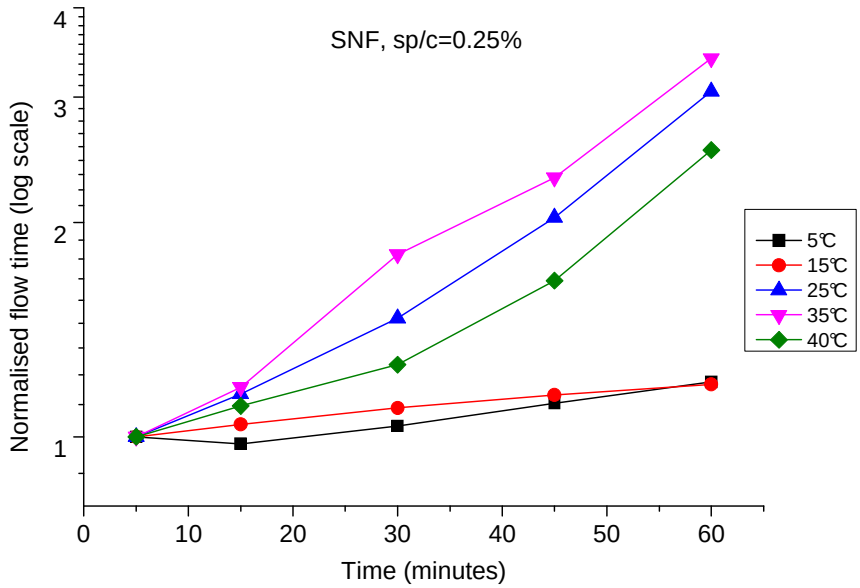
The previous section describes the loss in fluidity with temperature at the dosages of superplasticizer corresponding to the saturation dosage at each temperature and the coupled effect of temperature and dosage have been analysed. In order to study the effect of temperature alone on the loss in fluidity of cement paste, the (same) dosage of superplasticizer corresponding to the saturation dosage at 25°C was used at all temperatures, and the Marsh cone and mini-slump tests were performed as discussed earlier. These studies were conducted with a different batch of cement and superplasticizer and some difference in flow behaviour was consequently observed.

Figures 4.9 a-d shows the plots of the normalised Marsh cone flow time versus time after mixing for cement pastes prepared with the dosage of superplasticizer corresponding to the saturation dosage at 25°C. It is observed from the results that the flow retention generally decreases with an increase in temperature.

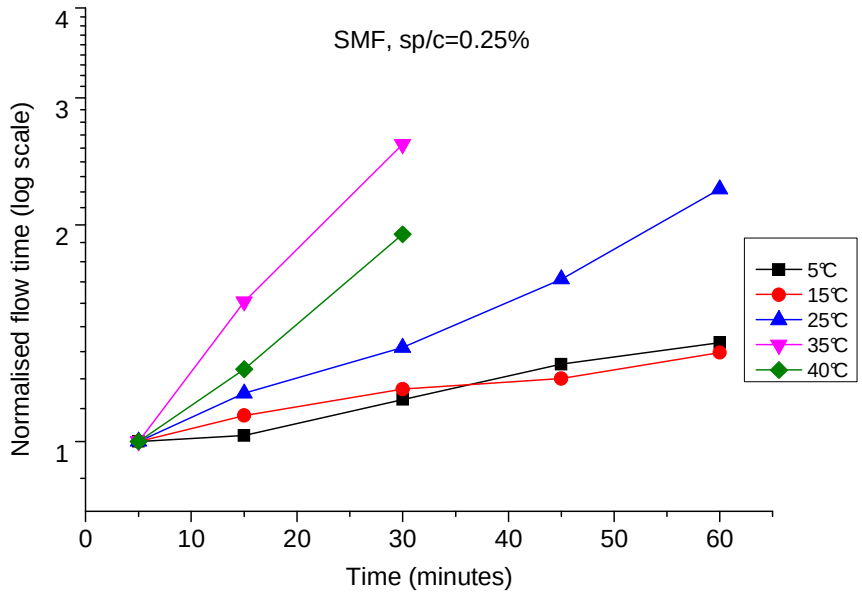


(a)

Figure 4.9 Curves of normalized Marsh cone flow time verses time at different temperatures for superplasticizers based on (a) PCE for dosages corresponding to the saturation dosages at 25°C

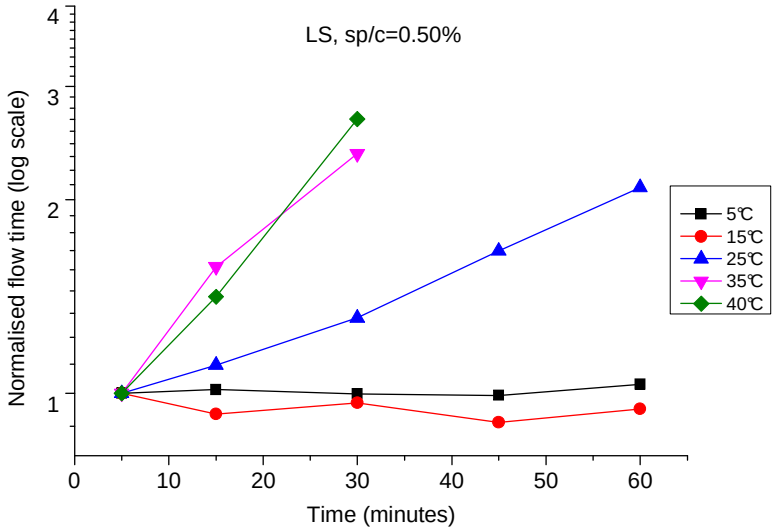


(b)



(c)

Figure 4.9 Curves of normalized Marsh cone flow time verses time at different temperatures for superplasticizers based on (b) SNF and (c) SMF for dosages corresponding to the saturation dosages at 25°C

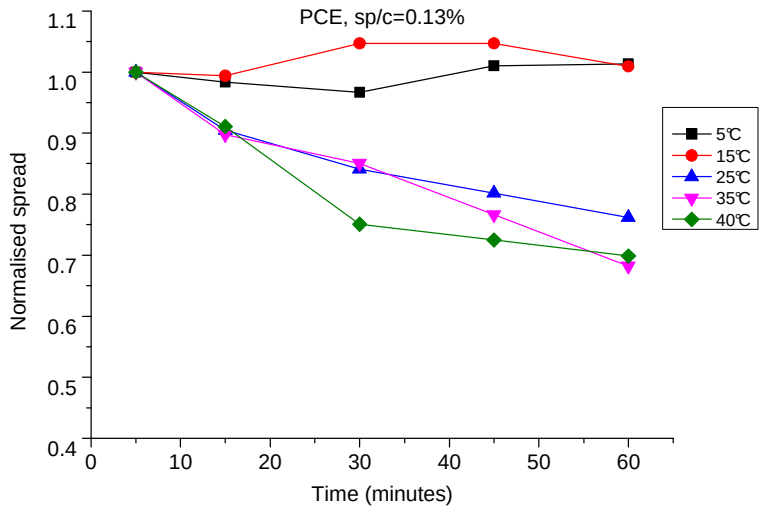


(d)

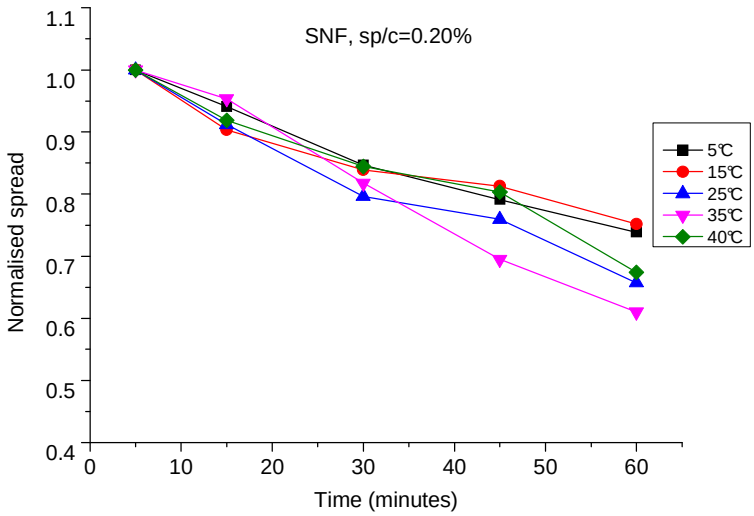
Figure 4.9 Curves of normalized Marsh cone flow time verses time at different temperatures for superplasticizers based on (d) LS for dosages corresponding to the saturation dosages at 25°C

In general, the loss in fluidity is low at 5ºC and 15°C in all the pastes with significant reduction in fluidity at 35°C and 40°C. In all the cases, the maximum reduction in fluidity is seen at 35°C. A similar trend was observed by Roncero et al. (1999) in their studies. From the flow pattern seen for the PCE based superplasticized cement pastes (Figure 4.9 a), it is observed that flow retention is good at 5ºC and 15°C up to one hour. However, at higher temperatures (25-40°C), the pastes exhibit considerable loss in fluidity with time. In the case of cement pastes with the SNF and SMF based superplasticizers (Figures 4.9 b&c) there is some loss in fluidity even at lower temperatures (5ºC and 15°C) and more significant loss in fluidity at higher temperatures (25-40°C). The SMF based superplasticizer does not give any flow after 30 minutes for the temperatures 35ºC and 40°C, which implies that the SMF based superplasticizers are the most susceptible to temperature in terms of flow retention. The LS based superplasticizer (Figure 4.9d) is able to maintain the fluidity for one hour at lower temperatures though at higher temperatures there is significantly higher loss.

The mini-slump spread was also measured over an hour for all the pastes to study its effect on loss in fluidity with time and temperature. The results thus obtained are shown in Figures 4.10 a-d. It is observed from the test results that the flow generally decreases with rise in temperature, which is similar to the observations inferred from the Marsh cone test.

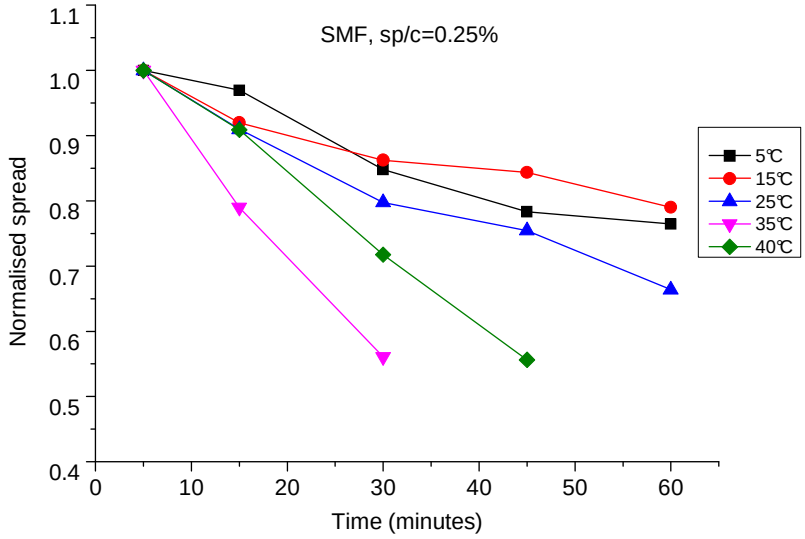


(a)

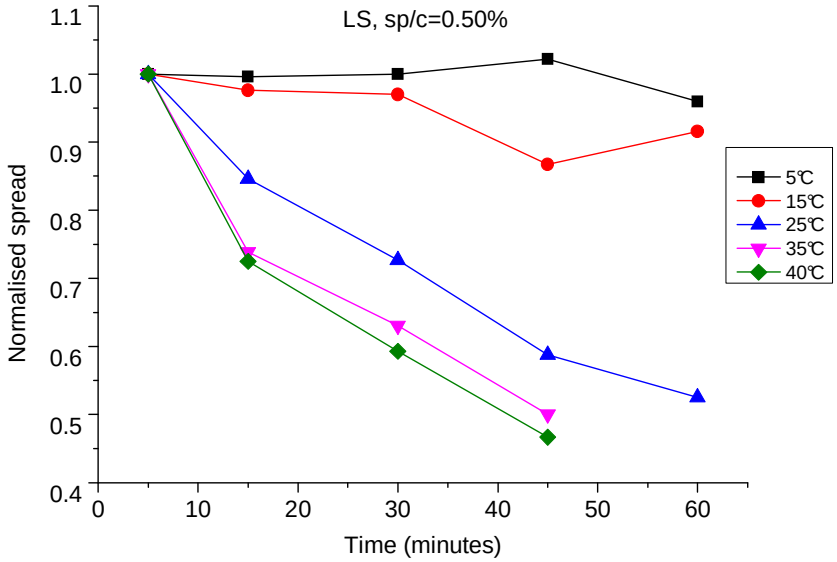


(b)

Figure 4.10 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (a) PCE and (b) SNF for dosage corresponding to the saturation dosage at 25°C



(c)



(d)

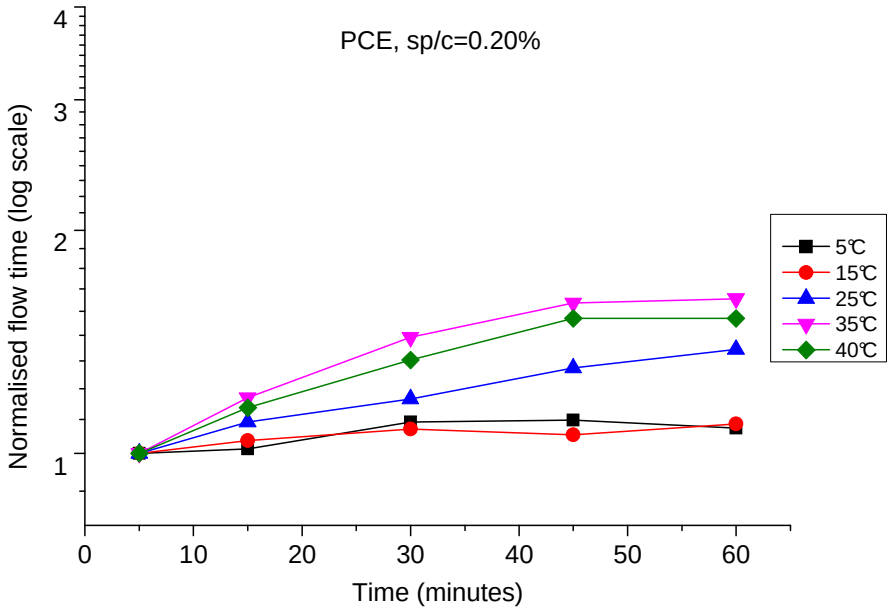
Figure 4.10 Curves of normalized mini-slump spread versus time at different temperatures for superplasticizers based on (c) SMF and (d) LS for dosage corresponding to the saturation dosage at 25°C

The SMF and LS based superplasticizers yielded the highest losses in flow at the higher temperatures, and the PCE based superplasticizer gives the best flow retention among the products studied.

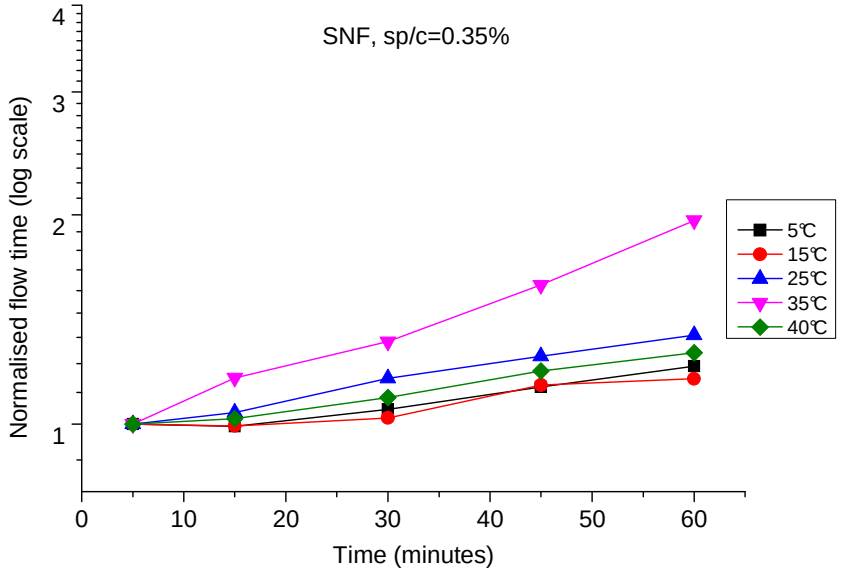
4.3.4 Effect of Temperature on the Evolution of Fluidity with Superplasticizer Dosage Corresponding to the Minimum Flow at 25°C

The previous sections explained the effect of temperature on the loss in fluidity with time for the saturation dosage of superplasticizer corresponding to each temperature and at the saturation dosage at 25°C, respectively. It was observed that the fluidity generally decreases with an increase in temperature. In order to study the effect of a dosage of superplasticizer that is higher than the saturation dosage on the loss in fluidity, the Marsh cone flow time and mini-slump spread were determined with a dosage of superplasticizer corresponding to the minimum flow at 25°C. (Note that in the case of LS, the dosage is same for both saturation and minimum flow at 25°C). The dosages selected are 0.2%, 0.35%, 0.35% and 0.5% for PCE, SNF, SMF and LS, respectively.

The results thus obtained for Marsh cone test are presented in Figures 4.11 a-d. From the results, it is observed that the loss in fluidity is, in general, less than that observed in the pastes with the saturation dosage corresponding to 25°C. All the superplasticizers, except LS, yielded flowing pastes up to an hour after mixing at the dosage corresponding to the minimum flow at 25°C, which was not always occurring with the saturation dosage at 25°C. There was no change in the case of the LS based superplasticizer because the saturation dosage and dosage corresponding to minimum flow at 25°C are the same. The results imply that some over-dosage of superplasticizer is better for flow retention, especially at higher temperatures, when the same dosage is to be maintained over all temperatures. The higher flow retention can be attributed to the superplasticizer available in the pore solution for the adsorption on the cement particles and newly formed hydrates at a later time.

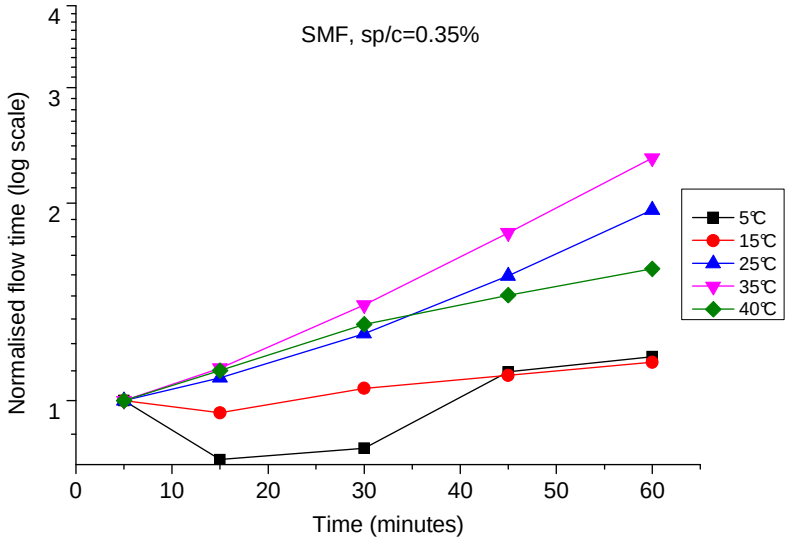


(a)

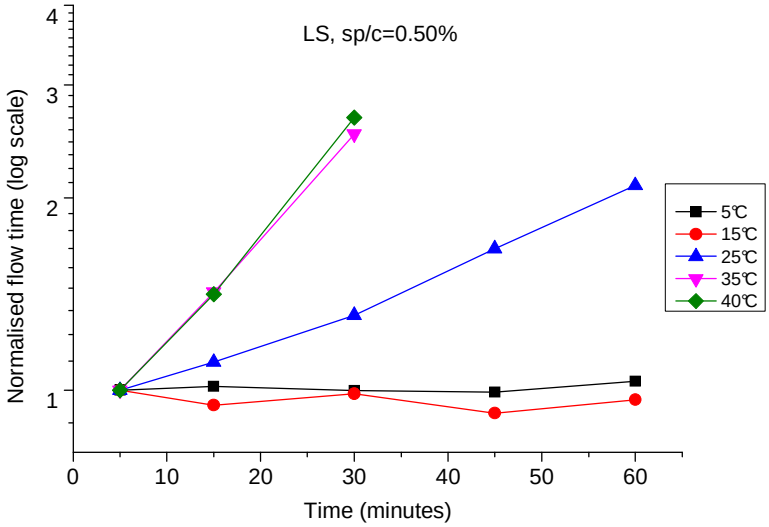


(b)

Figure 4.11 Curves of normalized Marsh cone flow time verses time at different temperatures for superplasticizers based on (a) PCE and (b) SNF for dosage corresponding to the minimum flow at 25°C



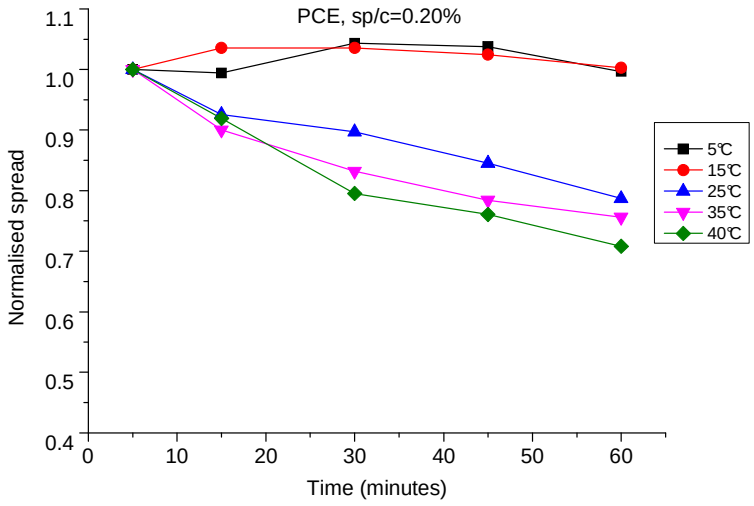
(c)



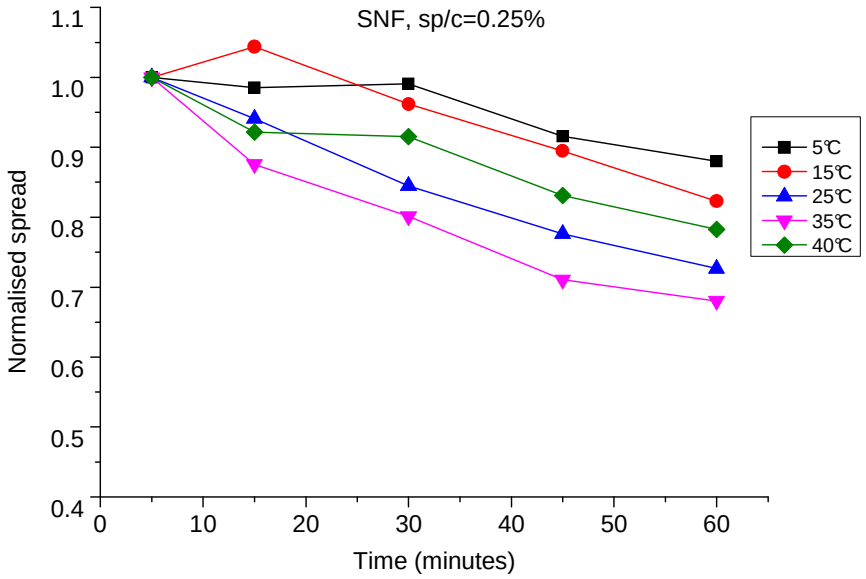
(d)

Figure 4.11 Curves of normalized Marsh cone flow time verses time at different temperatures for superplasticizers based on (c) SMF and (d) LS for dosage corresponding to the minimum flow at 25°C

The mini-slump test results (Figure 4.12) also show that the loss in spread with time is less when the results from the dosage corresponding to the minimum dosage are compared with those with the saturation dosage at 25°C, at all temperatures, which confirms the trends of the Marsh cone test results.

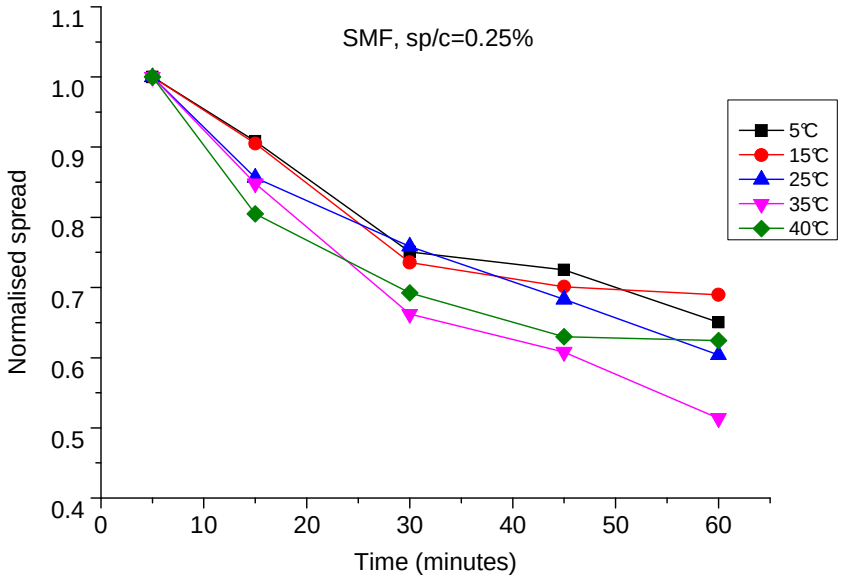


(a)

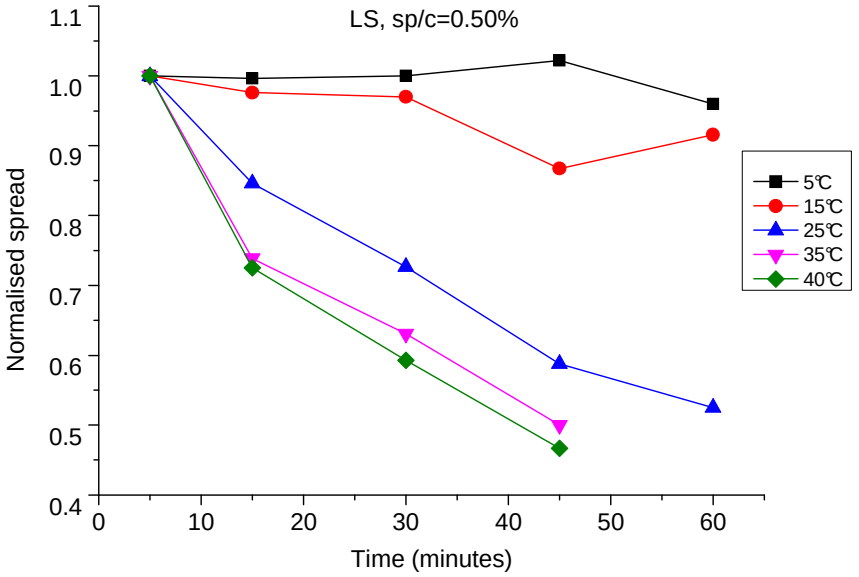


(b)

Figure 4.12 Curves of normalized mini-slump spread verses time at different temperatures for superplasticizers based on (a) PCE and (b) SNF for dosage corresponding to the minimum flow at 25°C



(c)

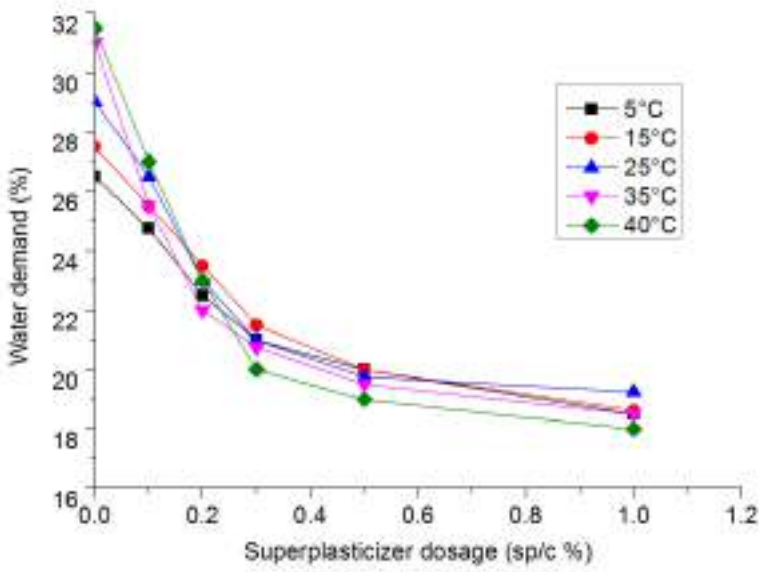


(d)

Figure 4.12 Curves of normalized mini-slump spread verses time at different temperatures for superplasticizers based on (c) SMF and (d) LS for dosage corresponding to the minimum flow at 25°C

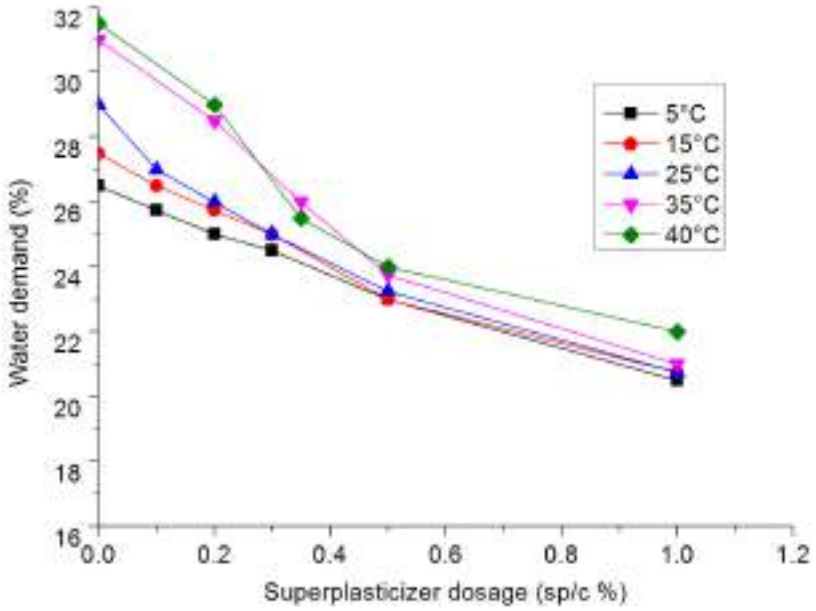
4.3.5 Effect of Temperature on Water the Demand of Cement Without and With superplasticizer

The water demand of cement is the measure of the minimum water content required to obtain a cement paste with a certain consistency (i.e., normal consistency) corresponding to a needle penetration of 6±1mm in the Vicat apparatus. The water demand is affected by the presence of superplasticizer and ambient temperature (Roncero et al., 1999). Here, the water demand of cement was determined at different temperatures with superplasticizer dosages varying from 0 to 1% by weight of cement. The test procedures are given in Section 3.3.1.3 of Chapter 3. The water demand values have been plotted against superplasticizer dosages in Figures 4.13 a-d.

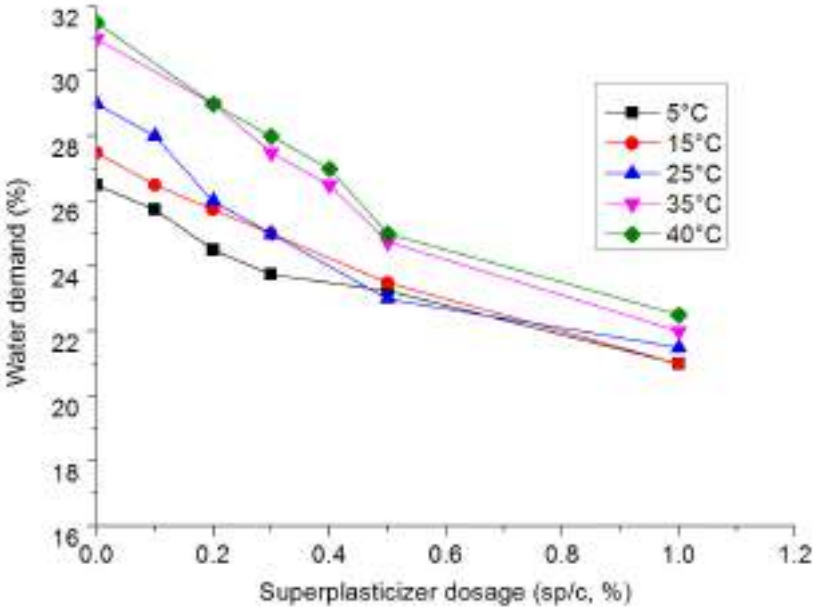


(a)

Figure 4.13 Water demand for different temperatures at varying sp/c dosage for superplasticizers based on (a) PCE (b) SNF

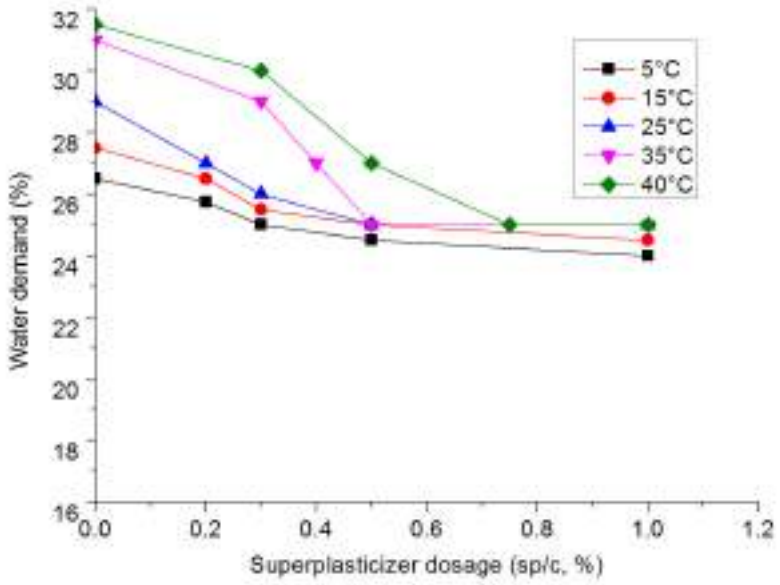


(b)



(c)

Figure 4.13 Water demand for different temperatures at varying sp/c dosage for superplasticizers based on (b) SNF and (c) SMF



(d)

Figure 4.13 Water demand for different temperatures at varying sp/c dosage for superplasticizers based on (d) LS

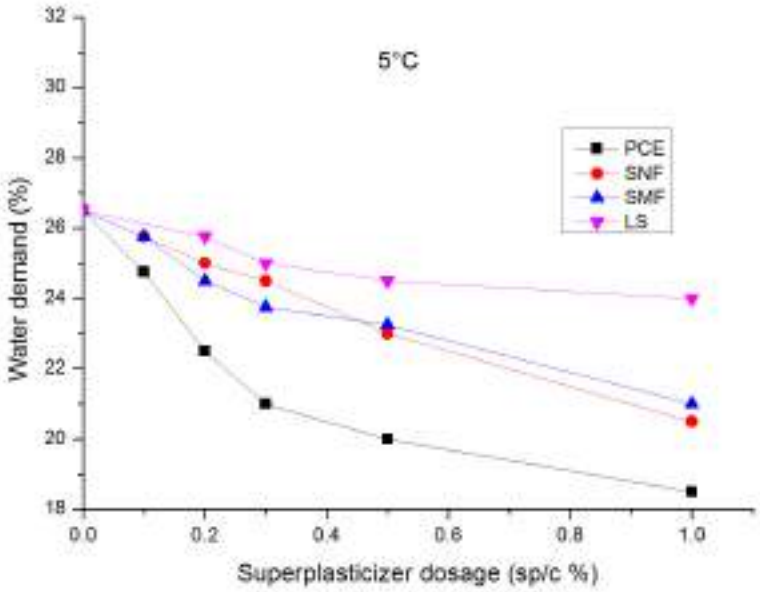
From the test results (Figure 4.13 a-d), it is observed that the water demand of cement generally increases with an increase in temperature. This is due to the increased rate of hydration of the cement at higher temperatures. The water demand is seen to increase from 26.5% to 31.5% as the temperature increases from 5°C to 40°C, which is similar to the increase observed by Roncero et al. (1999) for a type CEM I 52.5 R cement (European Standard ENV 197-1:92).

The incorporation of the superplasticizer decreases the water demand at all temperatures, with the amount of reduction varying with the chemical nature of the superplasticizer. The PCE based superplasticizer gave the highest reduction in water demand and the LS based superplasticizer gave the least reduction.

In the case of superplasticized cement pastes, the variations in the water demand with temperature are lower at higher dosages of superplasticizer. Roncero et al. (1999) also observed similar trends with SNF and PCE based superplasticizers. Figures 4.13 a-d show that for all superplasticizers, in general, an increase in temperature leads to an increase in the water demand at a given dosage of superplasticizer. This implies that

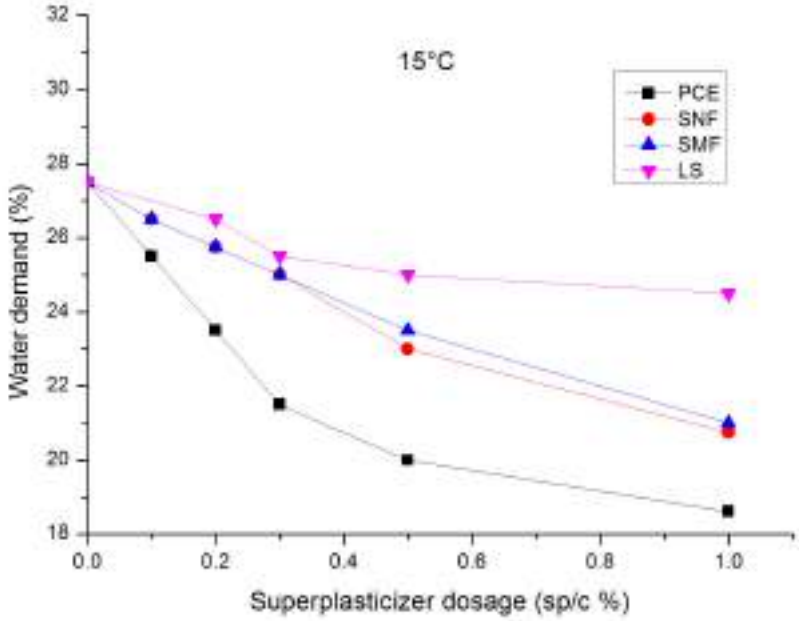
the quantity of water necessary to maintain a certain consistency of cement paste increases with an increase in temperature. Again, the decrease in water content with superplasticizer is a clear indication of the effectiveness of the superplasticizer in decreasing the water cement ratio for a fixed consistency at all temperatures. At higher temperatures and low dosages, all the superplasticizer yield higher water demand. The efficiency of the superplasticizer in decreasing the water demand seems to be more at higher temperatures. This effect could contribute to the increase in the fluidity of cement pastes observed at higher temperatures and higher dosages of superplasticizer in the Marsh cone tests (see Section 4.3.1).

In order to compare the effects of the different superplasticizers on the reduction in water demand at various temperatures, the data are plotted against sp/c dosage, for each temperature, in Figures 4.14 a-e. It is observed that the PCE based superplasticizer gives the maximum reduction in water demand at all temperatures, whereas the LS based superplasticizer gives the least, and the SNF and SMF based superplasticizers yield almost the same water reduction.

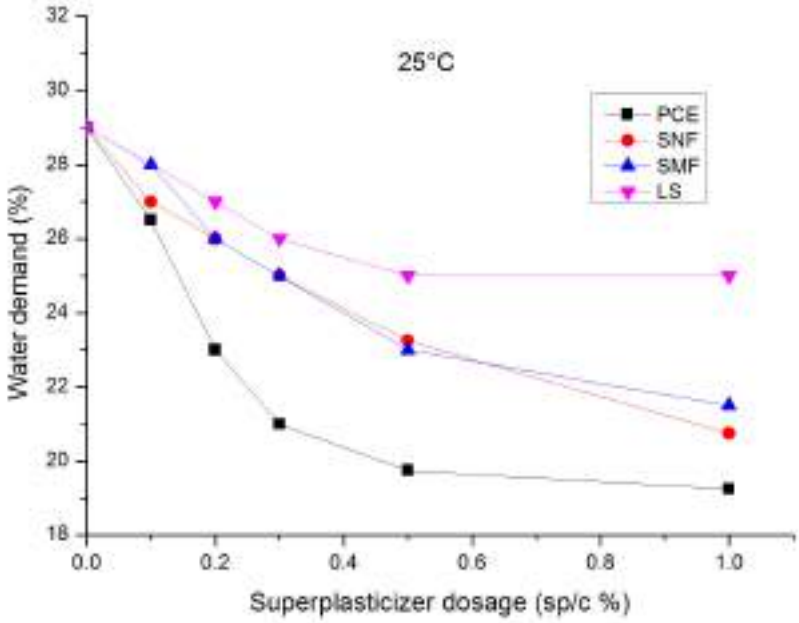


(a)

Figure 4.14 Water demand of cement with superplasticizers at different temperatures (a) 5°C

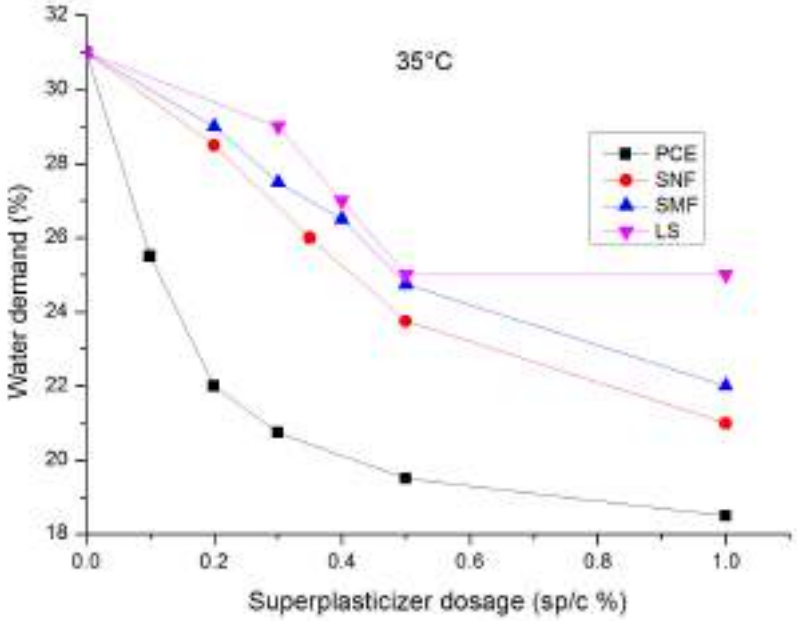


(b)

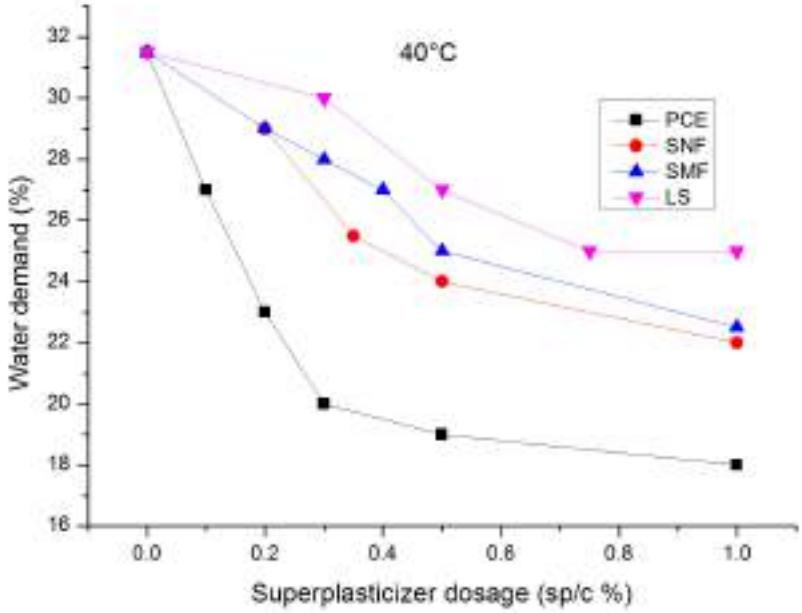


(c)

Figure 4.14 Water demand of cement with superplasticizers at different temperatures (b) 15°C and (c) 25°C



(d)



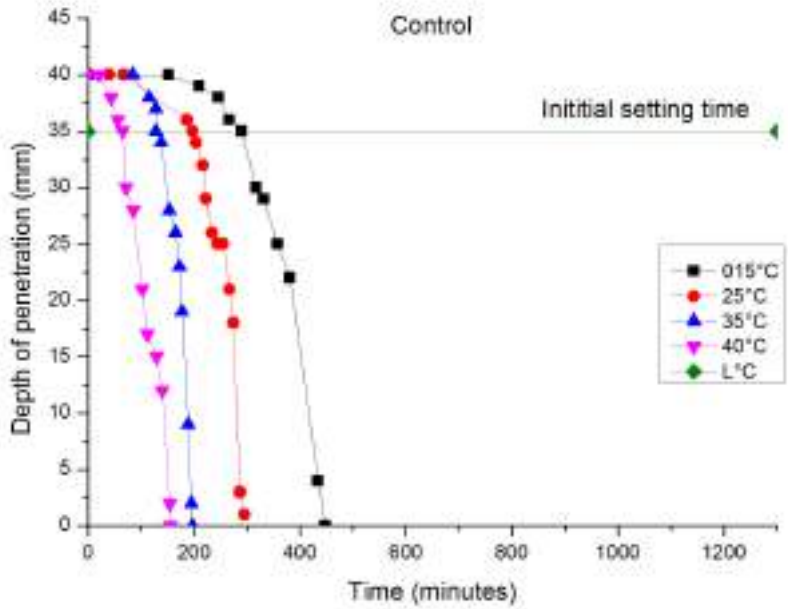
(e)

Figure 4.14 Water demand of cement with superplasticizers at different temperatures (d) 35°C and (e) 40°C

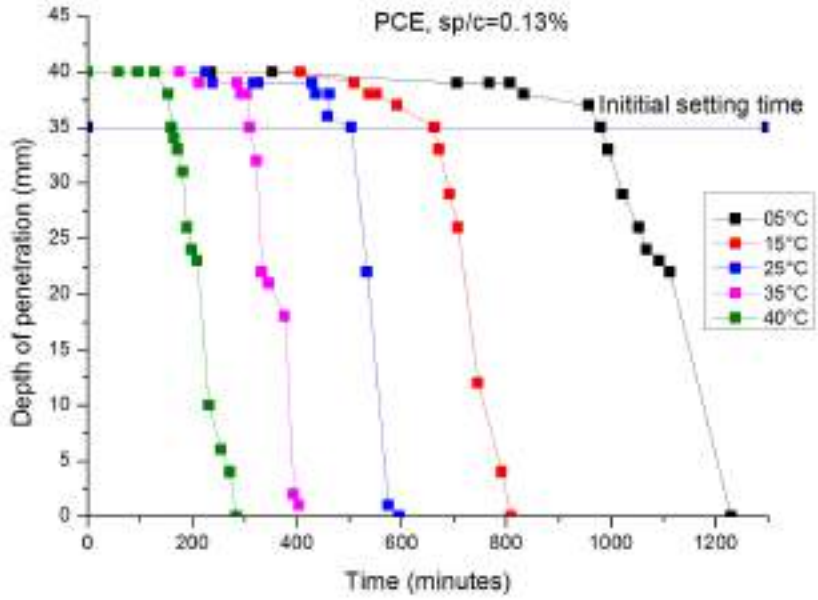
4.3.6 Effect of Temperature on Setting Time

Cement setting is a term used to describe the stiffening of cement paste, mortar or concrete due to hydration of cement. Temperature can affect the setting and hardening behavior of cement by altering the rate of hydration and evaporation of water from the paste. In order to study the effect of temperature on setting behavior, initial and final setting times were determined using the Vicat apparatus. The saturation dosage of superplasticizer obtained at 25°C (as given in Table 4.1) was used with pastes, which were tested under different temperatures. The details of the test procedures are given in Section 3.3.1.4 of Chapter 3.

The Vicat penetration for cement paste with and without superplasticizers is plotted against time for different temperatures in Figures 4.15 a-e. In all cases, there is a shift towards the left for all superplasticizers due to the increase in temperature. This implies that the setting times decrease with an increase in temperature, as expected. In each plot, the horizontal line drawn at 35 mm penetration indicates the initial setting time. It is interesting to note that the curves are practically parallel after the initial setting time. This could imply that the temperature basically affects the dormant stage of setting and the induction period, as also concluded by Vydra et al. (2007). Alshamsi (1994) also observed that higher temperature prepones the initiation of the acceleratory period and the amount of reactions taking place after that are affected to a lesser extent.

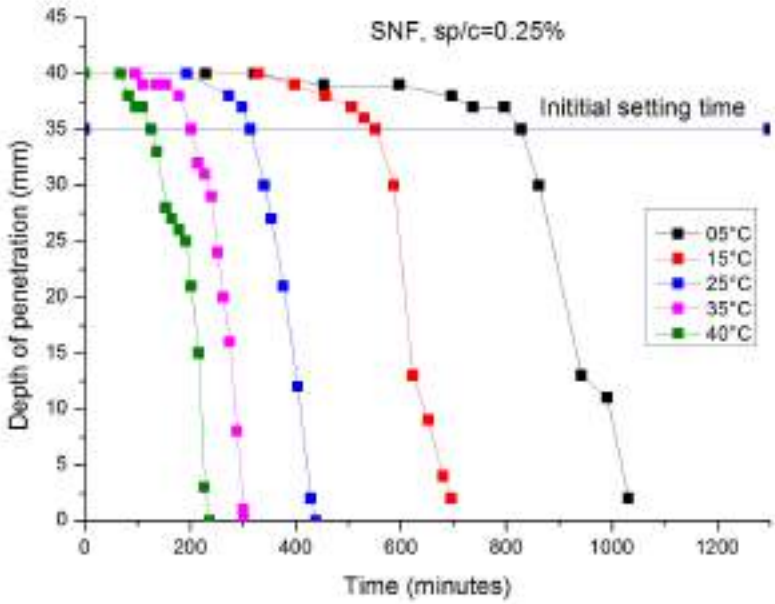


(a)

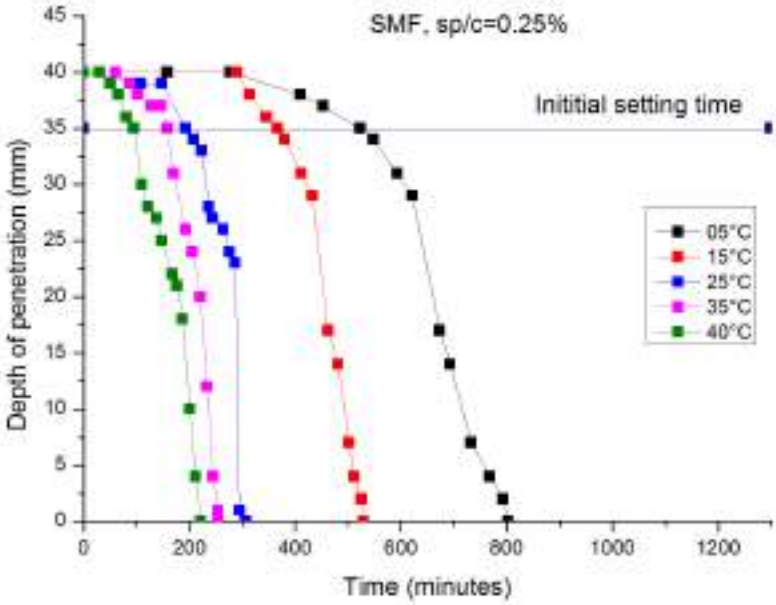


(b)

Figure 4.15 Evolution of Vicat penetration values for cement pastes with and without superplasticizer at various temperatures for (a) Control (b) PCE

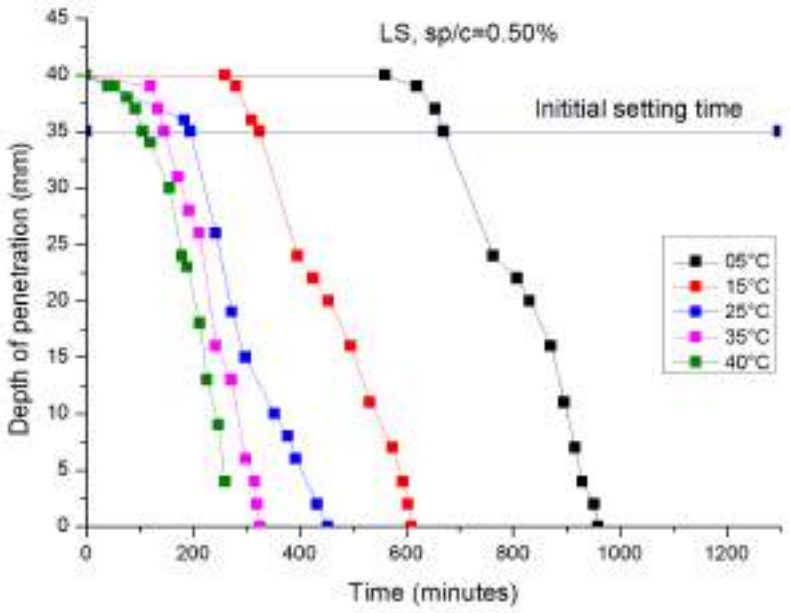


(c)



(d)

Figure 4.15 Evolution of Vicat penetration values for cement pastes with and without superplasticizer at various temperatures for (c) SNF (d) SMF



(e)

Figure 4.15 Evolution of Vicat penetration values for cement pastes with and without superplasticizer at various temperatures for (e) LS

The initial setting times obtained for the different pastes are plotted in Figure 4.16 as a function of ambient temperature. It shows the decrease in setting time with an increase in temperature mentioned earlier. Similar results were observed by many researchers (Alshamsi et al., 1993; Alshamsi, 1994; Escalante-García and Sharp, 1998; Soroka and Ravina, 1998; Roncero et al. 1999**;** Ahmadi, 2000; Mounanga et al., 2006). Mounanga et al. (2006) explain this phenomenon by the faster formation of a solid network due to the increase in the hydration rate as temperature increases, leading to more resistance to the penetration of the Vicat needle. The increase in hydration leads to the consumption of more water and formation of more hydration products (Soroka and Ravina 1998; Mounanga et al. 2006), which will result in more resistance to the penetration.

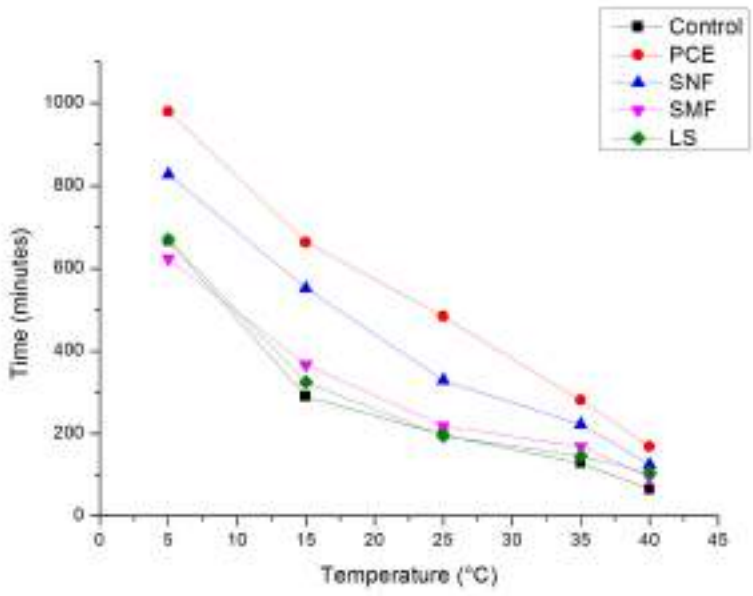


Figure 4.16 Initial setting time for different temperatures with different superplasticizers

From Figure 4.16, it is also observed that the addition of PCE and SNF based superplasticizers retard the initial setting time more, compared to the control paste. The retardation can be due to the formation of an adsorbed layer on the surface of the cement grains, which reduces the rate of dissolution of Ca^{2+} ions (Singh et al. 1992; Uchikawa et al. 1992; Gu et at. 1994). The SMF based superplasticizer does not cause significant retardation compared to PCE and SNF based superplasticizers, which conforms the understanding that the SMF based superplasticizers are good for achieving good initial workability but yield poor workability retention (e.g., Jayasree et al. 2011a). The LS based superplasticizer did not show much retardation, contrary to that expected, may be due to the low w/c (i.e., 0.25%). The trends are in accordance with those reported with the initial and final setting times of superplasticized concrete in the order of SMF <SNF < polyacrylates (Rixom and Mailvaganam 1999).

Fig. 4.17 shows the variation of final setting time with temperature, indicating a trend similar to that of the initial setting time; as the temperature increases, the final setting time decreases, and the final setting time of the cement paste increases due to the superplasticizer. The retardation is more (especially at lower temperatures) for the PCE based superplasticizer compared to the other superplasticizers. The SMF based

superplasticizer yielded the least retardation. At lower temperatures, the SNF based superplasticizer gave higher retardation compared to the LS based superplasticizer; however, at higher temperatures the LS based superplasticizer gave more retardation compared to SNF.

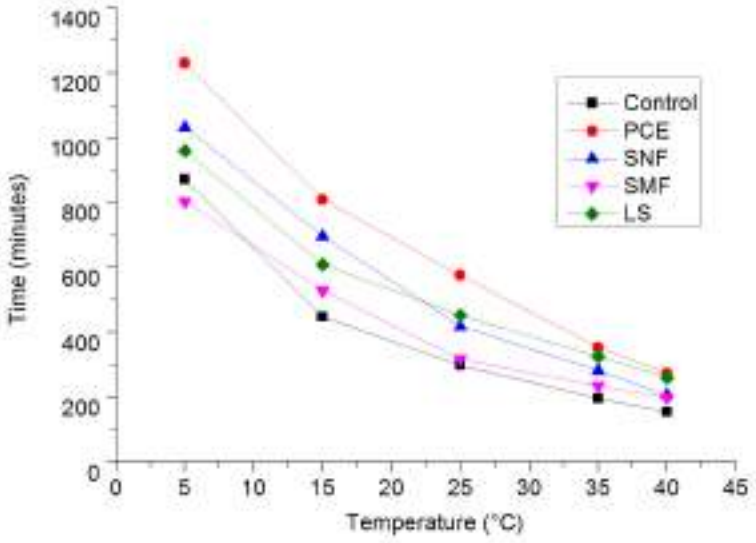


Figure 4.17 Final setting time for different temperatures with different superplasticizers

4.4 CONCLUSIONS

The effect of temperature on fluidity, water demand and setting time of cement paste with and without superplasticizer, were studied. One product from each of the four main families of superplasticizers, i.e. polycarboxylate, naphthalene, melamine and lignosulphonate, were investigated. The tests were conducted at 5, 15, 25, 35 and 40ºC. The following conclusions can be drawn from the study:

- The fluidity decreases with an increase in temperature at lower dosages of superplasticizer; however, the fluidity increases with an increase in temperature at higher dosages of superplasticizer. This may be due to two compensating mechanisms, the increase in water demand with an increase in temperature and the decrease in viscosity of the cement paste at higher temperature (or the increase in the efficiency of the superplasticizer with an increase in temperature).

- The saturation dosage of superplasticizer obtained from the Marsh cone test increases with an increase in temperature, for all the superplasticizers studied here. The PCE based superplasticizer had the least temperature sensitivity and LS based superplasticizer exhibited the most. The results emphasize that, the saturation dosage of superplasticizer needs to be determined over the range of ambient temperatures to which the ingredients and fresh concrete are exposed to for obtaining the required fluidity for concrete.

- The loss in flow with time increases as the temperature increases and decreases with an increase in the dosage of superplasticizer. Therefore, in order to get better flow retention, a slightly higher dosage of superplasticizer than the saturation dosage obtained from Marsh cone test can be used. Nevertheless, proper care has to be taken for deciding on the higher dosage to avoid adverse effects on concrete like segregation, delay in setting, etc.

- Water demand increases with increase in temperature, both with and without superplasticizer. The increase in water demand can be attributed to the increased rate of hydration at higher temperature. Nevertheless, there is a larger decrease in water demand due to the incorporation of a superplasticizer with an increase in temperature.

- The initial and final setting times decrease as the temperature increases, both with and without superplasticizer. However, the setting time increases with the addition of superplasticizer and varies with the type of superplasticizer.

Since the temperature affects the fluidity, loss in fluidity with time, and setting and hardening behavior of the cement, the ambient temperature of the concrete should be taken into consideration for designing the concrete for better performance. The dosage of superplasticizer needs to be selected by considering the ambient temperature to get the required workability and workability retention in concrete.

CHAPTER 5

EFFECT OF INITIAL TEMPERATURE ON THE PROPERTIES OF CEMENT MORTAR AND CONCRETE

5.1 **INTRODUCTION**

The influence of superplasticizer and temperature on the fluidity of cement paste has been discussed in the previous chapter. It is observed that temperature can influence the initial fluidity, loss in fluidity with time, water demand and setting time of the superplasticized cement paste significantly. The losses in fluidity and water demand of cement paste increase with an increase in temperature whereas the setting time decreases. The incorporation of superplasticizer increases the fluidity and setting time of cement paste whereas the lossess in fluidity and water demand decrease. In order to extend the results from the paste studies to concrete, it is necessary to study different properties of cement mortar and concrete so that a correlation can be made.

The specific objectives of the work in this chapter are to study the effect of temperature, superplasticizer and its coupled effects on initial fluidity, loss in fluidity with time and mechanical properties of cement mortar and concrete. The effectiveness of different types of superplasticizer with temperature have been studied. The preparation and various testing procedures adopted for mortar and concrete were explained in Chapter 3. The fluidity of cement mortar was analysed by determining the spread of mortar using flow table test. To study the influence of superplasticizer and temperature on the loss in fluidity, the spread of cement mortar was observed over an hour. The development of compressive and flexural strengths of cement mortar was also assessed. For concrete, the slump test using Abram's cone, and tests for the compressive and splitting tensile strength were performed.

5.2 **EXPERIMENTAL DETAILS**

Ordinary 53 grade portland cement conforming to IS 12269 (2004) and de-ionized water were used for this study. The chemical composition of the cement is given in Table 3.1. One commercially available superplasticizer each from the PCE, SNF, and SMF based families

was incorporated in the study of the effect of temperature and superplasticizer on cement mortar. The LS based superplasticizer was not incorporated in the study; The PCE and SNF based superplasticizers were used in the case of concrete, as these admixtures are commonly used in construction sites. The properties of the superplasticizers used are given in Table 3.2. The superplasticizer dosages are given as the ratio of the solid content of the superplasticizer to cement (sp/c), by weight, and the liquid phase in the superplasticizer has been accounted as part of the water cement ratio (w/c). Standard sand confirming to IS 650 (1991) was used to prepare the cement mortar. Three grades (Grades I, II and III) of sands were taken equally and mixed together to form the fine aggregate. A w/c of 0.35 was used for all mixes throughout the study.

The effect of temperature on cement mortar was studied at 5, 15, 25, 35 and 40°C, whereas for concrete, the tests were performed at 5, 25 and 40°C. A walk-in environmental chamber was used to maintain the temperature of the materials, mixing and measuring equipments and for conducting the experiments. The chamber was maintained at a constant humidity of 65%, except in the case of 5°C, where the condensation of water raised the humidity slightly. All the materials were maintained at the prescribed temperature for at least 48 hours prior to the test for preconditioning. The temperature of the materials were checked and found to be always within ±2°C of the prescribed temperature. The mixing, casting and determination of spread of mortar and slump of concrete were done inside the chamber, as per the procedures already explained in Chapter 3. The specimens were kept at the respective temperatures for 24 hours. Thereafter, the specimens were demoulded and cured in mist room till the designated ages of curing and then tested.

5.3 TEST RESULTS AND DISCUSSION

5.3.1 Effect of Temperature and Superplasticizer on the Fluidity of Cement Mortar

The fluidity of cement mortar was analysed in terms of the spread of mortar using the flow table test as explained in Section 3.3.3.2 of Chapter 3. The spread was determined for the cement mortar without superplasticizer, and with the superplasticizer dosage corresponding to the saturation dosage at 25°C (determined from Marsh cone test) for each type of superplasticizer. The saturation dosages of the different superplasticizers used are given in

Table 5.1. The initial spread (i.e., the spread of mortar immediately after mixing) obtained from the flow table test is plotted against temperature in Figure 5.1.

Table 5.1 Saturation dosages of superplasticizer at 25°C

Superplasticizer	Dosage (%)
PCE	0.13%
SNF	0.25%
SMF	0.25%

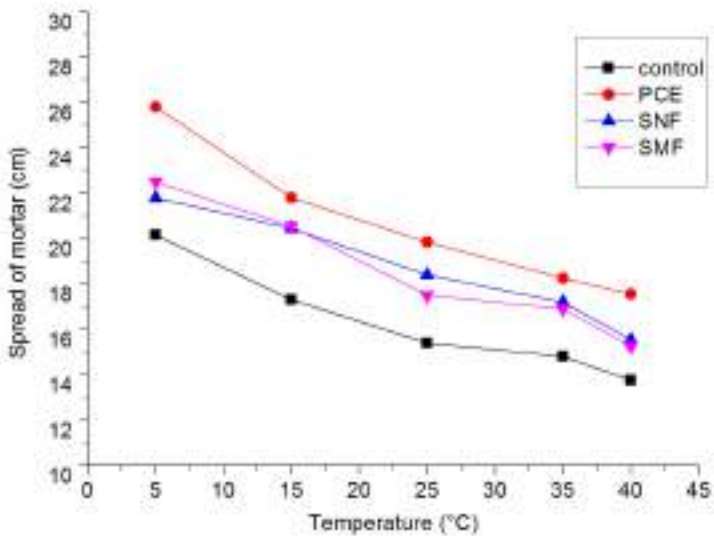


Figure 5.1 Initial spread of cement mortar in the flow table test for different temperatures

All the cement mortars studied (Figure 5.1) showed a decrease in the initial spread with an increase in temperature, which can be attributed to the higher water demand at higher temperatures that was observed in the paste study and explained in Section 4.3.5 of Chapter 4. The higher water adsorption of the cement leads to the decrease in the availability of free water and hence decreases the fluidity of mortar. Furthermore, the water absorption of the aggregates can also play a key role in the fluidity of mortar. Ortiz et al. (2009) attributed the decrease in workability of mortar at higher temperature to the higher water absorption of the aggregates at higher temperatures. When the aggregates are exposed to higher temperature, the pore structure expands and the size of the pores increase, which results in more absorption of water by the aggregates in less time. Since the properties of water, such as viscosity,

density and surface tension, vary with an increase in temperature, there is a higher rate of penetration of water into the pore structure of aggregate at higher temperatures (Ortiz et al. 2009).

The effect of temperature on the fluidity of cement mortar has been studied earlier in terms of rheological parameters (i.e., yield stress and plastic viscosity). Gołaszewski and Szwabowski (2004) observed an increase in yield stress and a decrease in plastic viscosity with an increase in ambient temperature, for cement mortar. The increase in yield stress at higher temperature indicates the decrease in the fluidity of mortar, confirming the trend seen in the present study.

It is also observed from the test results (Figure 5.1) that the fluidity increases with the addition of superplasticizer, as expected. The PCE based superplasticizers gave more spread compared to the SNF and SMF based superplasticizers, at the corresponding saturation dosage of superplasticizer determined for cement paste at 25°C. As expected, the better efficiency of the PCE based superplasticizer leads to higher fluidity, even at low dosages. Further, the higher reduction in water demand with the PCE based superplasticizer, as observed in paste study (Section 4.3.5 of Chapter 4), contributes to the higher mortar fluidity.

In order to study the influence of dosage of superplasticizer on the fluidity of cement mortar with temperature, a higher dosage (corresponding to the minimum flow time for cement paste at 25°C, as obtained in Marsh cone test) was also used and the spread of mortar was determined. The dosages of superplasticizer used are given in Table 5.2. The initial spread obtained with the dosage of superplasticizer corresponding to minimum flow time at 25°C is plotted against temperature in Figure 5.2. The initial spreads of mortar with the dosage of superplasticizer corresponding to saturation point and the minimum flow at 25°C are compared in Table 5.3 for the PCE, SNF and SMF based superplasticizers.

Table 5.2 Dosage of superplasticizer corresponding to minimum flow time at 25°C

Superplasticizer	Dosage (%)
PCE	0.20%
SNF	0.35%
SMF	0.35%

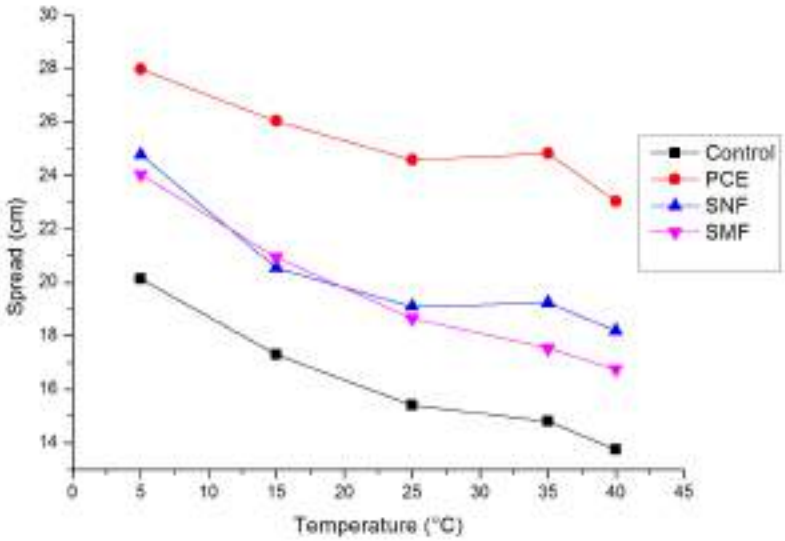


Figure 5.2 Initial spread of mortar in the flow table test for different temperatures (for superplasticizer dosage corresponding to the minimum flow at 25°C)

Table 5.3 Initial spread of mortar with dosage of superplasticizer corresponding to saturation point at 25°C and minimum flow at 25°C

Temp. (°C)	Initial spread of mortar (mm)						
	Control (without superplasticizer)	PCE		SNF		SMF	
		sp/c - saturation at 25°C	sp/c - minimum flow at 25°C	sp/c – saturation at 25°C	sp/c - minimum flow at 25°C	sp/c – saturation at 25°C	sp/c - minimum flow at 25°C
5	202	258	280	218	248	226	241
15	173	218	261	205	216	201	215
25	154	199	246	184	191	175	187
35	148	183	249	172	193	169	175
40	138	176	231	156	182	153	168

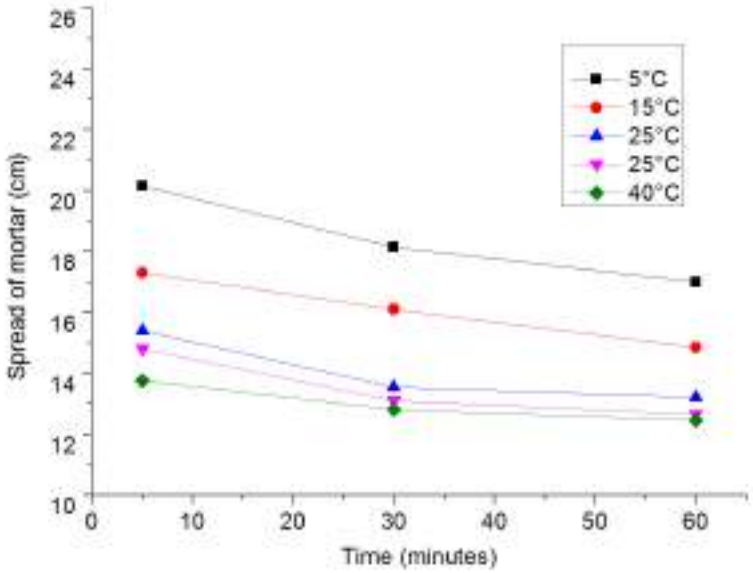
From the comparison between Figures 5.1 and 5.2, and from Table 5.3, it is observed that the fluidity of cement mortar increases with an increase in superplasticizer dosage. This can be attributed to the availability of more amount of superplasticizer for adsorption on the cement particles, due to the higher dosage. The saturation dosage of superplasticizer used was the dosage determined for the cement paste; however, in the case of mortar, a portion of the superplasticizers can be adsorbed on the aggregates and on the fines present in aggregates.

This can lead to a lower amount of superplasticizer available for the cement particles and hence a higher superplasticizer demand. The increase in spread of mortar with the increase in superplasticizer dosage is observed at all temperatures and for all the superplasticizers. The PCE based superplasticizer gave the maximum increase in fluidity at all temperatures with the higher dosage of superplasticizer compared to the other families.

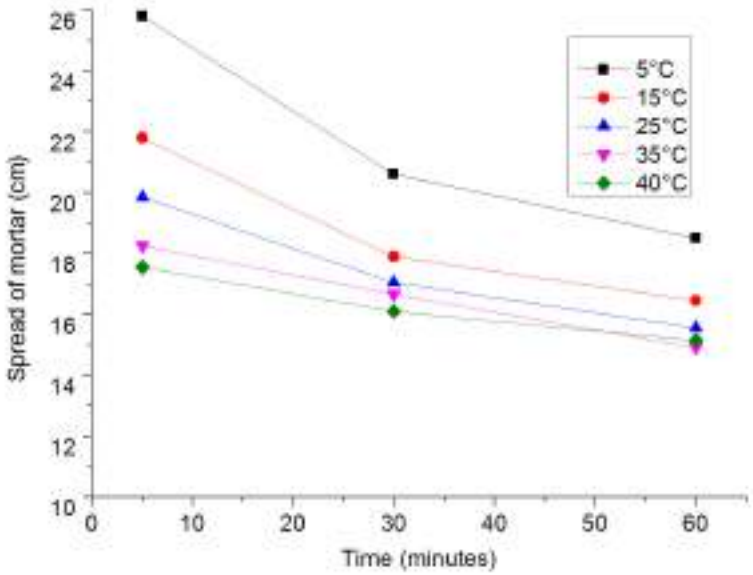
In the present study, the spread of mortar decreases with an increase in temperature and increases with an increase in superplasticizer content. This implies that higher dosages of superplasticizer than the saturation dosage obtained in the Marsh cone test of pastes are needed at higher temperatures. This reaffirms the conclusions from the study of cement paste (Chapter 4).

5.3.2 Effect of Temperature on the Evolution of Fluidity with Saturation Dosage of Superplasticizer at 25°C

The loss in fluidity with time is an important property of cement mortar and concrete as they have to be workable during transporting, placing, compacting and finishing. The loss in fluidity with time is studied here with the help of flow table test as explained in Section 3.4.2 of Chapter 3. The spread of cement mortar was measured immediately after mixing, and subsequently at 30 and 60 minutes after adding the water to the cement. The mortar was covered, to prevent the loss of water to the atmosphere, in between the measurements and mixed for 30 seconds at medium speed (with shaft speed of 285 rpm and planetary speed of 125 rpm) immediately before measuring the spread at each time. The spread of mortar obtained from the flow table test, with the saturation dosage of superplasticizer for cement paste at 25°C (given in Table 5.1), is plotted against time for different superplasticizers in Figure 5.3a-d and the data are given in Table 5.4.

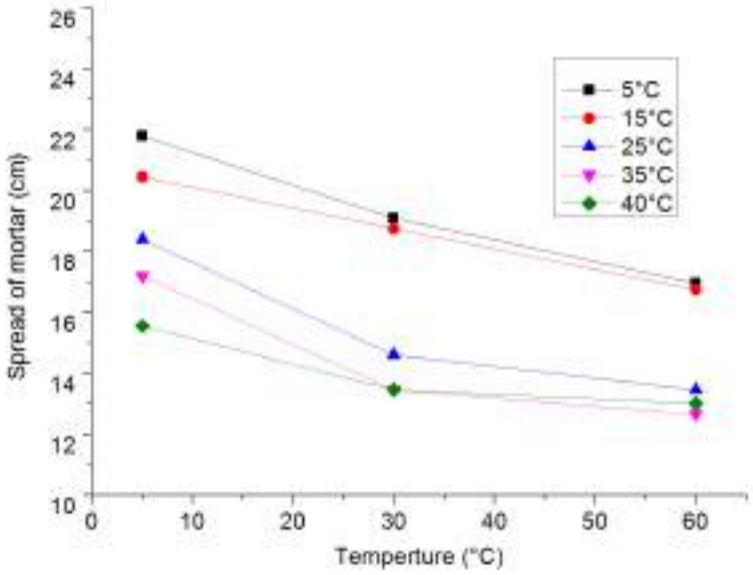


(a)

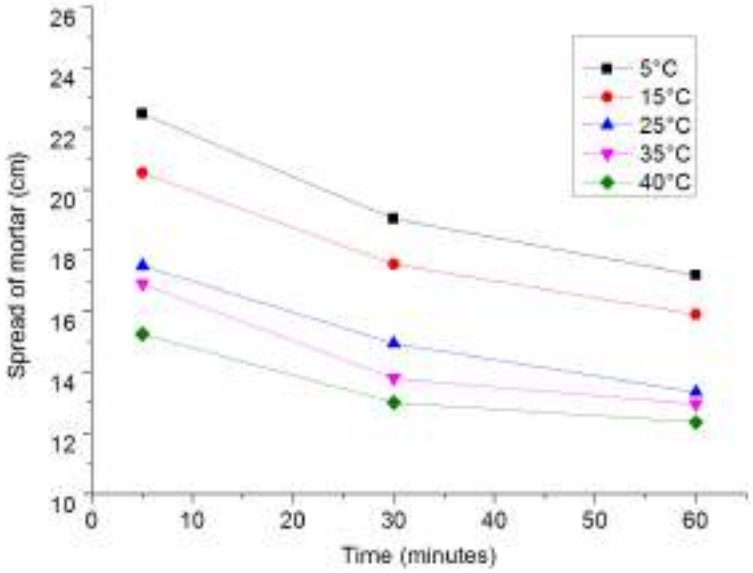


(b)

Figure 5.3 Spread of mortar with time at different temperature for superplasticizer dosage corresponding to the saturation dosage at 25°C for: (a) Control and (b) PCE



(c)



(d)

Figure 5.3 Spread of mortar with time at different temperature for superplasticizer dosage corresponding to the saturation dosage at 25°C for: (c) SNF and (d) SMF

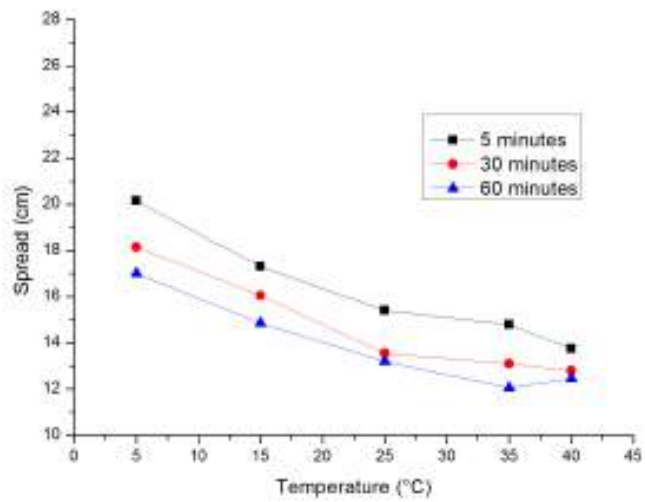
Table 5.4 Loss in spread of mortars with superplasticizer dosage corresponding to saturation point at 25°C

SP	Temperature (°C)	Saturation sp dosage at 25°C				
		Spread of mortar (mm)			Loss in spread (%)	
		5min	30min	60min	30min	60min
Control	5	202	182	170	9.9	15.6
	15	173	161	149	6.9	14.2
	25	154	136	132	12.0	14.3
	35	148	131	127	11.5	14.5
	40	138	128	125	6.9	9.5
PCE	5	258	206	185	20.2	28.3
	15	218	179	165	17.9	24.5
	25	199	171	156	14.1	21.7
	35	183	167	149	8.8	18.4
	40	176	161	152	8.3	13.7
SNF	5	218	191	170	12.4	22.2
	15	205	188	168	8.3	18.1
	25	184	146	135	20.7	26.9
	35	172	135	127	21.8	26.5
	40	156	135	130	13.5	16.4
SMF	5	225	191	172	15.3	23.6
	15	206	176	159	14.6	22.6
	25	175	150	134	14.6	23.7
	35	169	138	130	18.3	23.4
	40	153	130	124	14.8	19.0

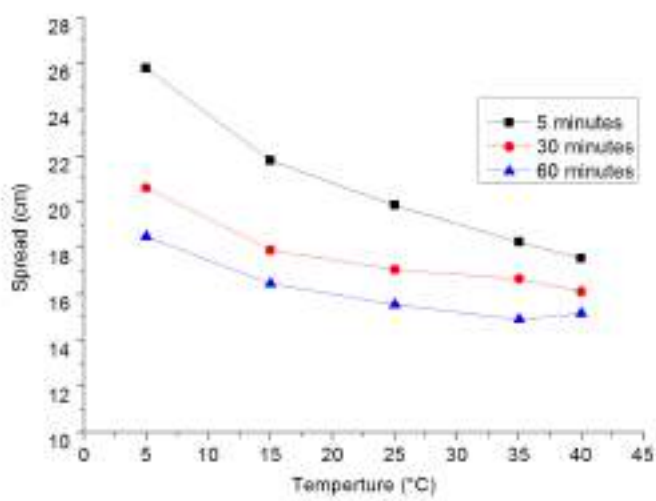
All the mortars studied (Figures 5.3a-d) show a higher spread at lower temperatures (5 and 15°C) than at the higher temperatures (25-40°C), during the entire period of measurement (i.e., one hour). As expected, the spread of mortar decreases with time. It is observed that the loss in spread with time is generally more significant in the first 30 minutes, especially at higher temperatures.

In order to assess the evolution of spread with temperature, the spreads at 5, 30 and 60 minutes are plotted against temperature for each superplasticizer in Figure 5.4(a-d). It is observed that the spread of mortar decreases with increase in temperature, at all ages. It is generally observed that the loss in fluidity (gap between 5 minutes and 30 minutes curve) is higher in the first 30 minutes compared to the second half hour, especially at higher

temperatures. The loss in fluidity with time depends upon the initial fluidity of the mortar to a large extent. The effect of temperature on the loss in fluidity is less for the mortars with lower initial spreads, which could be the reason for the lower loss in fluidity at higher temperatures. At higher temperatures, it is observed that the spread reaches almost the lowest value within 30 minutes itself.

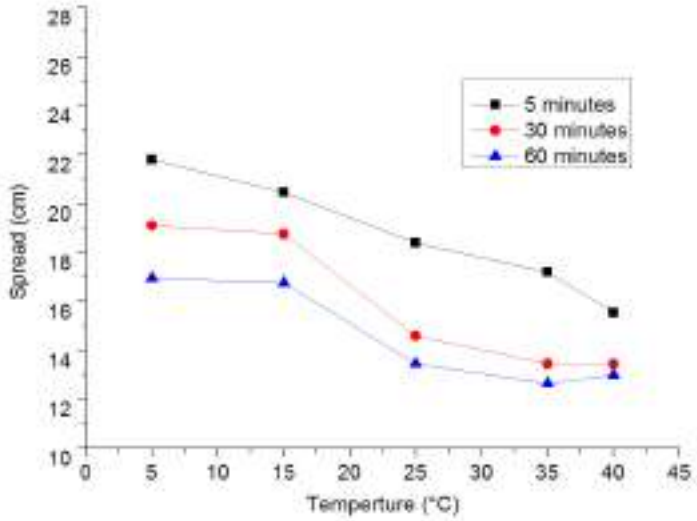


(a)

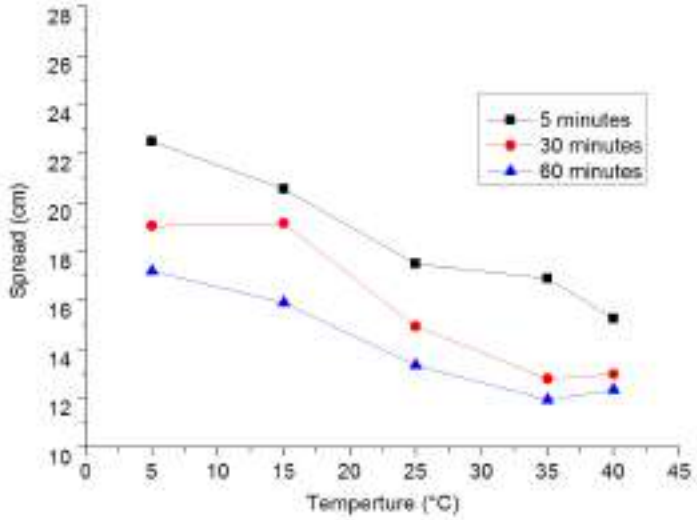


(b)

Figure 5.4 Spread of mortar with temperature for different age with superplasticizer dosage corresponding to the saturation dosage at 25°C for (a) Control (b) PCE



(c)

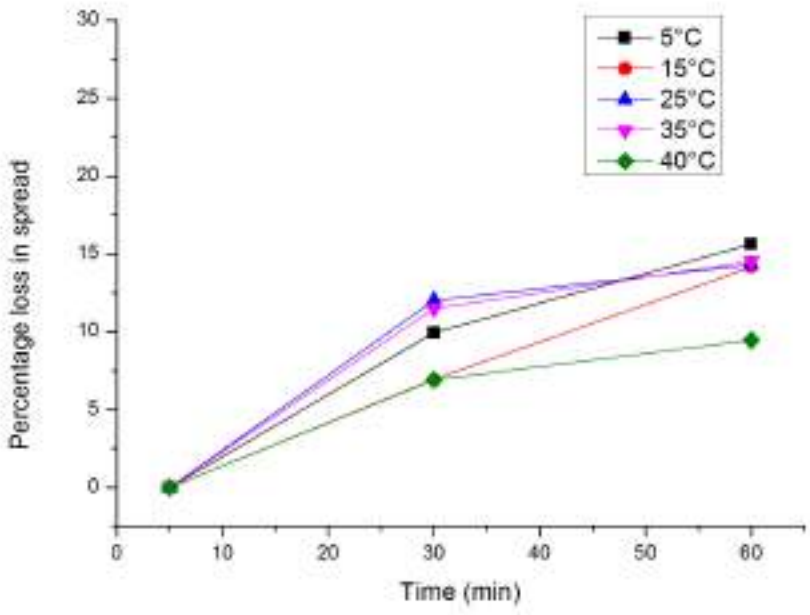


(d)

Figure 5.4 Spread of mortar with temperature for different age with superplasticizer dosage corresponding to the saturation dosage at 25°C for (c) SNF (d) SMF

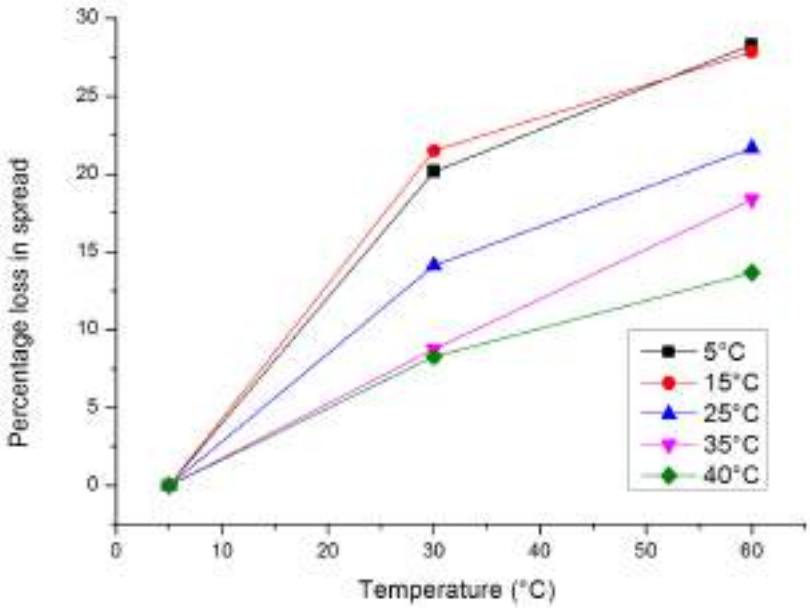
For a better comparison of the relative loss in fluidity with time, the spread of mortar has been normalised by the initial spread at that particular temperature in Figure 5.5 (a-d). The loss in normalised spread of mortar always increases with time, as observed earlier. In general, the loss in spread seems to be relatively less at higher temperatures though the data

does not yield a clear trend. The control and SMF based superplasticized mortars show similar trends after one hour. The control mortar showed a loss in spread of about 16% in the temperature range of 5°C to 35°C, whereas at 40°C, the loss in spread was 9%. In the case of SMF based mortar, the loss in spread was about 23% for the temperature range of 5°C to 35°C and 19% at 40°C. The lower loss in spread at higher temperature can be due to the lower initial spread. The loss in spread in the PCE based superplasticized cement (Figure 5.4b) mortar decreases with an increase in temperature. The SNF based superplasticized cement paste (Figure 5.4c) gave a loss in spread of about 22% at 5°C and 15°C, and 26% at 25°C and 35°C, whereas at 40°C, the loss in spread was 16%.

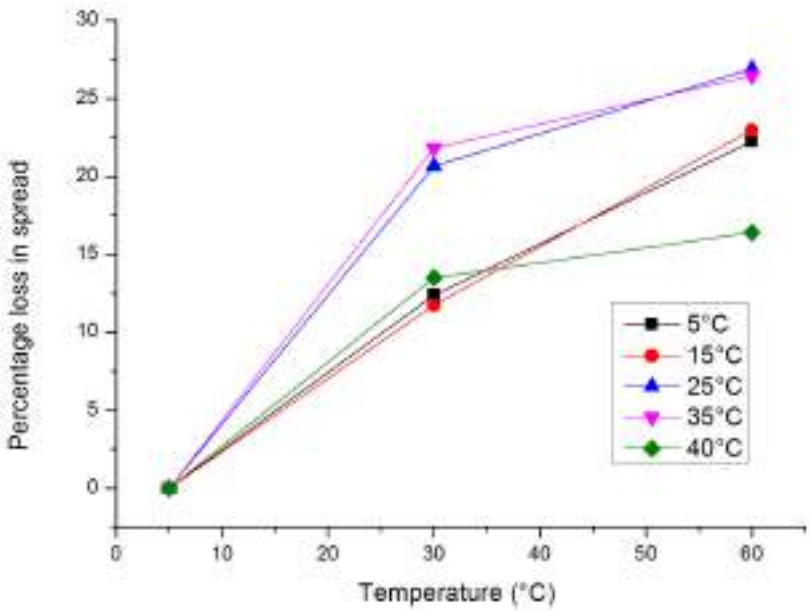


(a)

Figure 5.5 Normalised spread loss with time at different temperatures for mortars with superplasticizer dosage corresponding to the saturation dosage at 25°C for: (a) Control

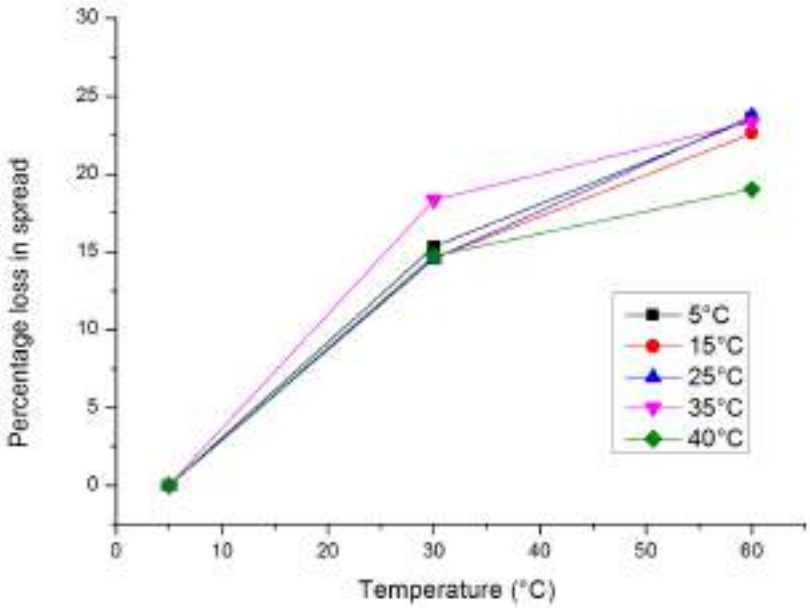


(b)



(c)

Figure 5.5 Normalised spread loss with time at different temperatures for mortars with superplasticizer dosage corresponding to the saturation dosage at 25°C for: (b) PCE and (c) SNF

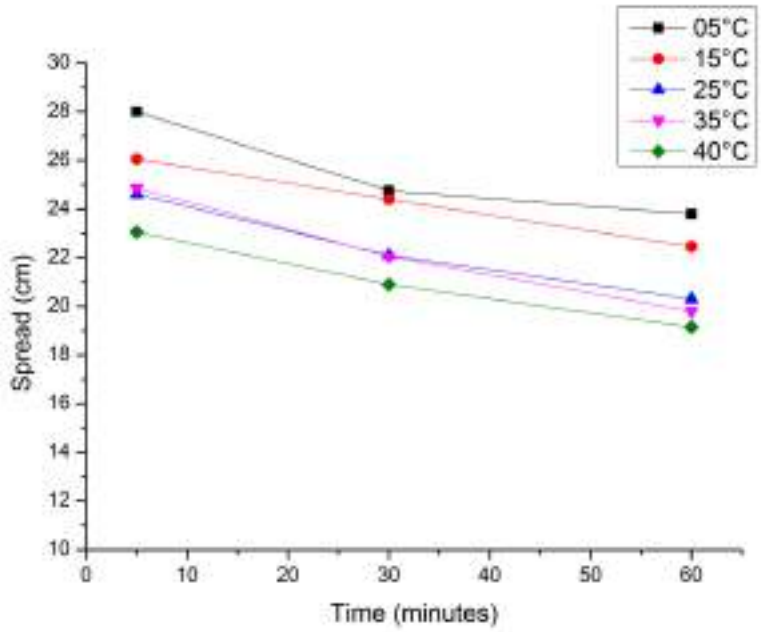


(d)

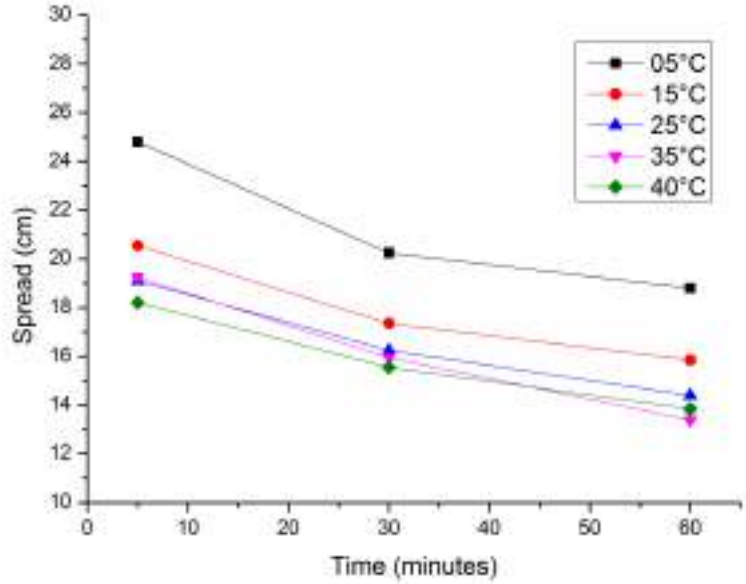
Figure 5.5 Normalised spread loss with time at different temperatures for mortars with superplasticizer dosage corresponding to the saturation dosage at 25°C for: (d) SMF

5.3.3 Effect of Temperature on the Evolution of Fluidity with Dosage of Superplasticizer Corresponding to Minimum Flow at 25°C

To evaluate the effect of superplasticizer dosage on the evolution of spread of mortar with temperature, a higher dosage of superplasticizer was also used (i.e., the dosage corresponding to the minimum flow of cement paste at 25°C determined from Marsh cone test). The spreads for the corresponding mortars are plotted against time in Figures 5.6a-d. The data for the spread and the loss in spread of mortar with time for the superplasticizer dosages corresponding to both the saturation point and minimum flow at 25°C are given in Table 5.5.

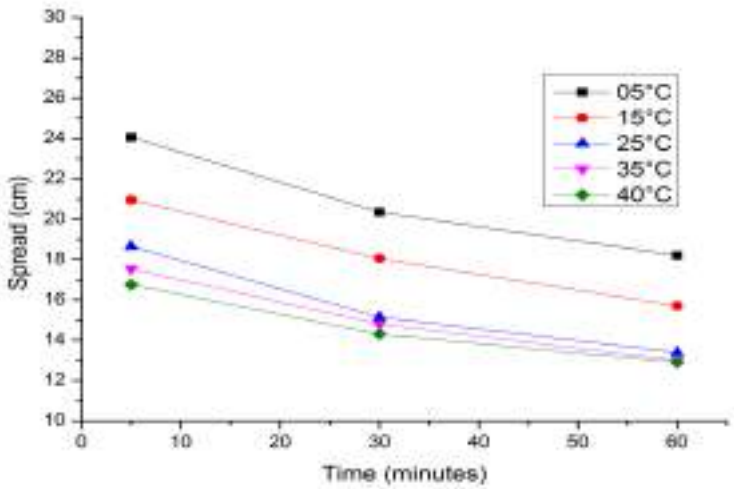


(a)



(b)

Figure 5.6 Spread of mortar with time and temperature for superplasticizer dosage corresponding to the minimum flow at 25°C for (a) PCE and (b) SNF



(c)

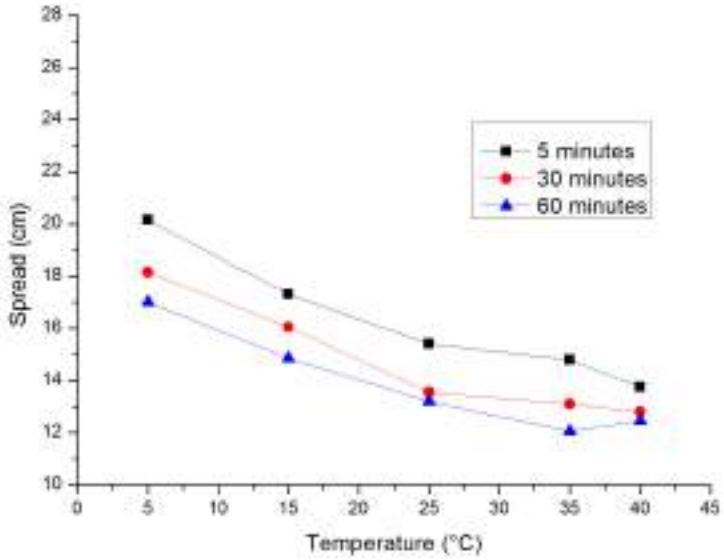
Figure 5.6 Spread of mortar with time and temperature for superplasticizer dosage corresponding to the minimum flow at 25°C for (c) SMF

Table 5.5 Comparison of spread of mortar at different ages with superplasticizer dosages at the saturation point at 25°C and minimum flow at 25°C

SP	Temp. (°C)	Saturation dosage at 25°C					Dosage corresponding to minimum flow at 25°C				
		Spread of mortar (mm)			Loss in spread (%)		Spread of mortar (mm)			Loss in spread (%)	
		5min	30min	60min	30min	60min	5min	30min	60min	30min	60min
PCE	05	258	206	185	20.2	28.3	280	248	238	11.6	15.0
	15	218	179	165	17.9	24.5	261	244	225	6.3	13.8
	25	199	171	156	14.1	21.7	246	221	203	10.2	17.5
	35	183	167	149	8.8	18.4	249	221	198	11.3	20.3
	40	176	161	152	8.3	13.7	231	209	192	9.3	16.9
SNF	05	218	191	170	12.4	22.2	248	203	188	18.3	24.2
	15	205	188	168	8.3	18.1	216	174	159	19.5	26.5
	25	184	146	135	20.7	26.9	191	163	144	14.9	24.6
	35	172	135	127	21.8	26.5	193	160	134	17.1	30.4
	40	156	135	130	13.5	16.4	182	156	139	14.6	23.9
SMF	05	225	191	172	15.3	23.6	241	204	182	15.4	24.3
	15	206	176	159	14.6	22.6	215	181	157	15.9	26.8
	25	175	150	134	14.6	23.7	187	152	134	18.8	28.2
	35	169	138	130	18.3	23.4	175	148	130	15.6	25.9
	40	153	130	124	14.8	19.0	168	143	129	14.6	23.0

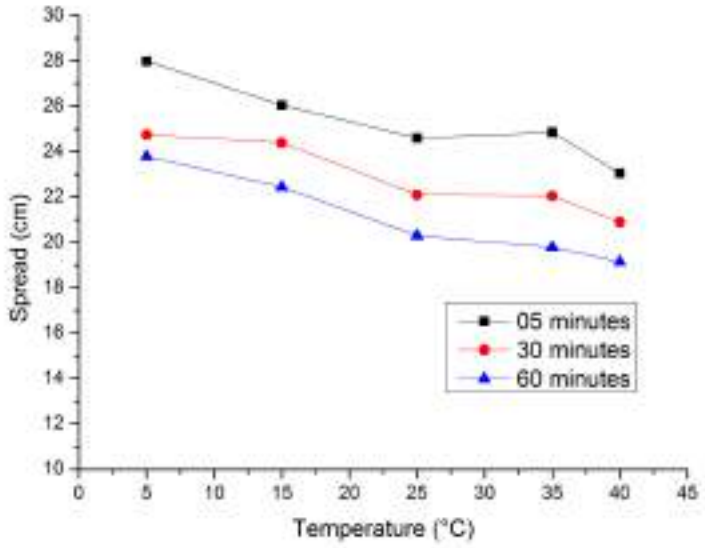
It is observed from the comparison of Figures 5.3 and 5.6, and from Table 5.5 that the spread of mortar increases with an increase in superplasticizer content initially, as well as throughout the measurement (i.e., one hour), for all the superplasticizers and at all temperatures. This increase in fluidity can be due to the higher amount of superplasticizer available for the adsorption on cement particles. As expected, the PCE based superplasticizer showed the highest increase in spread compared to the other superplasticizers.

In order to study the effect of dosage of superplasticizer on the evolution of fluidity of mortar with the dosage corresponding to minimum flow at 25°C, the spreads at 5, 30 and 60 minutes are plotted against temperature in Figure 5.7(a-d). It is observed that the spread also decreases with an increase in temperature at higher dosage of superplasticizer. It is observed from the comparison of Figures 5.5 and 5.8, and from Table 5.5 that the fluidity increases with an increase in the dosage of superplasticizer, at all temperatures, and the gap between the curves for 30 minutes and 60 minutes increases with an increase in superplasticizer dosage, especially at higher temperatures.

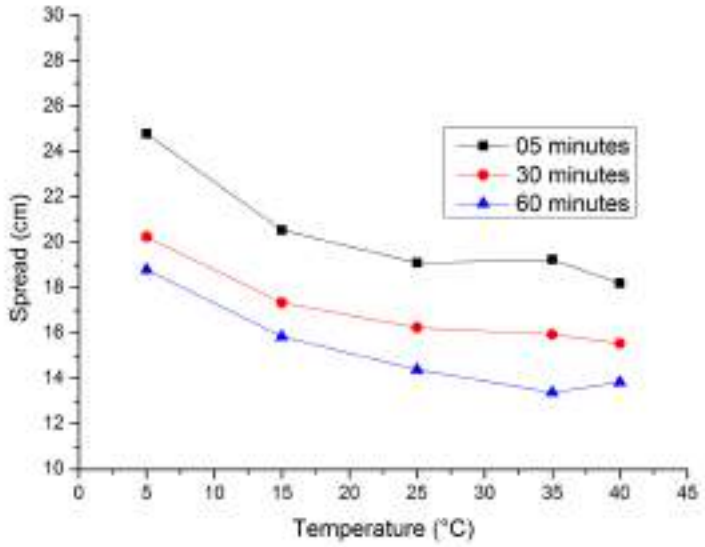


(a)

Figure 5.7 Spread of mortar with temperature at different ages for the superplasticizer dosage corresponding to the minimum flow at 25°C for (a) Control

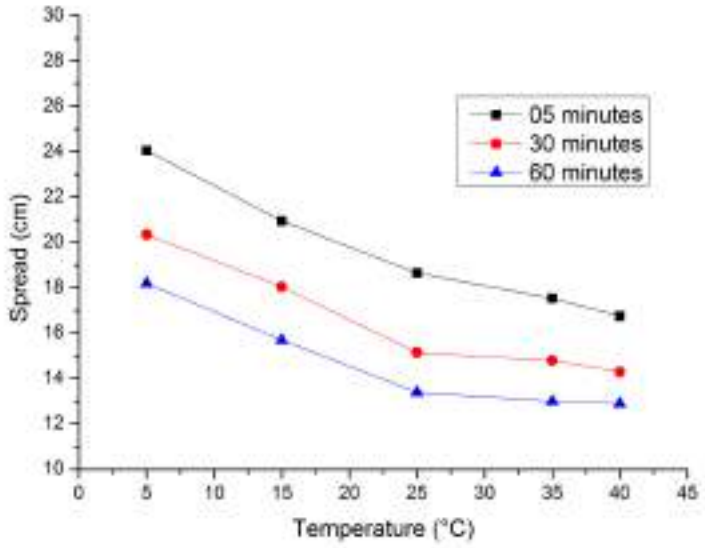


(b)



(c)

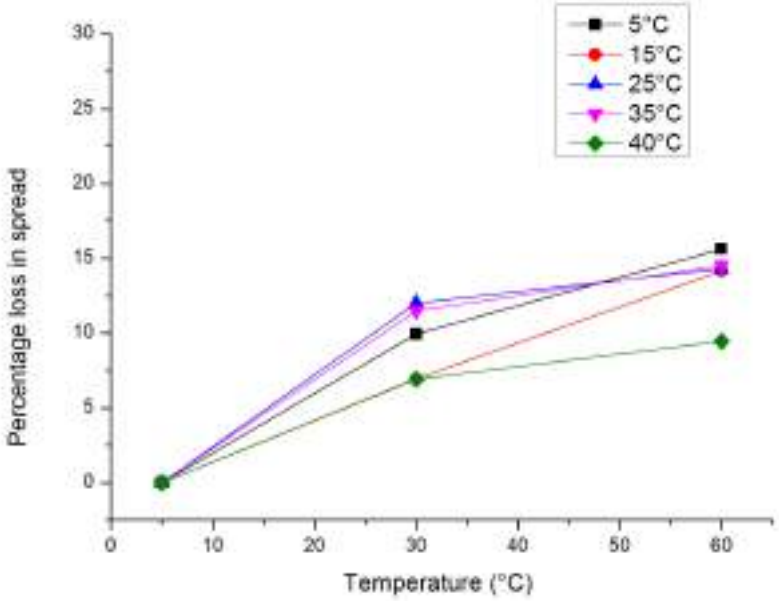
Figure 5.7 Spread of mortar with temperature at different ages for the superplasticizer dosage corresponding to the minimum flow at 25°C for CE (b) PCE and (c) SNF



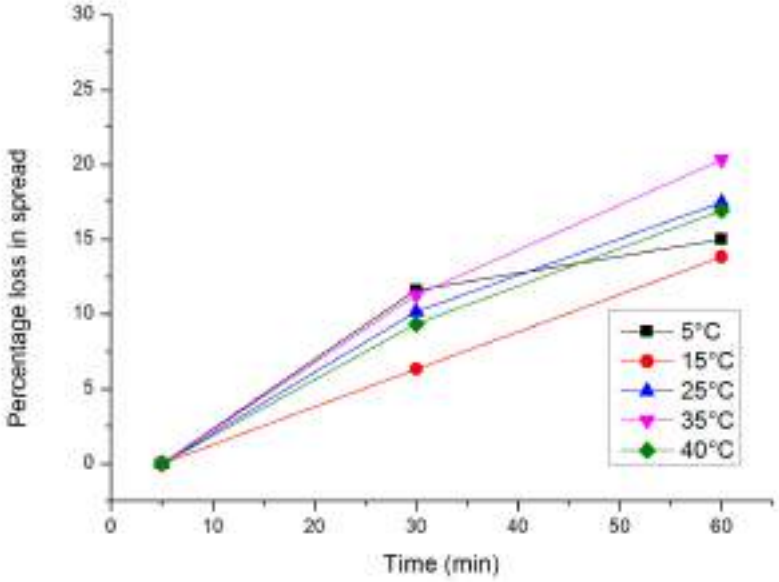
(d)

Figure 5.7 Spread of mortar with temperature at different ages for the superplasticizer dosage corresponding to the minimum flow at 25°C for (d) SMF

As the initial spread of mortar varies with temperature, the spread has been normalised to get a better comparison of the loss in spread with time at different temperatures. The normalized spreads of mortar versus time after mixing are plotted in Figure 5.8 (a-d). The PCE based superplasticized mortar (Figure 5.8b) had a higher loss in spread at higher temperatures, which can be due to the higher initial spread of mortar with the increase in superplasticizer content. The SNF based superplasticized mortar (Figure 5.8c) shows almost same loss in fluidity at all temperatures, except at 35°C, where a higher loss in spread is observed. A higher loss in spread is observed at 35°C for superplasticized mortars, which is in accordance with the observations from the Marsh cone tests on cement paste.

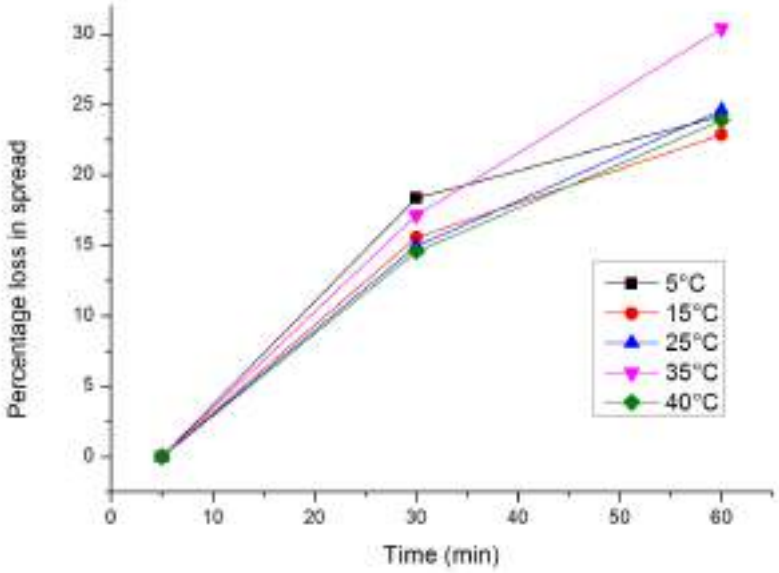


(a)

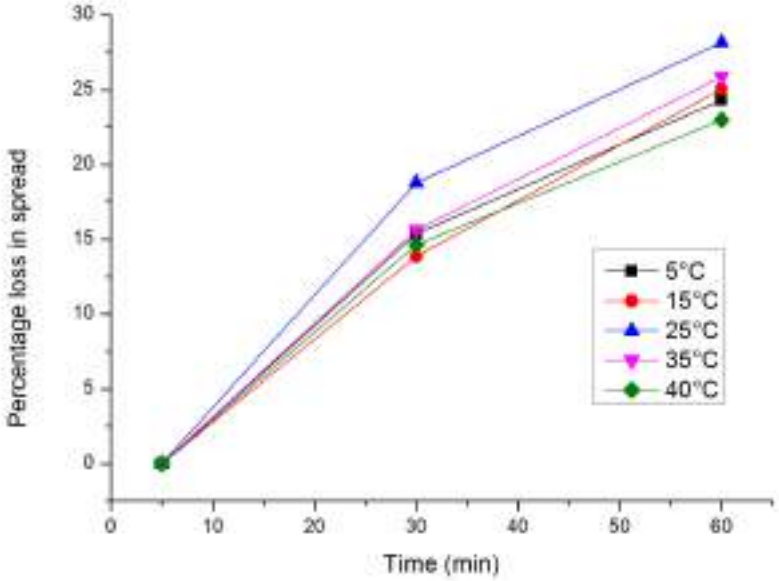


(b)

Figure 5.8 Normalised spread of mortar with time at different temperatures for superplasticizer dosage corresponding to the minimum flow at 25°C for (a) Control (b) PCE



(c)



(d)

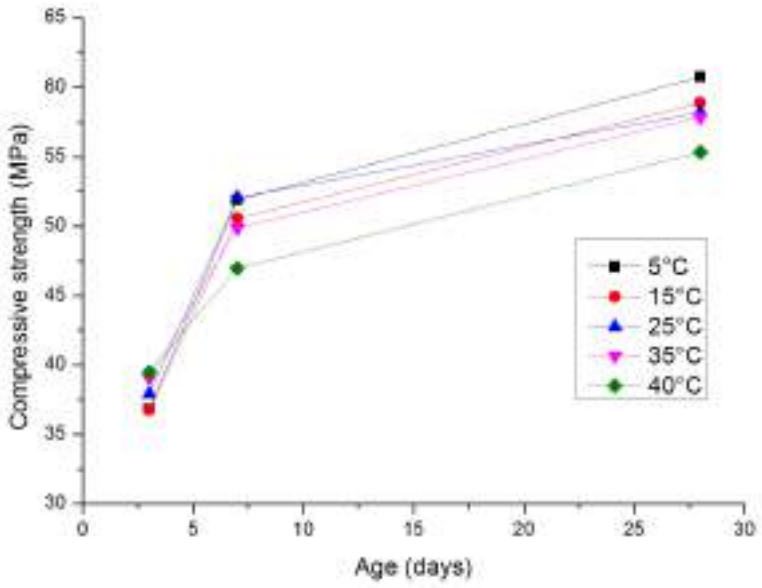
Figure 5.8 Normalised spread of mortar with time at different temperatures for superplasticizer dosage corresponding to the minimum flow at 25°C for (c) SNF (d) SMF

5.3.4 Mechanical Properties of Cement Mortar with Temperature

The ambient temperature affects the mechanical properties of superplasticized cement mortar due to the alteration of the hydration reactions of cement. To study the effect of superplasticizer and ambient temperature to which the mortar is exposed initially, on the mechanical properties of mortar, the compressive and flexural strength of mortar were determined. The results are discussed in the following sub-sections.

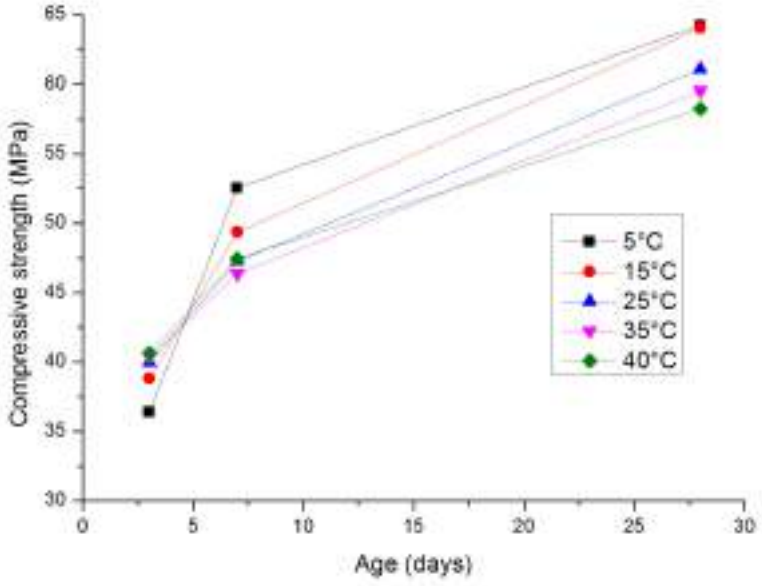
5.3.4.1 Effect of Temperature on the Compressive Strength of Cement Mortar

The compressive strength was determined as explained in Section 3.3.3.3 of Chapter 3 and the results are plotted against age for cement mortar, with and without superplasticizer, in Figure 5.9a-d.

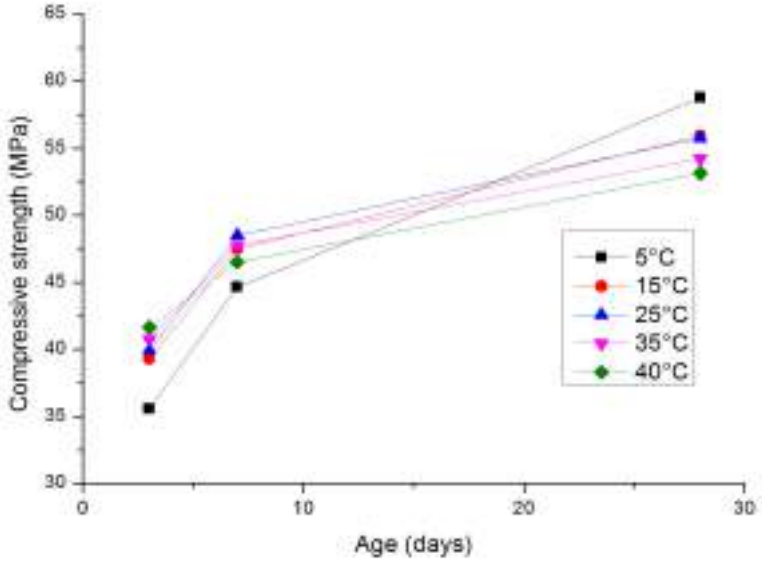


(a)

Figure 5.9 Compressive strength of cement mortar for superplasticizer based on (a) Control

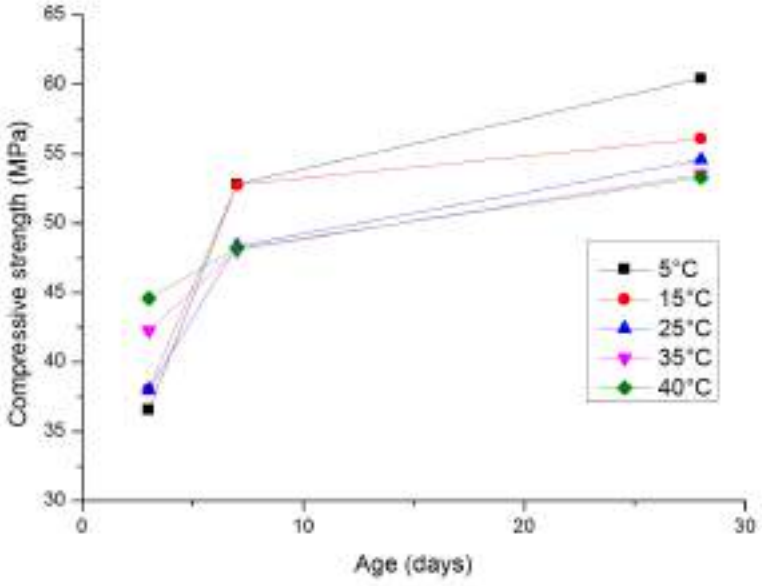


(b)



(c)

Figure 5.9 Compressive strength of cement mortar for superplasticizer based on (b) PCE (c) SNF



(d)

Figure 5.9 Compressive strength of cement mortar for superplasticizer based on (d) SMF

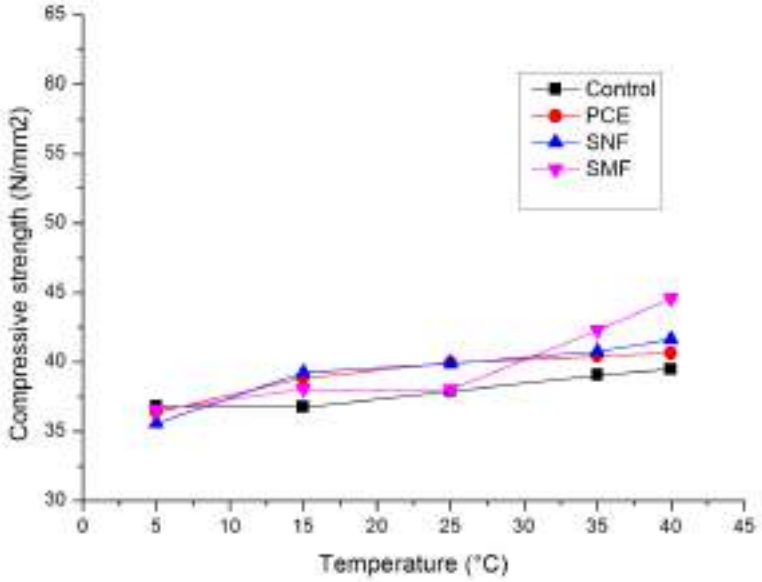
From the test results (Figure 5.9a-d), it is observed that the compressive strength is affected by the temperature to which the cement mortar is exposed initially. The initial compressive strength (3 day) of cement mortar increases with an increase in ambient temperature. However, at later ages, the strength decreases significantly with an increase in initial exposure temperature. There seem to be two competing mechanisms involved in the effect of temperature, and the strength of mortar at any age depends on whichever mechanism predominates at that time (Mirza et al. 1991). At early ages, the hydration of cement will be more due to the increased rate of reactions due to the higher temperature (up to 24 hours), which leads to higher strength initially. However, at later ages, the beneficial effects of the increased rate of hydration become equal to the detrimental effects of exposure to higher temperature and then the detrimental effects become dominant, which lead to reduction in strength. Kjellsen (1991) observed that the cement paste exposed to higher temperature can lead to a weaker, porous and non-uniform microstructure. It is evident that as porosity increases, the strength decreases (Sereda et al. 1980). Therefore, the more porous microstructure formed at higher temperature leads to decrease in strength possibly due to the more porous hydrated cement paste or due to a weakened cement paste-aggregate bond. The

lower strength at higher temperature can also be due to the incomplete hydration of cement particles due to the initial faster rate of moisture loss from the mortar (Mirza et al. 1991).

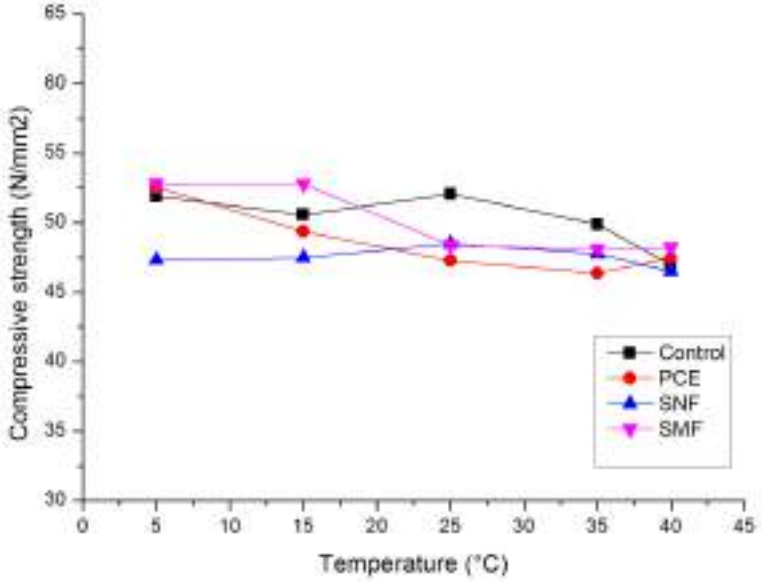
Earlier researchers also found an increase in early strength of mortar with an increase in curing temperature and a reduction in later age strength (Abd-El.Aziz 2012; Mirza et al. 1991; Maltais and Marchand 1997; Elkhadiri et al. 2009). Kjellsen and Detwiler (1992) observed that the effect of temperature is important only at the early ages and becomes less significant at later ages. A dense zone of hydration products are believed to form around the hydrating grains of cement at higher temperatures, and this formation of hydration shells would limit or even prevent further diffusion of ions, thereby reducing the ultimate degree of hydration (Kjellsen et al. 1991; Kjellsen and Detwiler 1992). Sajedi and Razak (2011) observed an increase in the initial compressive strength of mortar heated at 60°C for 24 hours immediately after demoulding, followed by a drop in strength, for mortar having almost same fluidity.

In the present study, the initial spread of mortar decreases at higher temperatures, which can also contribute to the decrease in the compressive strength, since the initial fluidity of mortar will influence the level of compaction of the mortar. It is observed from Figures 5.9a-d that the influence of temperature is more predominant in the case of superplasticized cement mortars. The cement mortar without superplasticizer (Figure 5.9a) showed only a marginal variation in 3 day compressive strength with temperature. However, the superplasticized mortars (Figure 5.9b-d) exhibited a significant increase in the 3-day compressive strength when exposed to higher initial temperatures.

In order to compare the compressive strengths of mortar at different ages, the values at 3, 7 and 28 days are plotted against temperature for different superplasticizers in Figure 5.10(a-c). From the graph (see Figure 5.10a), it is clearly observed that the 3 day compressive strength increases with an increase in temperature for cement mortar both with and without superplasticizer. At 7 days (see Figure 5.10b), the control mortar, and PCE and SMF based superplasticized cement mortars show a marginal decrease in compressive strength. The SNF based superplasticizer shows almost the same compressive strength at all temperatures after 7 days. At 28 days (see Figure 5.10c), the control as well as the superplasticized cement mortar gave lower compressive strength as the temperature increased.

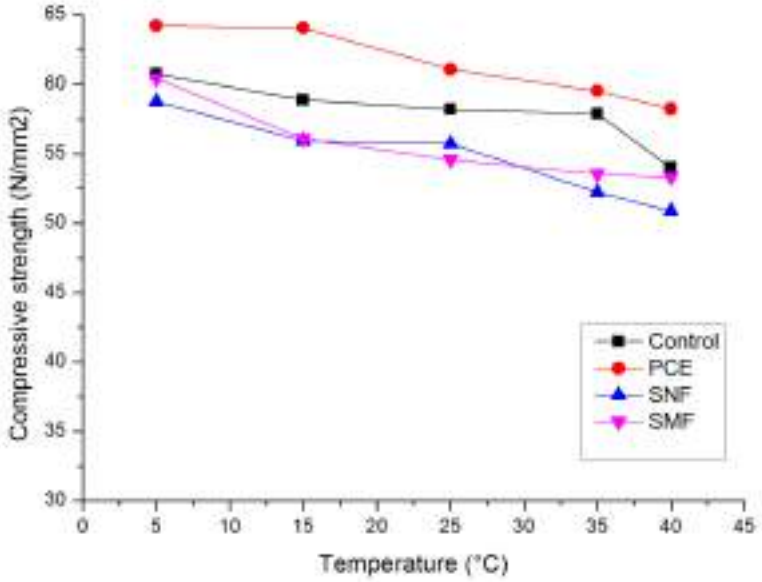


(a)



(b)

Figure 5.10 Compressive strength of mortar with temperature for specimen cured at (a) 3 days, and (b) 7 days

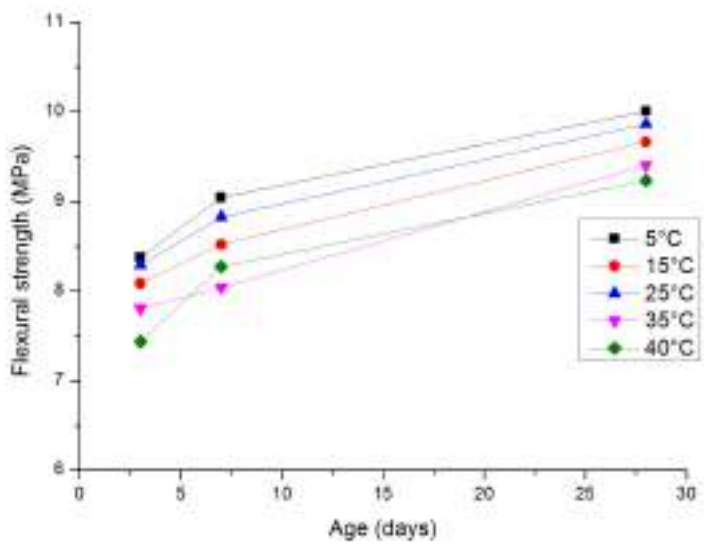


(c)

Figure 5.10 Compressive strength of mortar with temperature for specimen cured at (c) 28 days

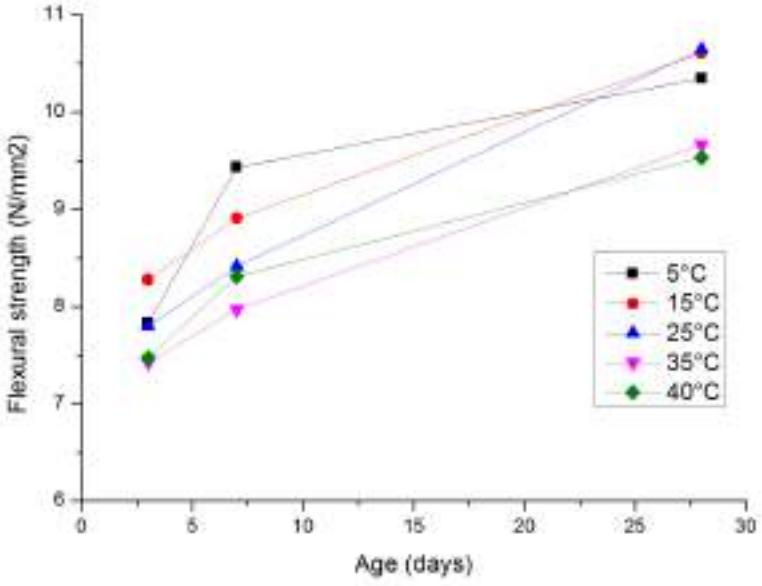
5.3.4.2 The Effect of Temperature on the Flexural Strength of Cement Mortar

The flexural strength of cement mortar was determined as explained in Section 3.3.3.3 of Chapter 3, and is plotted against age for different temperatures in Figure 5.11.

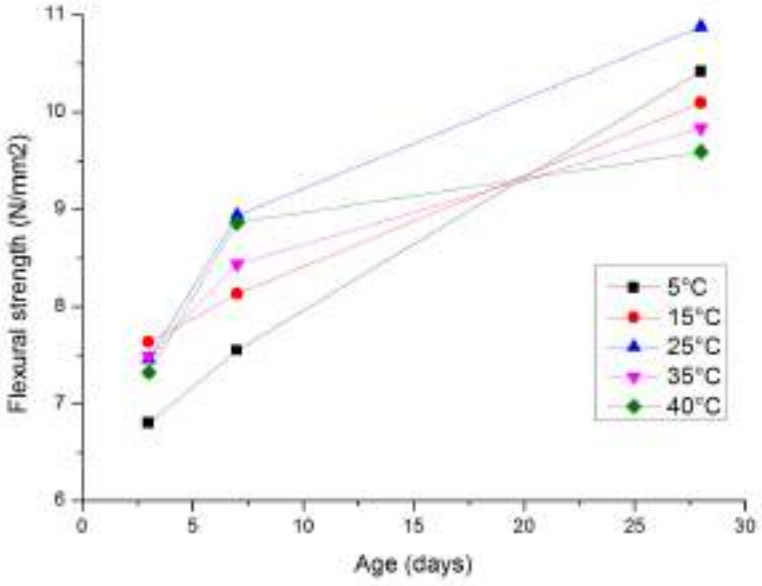


(a)

Figure 5.11 Flexural strengths of cement mortar for (a) Control

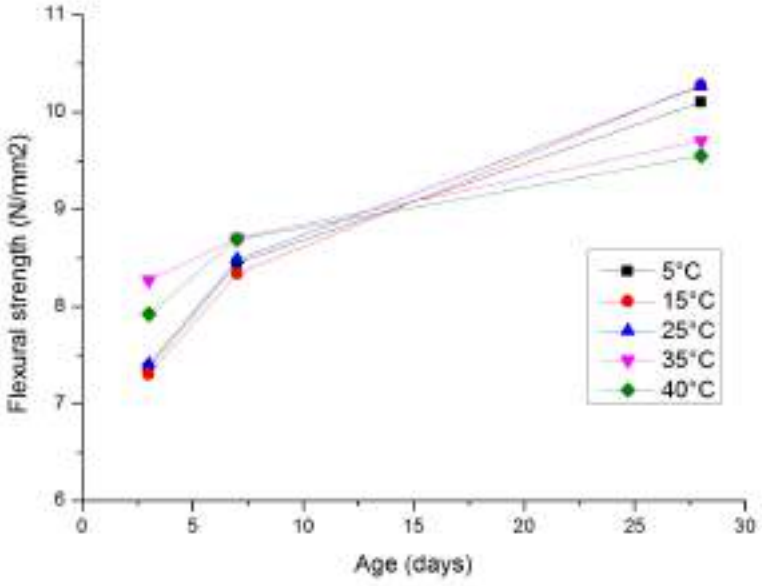


(b)



(c)

Figure 5.11 Flexural strengths of cement mortar for (b) PCE and (c) SNF



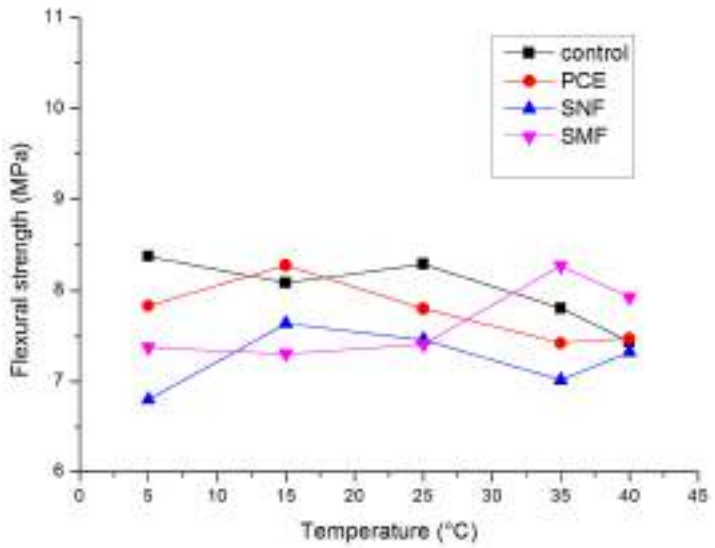
(d)

Figure 5.11 Flexural strengths of cement mortar for (d) SMF

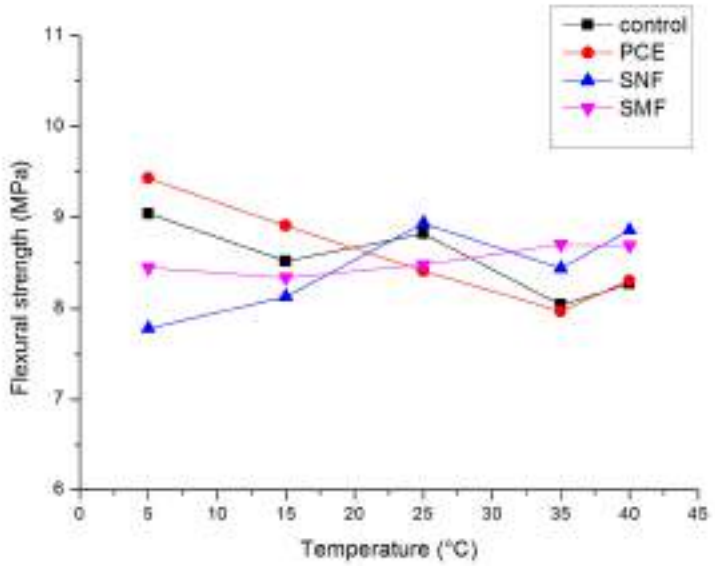
It is observed from the test results (Figure 5.11a-d) that, even though the compressive strength of mortar shows an increase in strength with temperature at early ages, the flexural strength does not show such a trend. It appears that the 28-day flexural strength is always lower for high initial temperatures. At the higher temperatures (i.e., 35 and 40°C), the SMF based superplasticized cement mortar shows higher flexural strength at early ages, whereas the control and PCE based superplasticized cement mortars exhibited lower flexural strengths when exposed to higher temperature initially.

To compare the flexural strengths of mortar at a certain age with temperature, the data for 3, 7 and 28 days are plotted against temperature in Figure 5.12(a-c). The results show that after 3 days of curing, the Control and SMF based superplasticized cement mortars (Figure 5.12a) showed almost the same flexural strength from 5°C to 25°C, and thereafter, the flexural strength increases with temperature for the SMF based mortar and decreases for the control mortar. The PCE and SNF based superplasticized mortars show an increase in flexural strength from 5°C to 15°C and thereafter a decrease with an increase in temperature after 3 days. The control mortar and the PCE based superplasticized cement mortar show a marginal decrease in flexural strength at 7 days, whereas the SNF and SMF based superplasticizers

yield a marginal increase in flexural strength (Figure 5.12b). Generally, the effect of initial temperature on the flexural strength at 3 and 7 days seems negligible. At 28 days, all the cement mortars exhibited a decrease in flexural strength at higher temperature (Figure 5.12c) but the values did not change much over the range of 5 to 25°C.

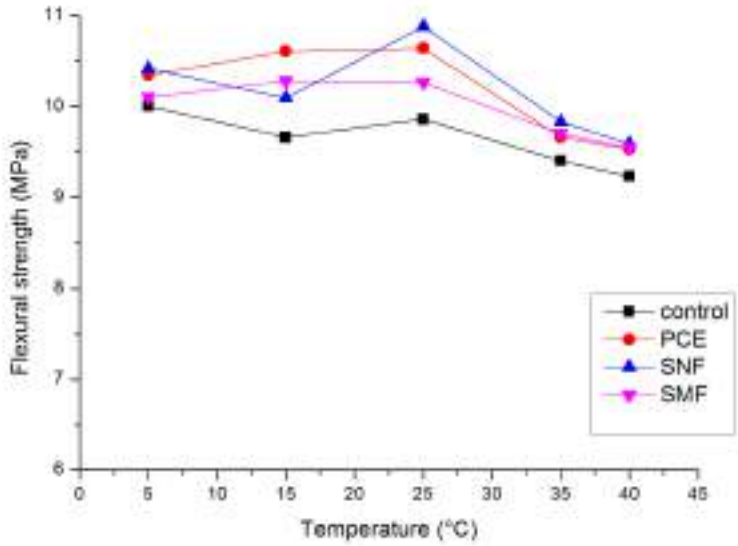


(a)



(b)

Figure 5.12 Flexural strength of mortars with temperature at (a) 3 days, (b) 7 days



(c)

Figure 5.12 Flexural strength of mortars with temperature at (c) 28 days

5.3. 5 Effect of Temperature on Concrete Properties

It is observed that the temperature can influence the fresh, as well as hardened state, properties of cement mortar significantly. In order to extend the conclusions to practical applications, it is essential to study the effects on the properties of concrete.

5.3.5.1 Effect of Temperature on the Fluidity of Concrete

To study the effect of ambient temperature, concrete was prepared as explained in Section 3.3.4.1 using the mix proportions given in Table 5.6. The fluidity of concrete was assessed with the slump test using the Abram's cone, as explained in Section 3.3.4.2 of Chapter 3. The compressive and splitting tensile strengths of concrete were determined, as explained in Section 3.3.4.3, to study the influence of temperature on the mechanical properties of concrete. Only the PCE and SNF based superplasticizers were used in this part of the study as these are the most common types of superplasticizers in the Indian context. The saturation dosage for cement paste at 25°C, as given in Table 5.1 (determined from Marsh cone test), was used as the dosage of superplasticizer for all temperatures. The measured slump of

concrete is plotted against temperature in Figure 5.13 (Note that two trials were conducted in each case).

Table 5.6 Mix proportions for concrete

Description	**Quantity (kg/m^3)**
Cement	440
Water	154
20 mm down aggregate	698
10 mm down aggregate	465
Sand	704

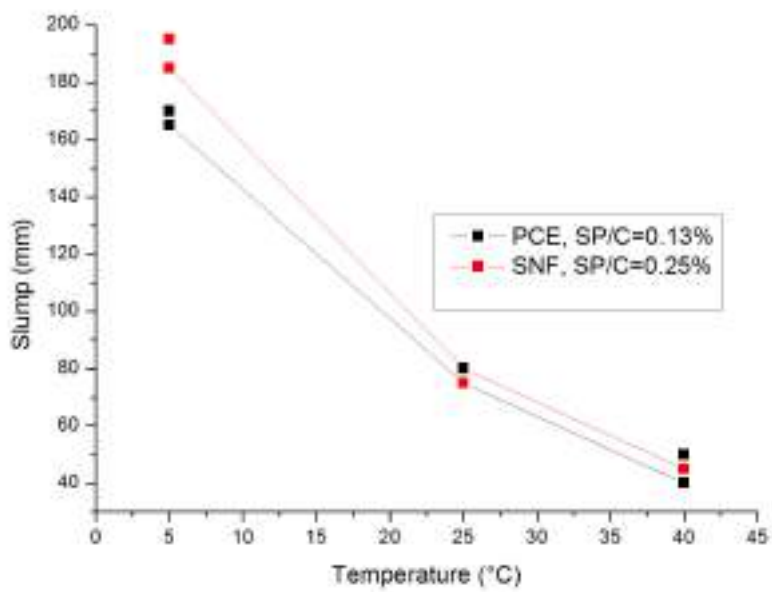


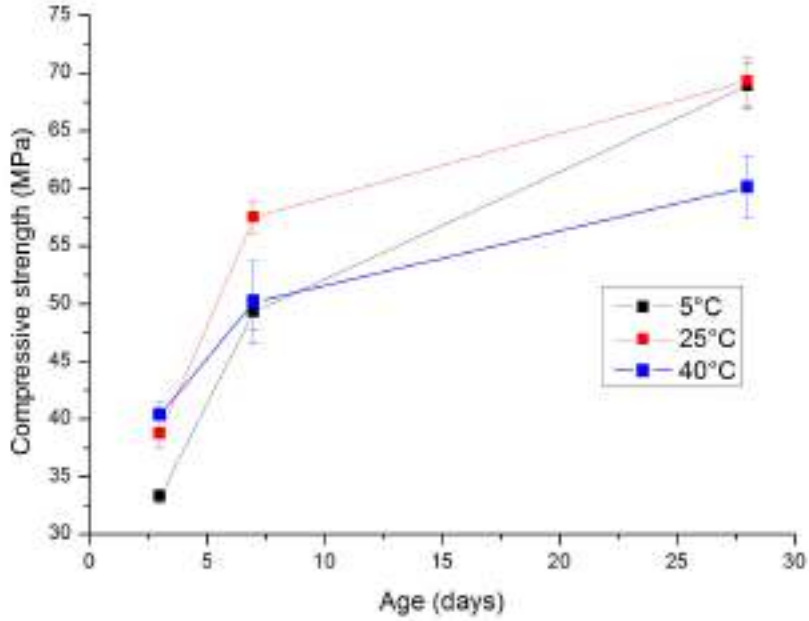
Figure 5.13 Change in slump of concrete with temperature

From Figure 5.13, it is observed that the slump of concrete decreases considerably with an increase in ambient temperature. Both the PCE and SNF based superplasticizers showed the same trend; as temperature increases, the slump decreases. It is also seen that the concrete

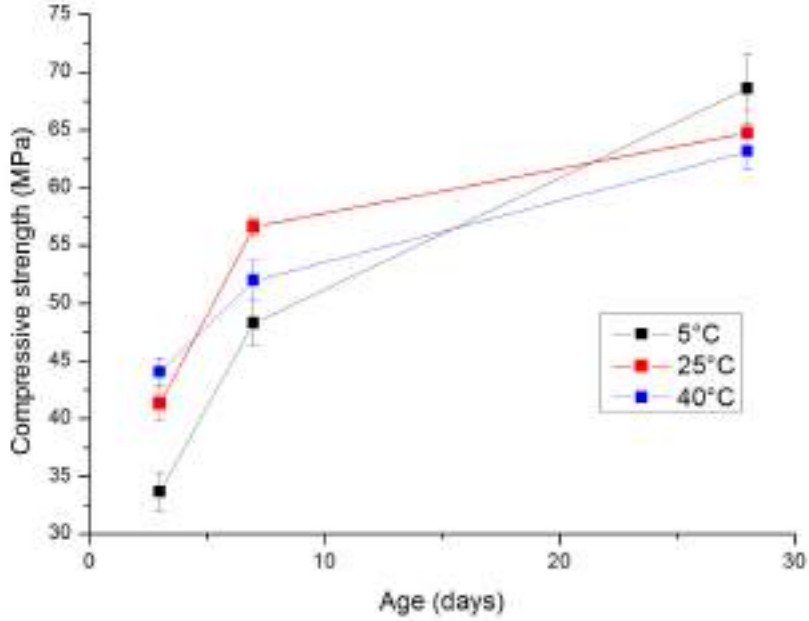
prepared with both PCE and SNF based superplasticizers with the saturation dosage of superplasticizer (for cement paste at 25°C) yielded almost the same slump at all temperatures studied, which reaffirms the usefulness of the Marsh cone test as a guideline for determining the saturation dosage of superplasticizer in concrete. The dosage of superplasticizer corresponding to the saturation dosage (of cement paste at 25°C), gave a slump of 75 and 80 mm for the PCE and SNF based superplasticizer, respectively, at 25°C, whereas the slump increases to 165 and 180 mm when the same mix was prepared at 5°C. When the temperature increased to 40°C, the slump reduced to 45 and 40 mm for the concrete with PCE and SNF based superplasticizer, respectively. Ghafoori and Diawara (2010) also observed a loss in flow at hot weather conditions (i.e., 21°C to 43°C) and an increase in flow with cold weather conditions (i.e., -0.5°C to 21°C) for self compacting concrete. They attributed this to the higher adsorption of the superplasticizer by the cement, the increase in absorption of water by the aggregates, and the higher evaporation rate of water at higher temperatures. Mouret et al. (1997) also observed an increase in water demand for a required consistency increases with an increase in aggregate temperature. An increase of water demand with an increase in temperature was reported by earlier researchers for concrete (Ravina and Soroko, 1994; Soroko and Ravina, 1998). The higher rate of hydration reactions and water demand at higher temperature will consume more water, and the consequent reduction in water increases the friction between the cement and aggregate particles leading to the stiffening of the fresh mix (Ravina and Soroko, 1994).

5.3.5.2 Effect of Temperature on the Mechanical Properties of Concrete

The compressive strength of concrete was determined as per the procedure explained in Section 3.3.4.3 and the results are shown in Figure 5.14 (as mean values and scatter bars). It should be noted that the exposure temperature was maintained for 24 hours after casting the specimen. After that, the specimens were demoulded and kept in a mist room for curing. The age of specimen is given here as the number of days after casting the specimen, which includes the 24 hours in the mould.



(a)



(b)

Figure 5.14 Compressive strength of concrete with temperature for superplasticizers based on (a) PCE and (b) SNF

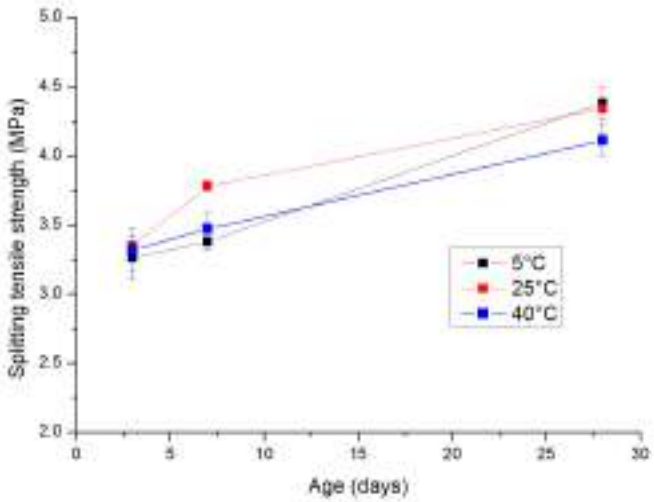
Figure 5.14 shows that the concrete exposed to a higher temperature initially (for the first 24 hours) attains a higher early-age strength but develops lower strength at later ages compared to the specimens exposed to initial lower temperatures. Kim et al. (1998) observed a similar trend in strength for concrete exposed to different temperatures initially. Shoukry et al. (2011) observed a decrease in the 28 day compressive strength with an increase in exposure temperature. Other studies have also shown that concrete cured at higher temperatures yield higher initial strength and lower long-term strength compared to concrete cured at lower temperatures (Mirza et al. 1991; Kim et al. 1998; Topçu and Toprak 2005).

The influence of temperature on cement hydration reactions and the strength development is still not completely clear. The increased rate of hydration of cement at higher temperature can lead to a layer of hydration products in the form of a ‘‘shell’’ on the surface of cement particles, which hinder the diffusion of hydration products further into the matrix (Kim et al. 1998; Ortiz et al. 2005). It is also reported that the porosity of the cement paste subjected to higher temperature increases as a result of the non-uniform diffusion and precipitation of the hydration products. The increase in early curing temperature increases the hydration rate of cement initially and the strength increases rapidly. However, the difference in expansion coefficients of various ingredients of concrete and the non-uniform distribution of hydration products lead to more porosity and formation of micro-cracks, eventually leading to a decrease in strength at later ages (Kim et al. 1998; Ortiz et al. 2005). In the present study, the concrete was exposed to higher temperature initially (i.e., 24 hours after casting) and then cured at room temperature. Therefore the difference in thermal contraction of different constituents of concrete due to the variation in thermal expansion coefficients can lead to the formation of micro-cracks, which in turn can reduce the long-term strength of concrete.

Verbeck and Helmuth (as cited in Ortiz et al. 2005; and Kjellsen and Detwiler 1991) observed that the rate of hydration is initially high at higher temperatures and slows down at the later ages, resulting in a non-uniform distribution of the hydration products within the paste. They explained this to be as a result of insufficient time for the diffusion products of hydration in the interstitial space to precipitate away from the cement particles due to increased rate of hydration at higher temperatures, whereas at lower temperatures, the hydration products will get sufficient time in the interstitial space for diffusion and precipitation, which results in a more uniform and homogeneous distribution of hydration

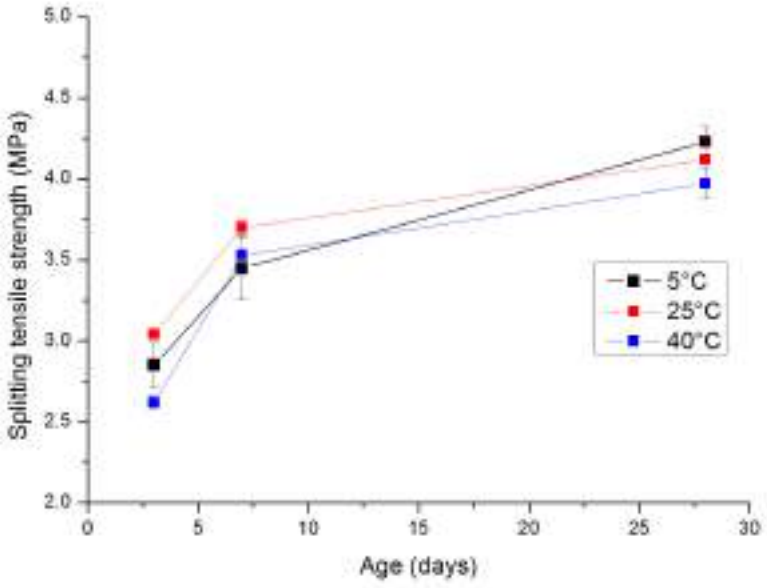
products at lower temperature. Kjellsen and Detwiler (1991) and Kjellsen et al. (1990) found a more uniform microstructure at lower temperatures compared to specimens exposed to high curing temperatures. They also observed that dense hydration shells formed around the cement particles and there is an increased porosity at higher temperatures. Elkhadiri et al. (2009) concluded that higher rate of hydration at the early ages (at higher initial temperatures) leads to the formation of dense hydration products near the hydrating cement particles.

The splitting tensile strength of concrete was determined as explained in Section 3.3.4.3 of Chapter 3 and results are plotted in Figure 5.15. The results showed that the splitting tensile strength generally decreases with an increase in temperature. This can be due to the higher amount of porosity and non-uniform microstructure of the concrete exposed to initial higher temperature. As the defects are more, there will be more possibility of larger defects to develop into cracks, causing failure to occur at lower stresses. The drop in tensile strength of the concrete with a rise in temperature may be partly attributed to a more pronounced weakness of the transition zone (Mouret et al. 1997). The present results are in accordance with the results of Abbasi and Al-Tayyib (1985) and Shoukry et al. (2011) who have observed a decrease in splitting tensile strength of concrete with an increase in the preparation and curing temperature of concrete.



(a)

Figure 5.15 Splitting tensile strength of concrete at different temperatures for superplasticizers based on (a) PCE

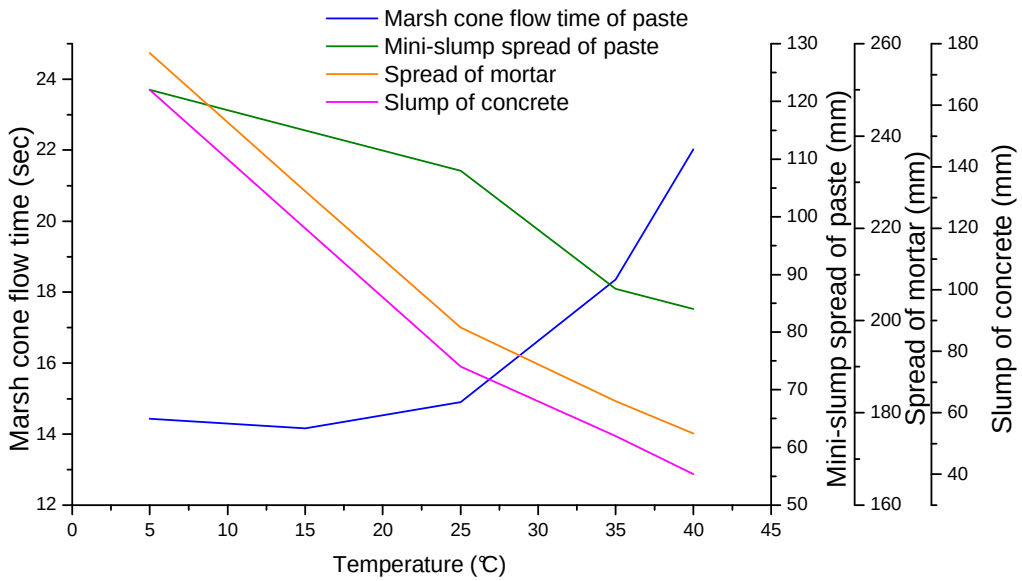


(b)

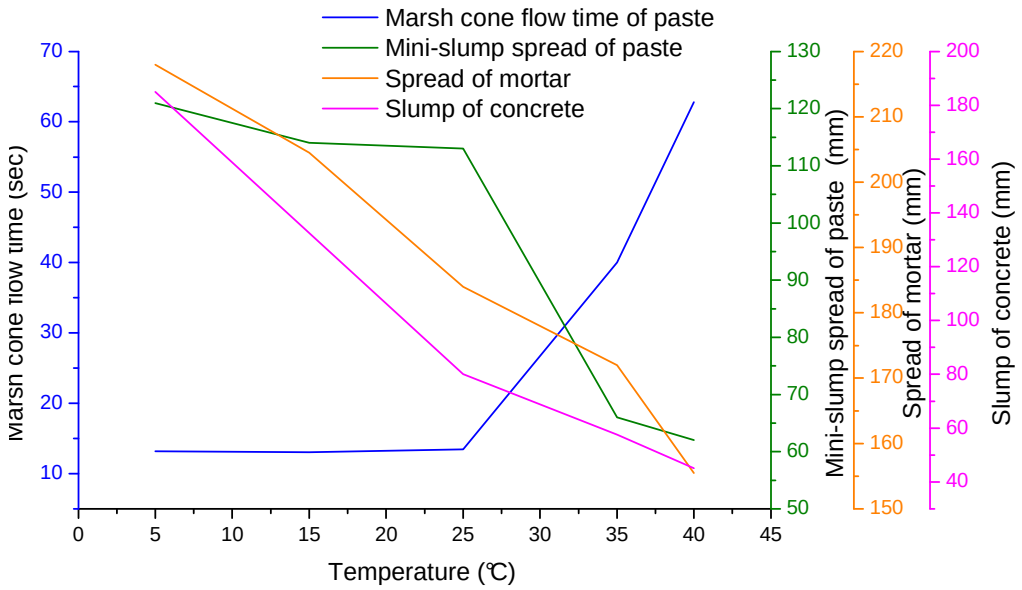
Figure 5.15 Splitting tensile strength of concrete at different temperatures for superplasticizers based on (b) SNF.

5.4 Correlation Between Initial Fluidity of Cement Paste, Mortar and Concrete

The previous sections described the effect of temperature on different properties of cement mortar and concrete, and the previous chapter discussed the influence of temperature on cement paste. It will be interesting to correlate the fluidity of cement paste, mortar and concrete in order to predict the fluidity of concrete from simple tests on the cement paste or mortar. In this study, the paste composition was maintained in the mortar and concrete for comparison. Also, a fine aggregate to cement ratio of 1.6 was used for both cement mortar and concrete. The results from the Marsh cone and mini-slump tests of cement paste, flow table test of mortar and slump test of concrete are plotted as a function of ambient temperature for PCE and SNF based superplasticizer in Figures 5.16.



(a)



(b)

Figure 5.16 Correlation between fluidity of cement paste, mortar and concrete with temperature for superplasticizer based on (a) PCE (b) SNF

The results of the Marsh cone and mini-slump tests on cement paste were discussed in detail in Chapter 4. It is observed that there exists a good correlation (Figure 5.16) between the Marsh cone and mini-slump test results, with the Marsh cone flow time increasing with an increase in temperature and the mini-slump spread decreasing at about the same rate. The fluidity of cement paste is not affected significantly at the lower temperatures (i.e., 5°C to 25°C) but is severely affected at temperatures higher than 25°C. Note that the dosage of superplasticizer used is the dosage corresponding to the saturation dosage of superplasticizer at 25°C. It can be concluded that the fluidity is not affected adversely at temperatures lower than the temperature at which the saturation dosage is determined and the fluidity will change significantly only for temperatures above that. The decrease in fluidity at higher temperatures can be due to the increased rate of hydration and the unavailability of sufficient superplasticizer to adsorb on the cement particles and the newly formed hydrates, as discussed earlier. The higher water demand at higher temperatures can reduce the free water in the mix and increase the superplasticizer demand also leading to a decrease in fluidity (when the dosage is not changed).

The presence of aggregates significantly affects the fluidity of the material (see Figures 5.16). Both mortar and concrete exhibited lower fluidity with an increase in ambient temperature that is much more significant than in the cement paste. This can be due to the absorption of a part of superplasticizer on the aggregate and due to higher water absorption of the mixing water by the aggregates at higher temperature (Ortiz et al., 2009). The higher water absorption could also lead to the decrease observed in setting time when the ambient temperature increases.

A good correlation can be observed between the spread of mortar and slump of concrete with temperature; as temperature increases both these parameters decrease in a similar manner. Both the PCE and SNF based superplasticizer gave the same trend and correlation between cement mortar and concrete because the dosages were the corresponding saturation dosages.

5.5 Comparison Between the Strength of Cement Mortar and Concrete

It was seen in the previous sections that the later-age (i.e., 7- and 28-day) strengths of cement mortar and concrete decrease with an increase in initial temperature. It will be interesting to compare the development of strength of cement mortar and concrete at different ages with

varying temperature. Therefore, the change in strength of the cement mortar and concrete were calculated as a percentage increase/decrease from the strength at 5°C and the values are given in Table 5.7.

Table 5.7 Comparison between the compressive strengths of cement mortar and concrete

SP	Age (days)	Cement mortar					Concrete				
		Temperature (°C)			Percentage change in strength (with respect to the 5°C value)		Temperature (°C)			Percentage change in strength	
		5	25	40	25	40	5	25	40	25	40
PCE	3	36.4	40.0	40.7	9.8	11.7	33.3	38.7	40.4	16.3	21.2
	7	52.6	47.3	47.5	-10.1	-9.7	49.3	57.5	49.2	16.7	-0.2
	28	60.8	58.2	54.0	-4.2	-11.1	68.9	69.3	60.1	0.6	-12.7
SNF	3	35.6	39.9	41.6	12.2	17.0	33.7	41.2	44.1	22.4	30.9
	7	47.3	48.5	46.5	2.5	-1.7	48.3	56.6	52.0	17.3	7.6
	28	64.2	61.1	58.2	-4.9	-9.4	68.6	64.7	63.1	-5.7	-8.0

The compressive strengths of cement mortar and concrete generally gave a similar trend. The short-term (3 day) compressive strength of cement mortar and concrete was observed to increase with initial ambient temperature (Note that the negative sign in the table indicates loss in strength). The concrete shows a higher increase in compressive strength compared to cement mortar at 3 days. The PCE based cement mortar shows a lower strength after 7 days of curing at 25 and 40°C compared to 5°C; however, the concrete shows an increase in strength at 25°C and has almost the same strength at 40°C and 5°C at 7 days. For the SNF based superplasticizer, the cement mortar shows a marginal gain in strength at 25°C and a marginal loss in strength at 40°C compared to 5°C after 7 days of curing, whereas the concrete with the SNF based superplasticizer shows a gain in strength at both 25 and 40°C. The 28 day compressive strength shows a good correlation between cement mortar and concrete. The PCE based superplasticizer gave a marginal decrease in compressive strength for mortar at 25°C, while the concrete has almost the same strength at 5 and 25°C. At 40°C, both mortar and concrete had significantly lower strengths. It can be observed from the results that the gain in strength at the early ages due to increase in temperature reduces at a faster rate in the case of cement mortar compared to concrete.

The flexural strength of mortar and splitting tensile strength of concrete were also compared to get a qualitative idea about the development of tensile strength of concrete with age for specimens exposed to different temperatures. The change in strength compared to 5°C for each age was calculated for 25 and 40°C, and the values are given in Table 5.8.

Table 5.8 Comparison between the flexural strength of cement mortar and splitting tensile strength of concrete

SP	Age (days)	Flexural strength of cement mortar					Splitting tensile strength of concrete				
		Temperature (°C)			Percentage change in strength (with respect to the 5°C value)		Temperature (°C)			Percentage change in strength	
		5	25	40	25	40	5	25	40	25	40
PCE	3	7.8	7.8	7.5	-0.4	-4.6	3.3	3.4	3.3	3.4	1.8
	7	9.4	8.4	8.3	-10.8	-11.9	3.4	3.8	3.5	11.8	2.7
	28	10.4	10.6	9.5	2.8	-7.9	4.4	4.5	4.1	2.5	-6.2
SNF	3	6.8	7.5	7.3	9.7	7.7	2.9	3.0	2.6	6.3	-8.1
	7	7.8	8.9	8.9	14.9	13.9	3.5	3.7	3.5	7.3	2.3
	28	10.4	10.9	9.6	4.4	-7.9	4.1	4.1	4.0	0.5	-3.2

The cement mortar and concrete had lower 28 day strengths for the specimens exposed to higher temperature initially. There exists a good correlation between the strength of cement mortar and concrete. The 28-day flexural strength of mortar and splitting tensile strength of concrete also show trends similar to that of the compressive strength.

5.6. CONCLUSIONS

The influence of temperature and superplasticizer, and its coupled effect on the different properties of cement mortar and concrete were studied. The results of the initial fluidity of cement paste, cement mortar and concrete were correlated to establish a relation between them. The study has lead to the following conclusions:

- The temperature has a significant influence on the initial fluidity and loss in fluidity of cement mortar with time. The fluidity decreases with an increase in temperature, with and without superplasticizer. The loss in fluidity is more predominant in the first half hour compared to the second half hour, especially at higher temperatures. Therefore,

the ambient temperature should be taken into consideration while finalising the proportions of the mix to get the required fluidity for cement mortar.

- Higher superplasticizer dosage can increase the fluidity of cement mortar. A higher dosage of superplasticizer can be adopted, if necessary, for obtaining the required fluidity for cement mortar; however, care should be taken to avoid problems like segregation and retardation due to over dosage. The dosages used in this study are those corresponding to the saturation dosage and the dosage corresponding to the minimum flow, both obtained at 25°C. Following the work of Jayasree (2008) and Jayasree and Gettu (2012), it is recommended that when superplasticizer dosages higher than the saturation dosage need to be used, the dosage should not exceed 150% of the saturation dosage, in order to limit retardation and probable segregation, as well as cost.

- The compressive strength of cement mortar increases initially with an increase in temperature; however, the long term strength decreases with an increase in initial exposure temperature. The higher rate of hydration due to higher temperature at early ages can be the reason for the higher early strength; however, at later ages, this effect is neutralised and the detrimental effects of higher temperature exposure become more predominant. The changes in the microstructure due to rapid hydration at higher temperatures and the effect of variation in the compaction due to low fluidity can be the reason for the lower strength for the specimens exposed to initial higher temperatures. Therefore, proper studies have to be done to make sure that the required strength will be obtained at the actual exposure conditions. The flexural strength of mortar also decreases with an increase in temperature.

- The slump of concrete decreases rapidly with an increase in temperature. The higher hydration of cement, increased absorption of the aggregates and the increased evaporation of water from the mix at higher temperature can be the reason for the decreased slump at higher temperature.

- The compressive strength of concrete increases initially with an increase in ambient temperature to which the concrete is exposed; however, the long term strength reduces with increase in initial temperature. The splitting tensile strength of concrete

was also found to decrease with an increase in ambient temperature to which the concrete is exposed initially. Therefore, the ambient temperature to which the concrete is subjected should be considered in the determination of the proportioning of the ingredients of concrete. The methodology for selecting a compatible cement-superplasticizer combination can follow that suggested by Jayasree (2008) and Jayasree and Gettu (2012), with the tests conducted at the temperature of interest. It is reiterated that the testing should be done at the temperature to which the concrete is going to be exposed at the site in the fresh state in order to get the most appropriate results.

- There exists a good correlation between the initial fluidity of cement paste, mortar and concrete. Studies on fluidity of cement paste give a guideline for the superplasticizer demand for the mortar and concrete at varying temperatures; however, at lower temperatures compared to the temperature at which the saturation dosage of cement paste is determined, there is practically no loss in flow for cement paste, whereas the cement mortar and concrete exhibited lower in fluidity.

- The influence of temperature on the 28-day compressive strengths of cement mortar and concrete can be generally comparable even though the development of strength varies marginally. The advantage of an initial higher rate of hydration due to higher temperatures is negated early in the case of cement mortar, whereas higher strength is observed for longer time for concrete.

Generally, it can be concluded that the mix proportioning of concrete should be done by considering the ambient temperature to which the concrete is exposed to. Increase in temperature can affect the fresh and hardened state properties of concrete drastically. The fluidity of cement mortar and concrete decreased significantly with an increase in temperature. Hence, the superplasticizer dosage should be selected by considering the temperature also as a factor, to get the required slump, and proper care has to be taken to ensure the required strength at later ages. Again, the strength of mortar and concrete decreased with an increase in initial temperature.

CHAPTER 6

EFFECTS OF THE FINENESS AND SO_3 CONTENT OF CEMENT

6.1 INTRODUCTION

The previous chapters dealt with the effect of temperature on the different properties of cement paste, mortar and concrete. In addition to the environmental conditions, the properties depend on the characteristics of the ingredients, especially cement, to a large extent. There are many brands of cement available in the market, which vary in their physical properties and chemical composition within the ranges specified in the codes. Moreover, there are various types of superplasticizer available in market, which are significantly different in composition and performance.

The effects of the fineness and SO_3 content of cement on the properties of superplasticized cement paste, mortar and concrete are discussed in this chapter. These factors have been selected to cover the usual range of fineness and SO_3 content seen in the cements available in Indian market. Fresh cement paste properties such as fluidity, loss in fluidity with time, water demand and setting time have been studied. The fluidity of cement paste has been characterized with the help of Marsh cone and Mini slump tests. The Vicat apparatus was used to study the water demand and setting time of cement paste. The flow table test was employed to study the effect of these parameters on the workability of mortar. The compressive and flexural strengths of the mortars were determined to study the mechanical properties of mortar. The slump test was employed in concrete to study the superplasticizer requirement; all concretes had an initial slump of 150 ±20 mm. The compressive strength of concrete was also determined. The procedures of the various tests conducted have been presented in Chapter 3.

6.2. EXPERIMENTAL DETAILS

6.2.1 Materials Used

6.2.1.1 Cement

Tailor-made cement samples were prepared in a cement manufacturing plant from the same batch of clinker so as to keep the manufacturing process and the temperature during grinding the same, which is important as these parameters can influence the properties and performance of cement (Bensted 1982). All the cements can be classified as 53 grade ordinary portland cement, satisfying the requirements of IS 12269 (2004). The fineness of cement was varied by altering the duration of grinding in the ball mill and the SO_3 content of cement was varied by altering the gypsum content in the feed. The chemical properties of the cement samples are given in Table 6.1, as determined by the National Test House, Taramani, Chennai. The fineness of cements (average of three tests) as determined through the Blaine's air permeability test is given in Table 6.2. The water demand of cement for a standard consistency (here, corresponding to a Vicat needle penetration of 35±1 mm) was determined as per the procedure explained in Section 3.3.3.2.4 of Chapter 3. The water demand for cements with different fineness values is given in Table 6.2.

From Table 6.1, it is clear that the compositions of all the samples are within the range specified in IS 12269 (2004). The samples, designated as S1, S2, S3 and S4, have SO_3 contents (Table 6.1) of 1.70, 1.88, 2.19 and 2.53%, respectively, and were used to study the effect of SO_3 content of cement. The samples F1, F2, F3 and F4 have fineness values (Table 6.2) of 270, 290, 340 and 360 m^2/kg, respectively, and were used to study the effect of fineness of cement. It is also observed from Table 6.2 that all the cement samples had practically the same water demand.

Table 6.1 Chemical composition of the cement samples used

Characteristics	Quantity (% by mass)							
	S1	**S2**	**S3**	**S4**	**F1**	**F2**	**F3**	**F4**
Calcium oxide (CaO)	61.	60.2	60.4	59.3	60.2	59.5	60.0	59.4
Silica (SiO_2)	21.	21.4	21.5	21.5	20.9	21.9	21.9	21.4
Alumina (Al_2O_3)	4.4	5.72	4.95	4.94	5.96	6.01	7.14	6.63
Iron oxide (Fe_2O_3)	4.7	4.34	4.22	4.25	4.38	4.08	4.08	4.16
Magnesia (MgO)	1.9	2.16	1.99	2.01	1.85	2.01	2.31	2.14
Sulphuric anhydride (SO_3^{2-})	1.7	1.88	2.19	2.53	1.71	2.19	2.38	2.57
Insoluble residue	0.6	0.81	0.78	1.39	0.64	0.79	0.13	1.18
Total loss on ignition	2.2	2.69	2.32	1.83	2.04	2.64	1.41	1.77
Total chloride content (Cl^-)	0.0	0.06	0.05	0.05	0.06	0.04	0.03	0.03
Sodium oxide (Na_2O)	0.1	0.21	0.26	0.44	0.13	0.27	0.16	0.13
Pottassium oxide (K_2O)	0.5	0.55	0.14	0.41	0.16	0.75	0.48	0.37
Total alkalies $(Na_2O)_{eq}$	0.5	0.57	0.35	0.71	0.24	0.76	0.48	0.37

Table 6.2 Fineness and water demand of cement samples

Sample	**S1**	**S2**	**S3**	**S4**	**F1**	**F2**	**F3**	**F4**
Fineness in m^2/kg	270	290	290	290	270	290	340	360
Water demand at normal consistency in %	29	29	29	29	29	29	30	30

6.2.1.2 Superplasticizer

Two types of widely used superplasticizers (i.e., PCE and SNF), as specified earlier in Table 3.2 of Chapter 3, were used in the study to obtain representative results. The superplasticizer dosages (sp/c) given in this work are all in terms of the solid content of the superplasticizer. The liquid content in the superplasticizer was compensated for in the water cement ratio.

6.2.1.3 Water

Distilled water is used in the study to eliminate the effects of chemicals present in the water.

6.2.2 Testing Conditions

All tests were performed at a temperature of 27±2 °C and relative humidity of 65±5% to avoid the effect of the ambient conditions on the results. A walk-in environmental chamber (see Fig. 3.3) was used to maintain the temperature of the materials, mixing and measuring equipments and for conducting the experiments. The materials were maintained at the prescribed temperature for at least 48 hours prior to the test for preconditioning. The temperature of the materials was verified to confirm that it is within the allowable limit (±2°C). The ambient humidity was monitored using a sensor to make sure that it is within the allowable limit (±5%). The mixing and testing of the samples were done as per the procedures already explained in Chapter 3. The mortar cubes and prisms were also prepared inside the walk-in chamber under controlled conditions. After demoulding (at the age of 24 hours), the specimens were shifted to a mist room for curing. For concrete, all the materials were preconditioned inside the chamber and the mixing was done outside, at room temperature, due to practical constraints.

6.3 RESULTS AND DISCUSSIONS

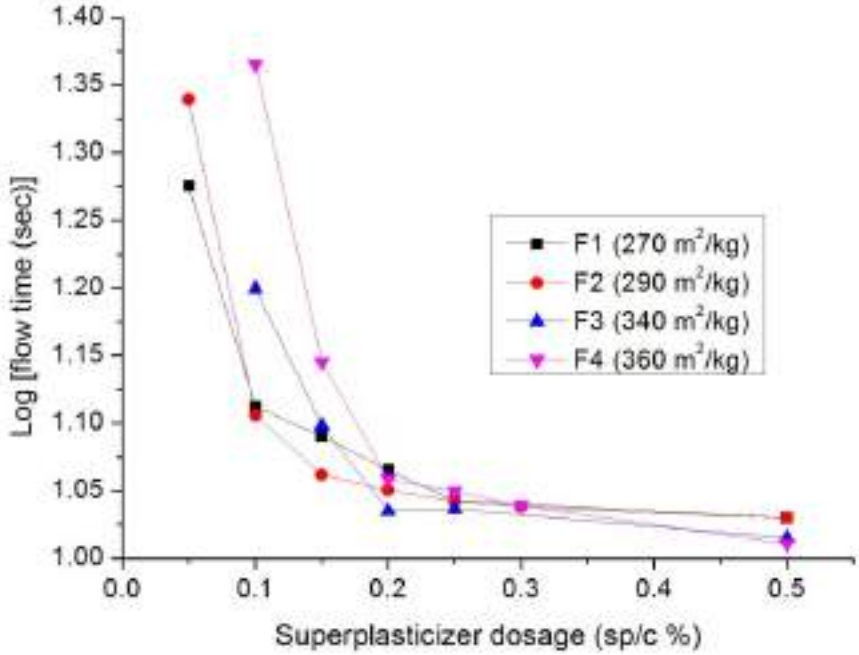
This section discusses the results obtained from the various tests conducted. The fluidity, loss in fluidity with time, water demand and setting time were determined in cement paste to study the influence of its behavior. The spread, loss in spread with time, compressive strength and flexural strength were assessed in cement mortar, whereas the slump, loss in slump with time and compressive strength were studied in concrete.

6.3.1 Effect of Fineness of Cement on the Properties of Paste, Mortar and Concrete

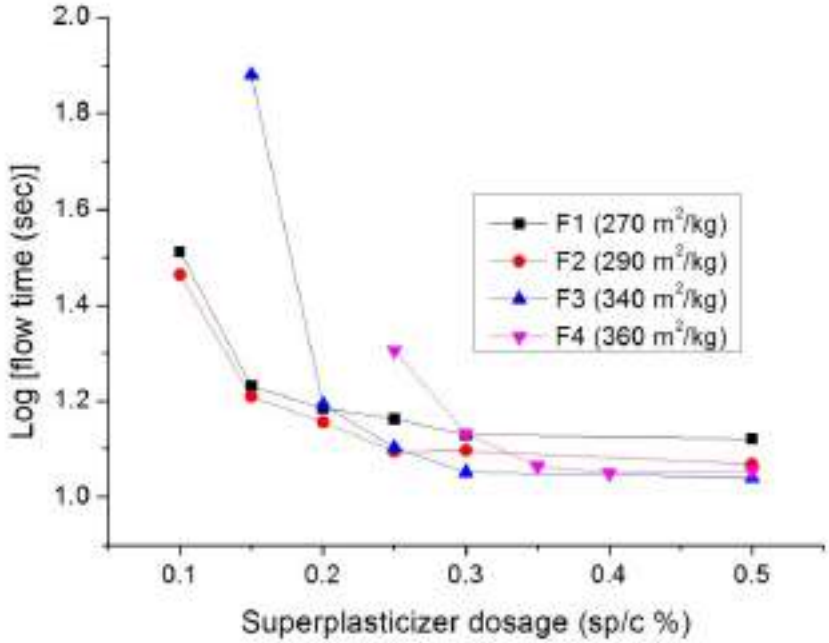
6.3.1.1 Effect on the Fluidity of Superplasticized Cement Paste.

The Marsh cone and mini-slump tests were used to study the fluidity of the superplasticized paste with the cement samples F1, F2, F3 and F4. The logarithm of Marsh cone flow time for each superplasticizer dosage is plotted against the sp/c dosage for the different cement pastes in Figure 6.1 (a and b). Two trials were done for each case and the typical curves for the PCE and SNF based superplasticizers are given in the plots; the complete set of flow time curves are given in Appendix B. The

average saturation dosage of superplasticizer corresponding to the internal angle of 140°±10° (as suggested by Gomes et al., 2001) was determined, and the values are given in Table 6.3.



(a)



(b)

Figure 6.1 Marsh cone flow time versus superplasticizer dosage for cements with various fineness for the superplasticizers (a) PCE and (b) SNF

Table 6.3 Saturation dosages of superplasticizer with fineness

Cement	Saturation dosage (sp/c, %)	
	PCE	SNF
F1 (270 m^2/kg)	0.10	0.15
F2 (290 m^2/kg)	0.10	0.15
F3 (340 m^2/kg)	0.19	0.30
F4 (360 m^2/kg)	0.21	0.35

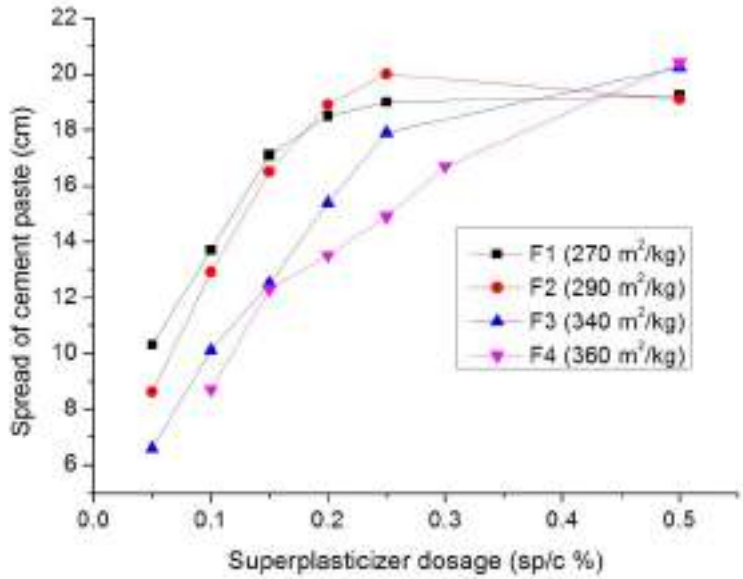
From Figure 6.1, it is observed that, in all the cases, the fluidity increases with an increase in the dosage of superplasticizer up to the saturation point and does not increase significantly thereafter, as expected and observed earlier. It is also seen that the fluidity decreases (i.e., flow time increases) with an increase in the fineness of cement at lower dosages of superplasticizer. This is in accordance with the observation of Skvara et al. (1981) that the viscosity of cement paste increases with an increase in the fineness of cement without superplasticizer, and those of Aitcin (1998). However, it is seen here that at higher dosages of superplasticizer, the fluidity is unaffected by or increases marginally with an increase in the fineness of cement. The marginal increase observed here in some cases was also seen by Aitcin (1998) and Aydin et al. (2009). Aydin et al. (2009) attributed the decrease in flow time to the decrease in viscosity of cement paste with an increase in cement fineness possibly due to better dispersion of the finer cement at higher superplasticizer dosages. The increase in fluidity at higher superplasticizer dosages is more evident in the case of an SNF-based superplasticizer than for the PCE. Further, Neville (2007) also noticed a slight increase in workability of concrete with an increase in fineness of cement.

From Figure 6.1 and Table 6.3, it is clear that the saturation dosage of superplasticizer increases with an increase in the fineness of cement. Nkinamubanzi and Aïtcin (2004) also observed an increase in the saturation dosage of an SNF-based superplasticizer for cements having high Blaine specific surface area. Aydin et al. (2009) reported an increase in superplasticizer demand with an increase in the fineness of cement after 60 minutes though they did not find any significant effect immediately after mixing (i.e.,

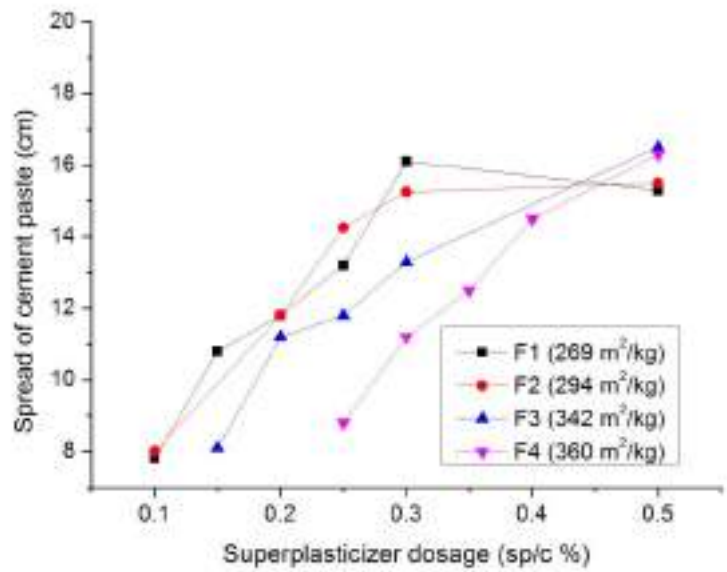
5 minutes). They attributed this is to the increased adsorption of the superplasticizer on the cement particles; i.e., higher the fineness, more will be the adsorption. The increase in saturation dosage is not observed in the case of samples F1 and F2, as the difference in fineness between them (i.e., 20 m^2/kg) is not large enough to cause an increase in the saturation dosage. However, the increase in saturation dosage is clearly significant in samples with higher fineness (i.e., F3 and F4), which implies a higher superplasticizer requirement for better fluidity of cement with higher fineness. This can be attributed to the higher adsorption of water and superplasticizer on the surface of cements with higher fineness. Again, the higher surface area of the finer cement leads to an increase in hydration reactions (Bentz et al. 1999, Aydin et al. 2009). As the reactions are faster, more initial reaction products are formed, resulting in more superplasticizer being adsorbed on the surface of the hydration products.

From Table 6.3, it is observed that the dosage of superplasticizer at saturation was lower for the PCE-based superplastizer compared to the SNF-based superplasticizer, as expected and observed earlier. This is attributed to the better efficiency of the steric hindrance mechanism of action of the PCE-based superplasticizer. However, both superplasticizers yielded the same trend, i.e., the saturation superplasticizer dosage increases with an increase in the fineness.

The mini slump test was also employed to assess the fluidity of cement paste and the results are plotted in Figure 6.2. The mini slump spreads (Figure 6.2a & b) gave trends similar to those of the Marsh cone tests, i.e., the flow decreases as the fineness increases at lower dosages of superplasticizer, which is in accordance with the observations of Aydin et al. (2009). However, at higher dosages of superplasticizer, the cement with higher fineness gave marginally higher fluidity compared to that of the cements with lower fineness. Both PCE and SNF yielded the same trend with variation in fineness of cement. Pastes with cement F1 and F2 had almost the same spread; however, the pastes with F3 and F4 had lower spreads at lower dosages of superplasticizer, which is in accordance with the observations of Marsh cone test. This confirms the higher requirement of superplasticizer in cements with more fineness. At higher dosages of superplasticizer, the finer cements (i.e., F3 and F4) gave higher fluidity with both PCE and SNF based superplasticizers.



(a)



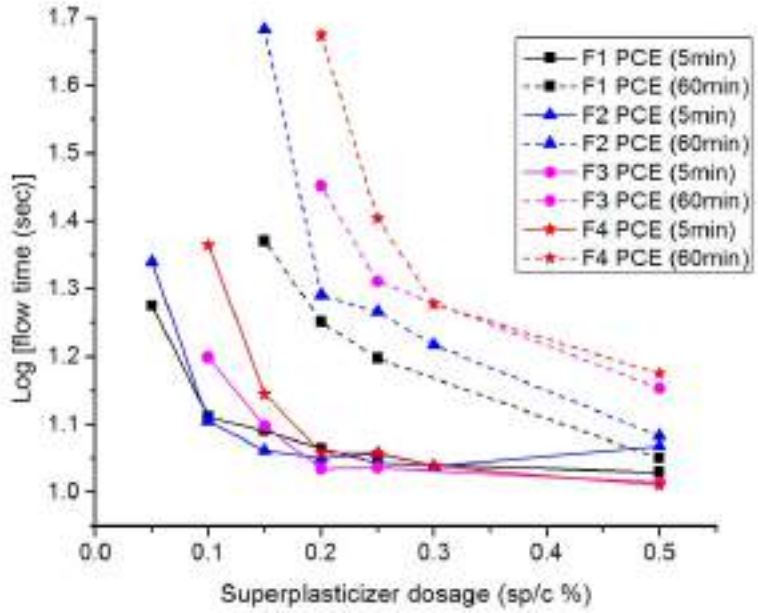
(b)

Figure 6.2 Curves of mini-slump spread versus superplasticizer dosage for cements with various fineness for the superplasticizers (a) PCE and (b) SNF

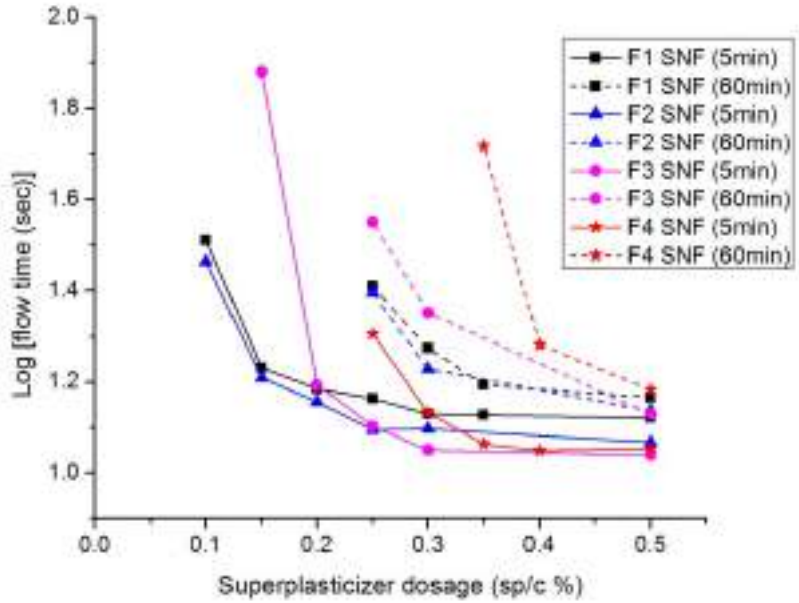
6.3.1.2 Effect on the Evolution of Fluidity of Superplasticized Cement Paste

In order to study the effect of fineness of cement on the loss in fluidity of cement paste with time, the Marsh cone flow time of cement paste was measured immediately after mixing and 60 minutes after the addition of water to cement. The cement paste was kept in air tight containers until one hour after the initial measurement and then mixed for 30 seconds at medium speed (with a shaft speed of 285 rpm and a planetary

speed of 125 rpm) before the second measurement. The results are plotted in Figures 6.3a and b; the continuous lines give the flow curves immediately after mixing (5 minutes) and the dotted lines represent the flow after 60 minutes.



(a)



(a)

Figure 6.3 Loss in fluidity in cement pastes with cements having varying fineness for (a) PCE and (b) SNF

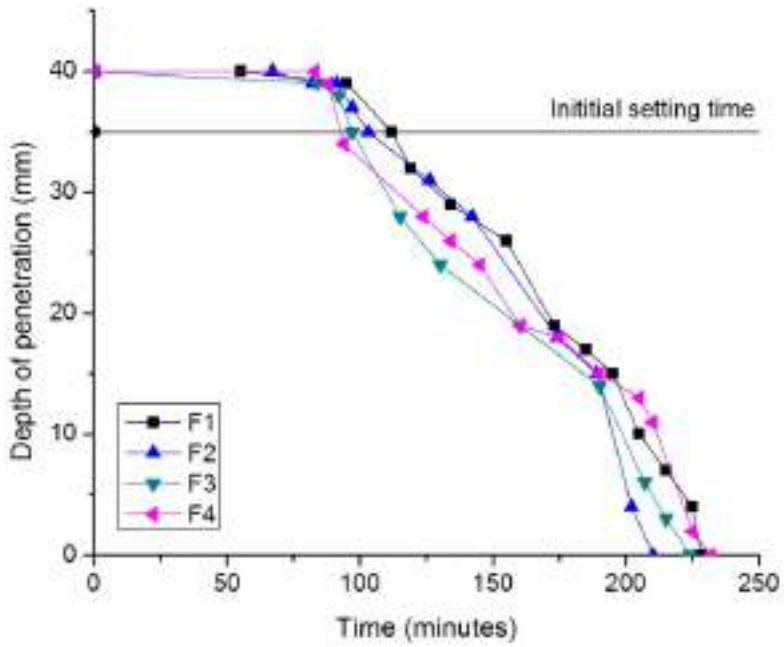
In Figure 6.3, the curves after 60 minutes shift towards the right and above the initial curves, in all the cases, indicating the loss in fluidity with time. From the test results (Figure 6.3), it is clear that the loss in fluidity with time for cement paste increases with an increase in fineness of cement for the same dosage of superplasticizer (i.e., the gap between the initial and 60 minute curves increases with an increase in cement fineness). This is in accordance with the observations of Kim et al. (2000), who found that the effectiveness of the superplasticizer adsorbed on the cement surface reduces as hydration proceeds, due to the incorporation of the new hydrates. In finer cements, it can be expected that there will be higher early adsorption of the superplasticizer, leaving less superplasticizer in the interstitial solution for replacing that consumed by the newly formed hydrates. In addition to this, the hydration rate will also be more for cements with higher fineness due to greater specific surface area (Bentz et al. 1999, Aydin et al. 2009). Further, the acceleration in hydration process also produces a higher flow loss (Chandra and Björnström 2002, Aydin et al. 2009). Jayasree and Gettu (2008) also observed an increase in Marsh cone flow time with age and suggested that for a particular application when the flow behavior at 60 minutes is more significant than the immediate flow, the saturation point could be defined based on the flow time curves at 60 minutes, or similarly for any other critical time.

The difference in loss in fluidity between the pastes with F1 and F2 cements (Figure 6.3a and b) was marginal as their difference in fineness is small (i.e., 20 m^2/kg). However, for the cements with higher fineness (i.e., for F3 and F4), the loss in fluidity is significantly affected. Further, it is observed (see Figure 6.3) that the fluidity loss also depends on the dosage of superplasticizer (i.e., the gap between the initial and 60 minute curves decreases with an increase in the dosage of superplasticizer); at higher superplasticizer dosages, the loss in fluidity is significantly reduced. The pastes with the samples F1 and F2 do not exhibit any flow after 60 minutes with the saturation dosage of both PCE and SNF based superplasticizers. The flow time for F3 and F4 increased by about 75% at the saturation dosage of the PCE based superplasticizer, whereas the paste with F3 did not flow after 60 minutes and F4 exhibited an increase of about 80% in flow time at the saturation dosage of SNF based superplasticizer. With 0.5% PCE dosage, the pastes with F1 and F2 had almost the same flow time over an hour, i.e., loss in fluidity over one hour is marginal. All the samples exhibited the similar trend; i.e., as the dosage of superplasticizer increases, the loss in flow with

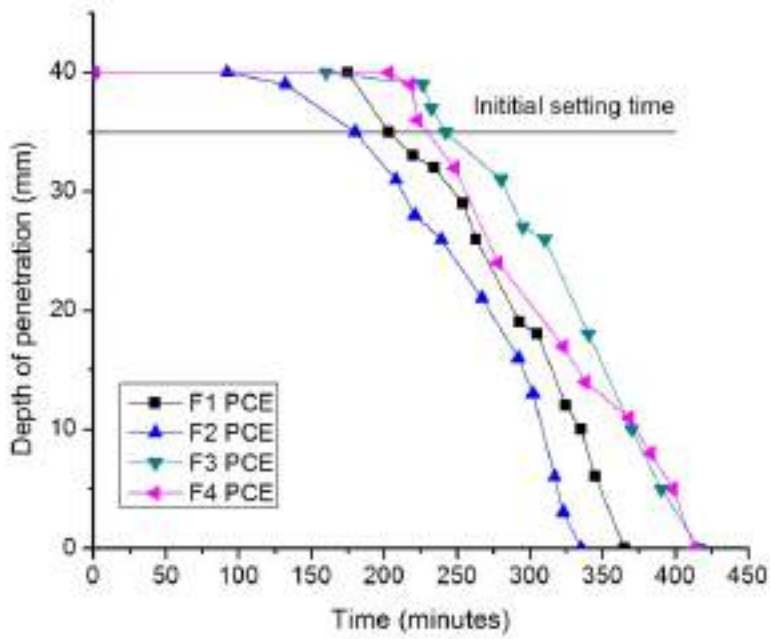
time decreases. This phenomenon can be attributed to the availability of superplasticizer in the interstitial solution, at higher dosages, for later adsorption on the newly formed hydration products, leading to better retention of fluidity.

6.3.1.3 Effect on the Setting Time of Cement Paste

The setting time of cement is an important property as the mix should be workable for a sufficient time after mixing. The setting is controlled by the formation of a network of partly hydrated cement paste, having hydration products that can resist shearing. The initial and final setting times of the cements were determined with and without superplasticizer. The saturation dosages of superplasticizer determined from Marsh cone test for each of the samples (see Table 6.3) was used in the superplasticized pastes. The Vicat penetration for cement pastes with and without superplasticizers is plotted against time for each cement, in Figures 6.4 a-c. The horizontal line drawn at 35 mm penetration in each of the plots indicates the criterion for the initial setting time. It is observed from the test results of cement paste without superplasticizer (Figure 6.4a) that the initial setting time decreases with an increase in the fineness of cement, as expected. For the superplasticized cement pastes, the data are plotted for the PCE in Figure 6.4b and for the SNF in Figure 6.4c. When we compare the results for cements F1 and F2, which have the same superplasticizer dosage, it is seen that the setting time decreases with an increase in fineness of cement. However, the overall trends are not clear as both the dosage of superplasticizer and cement fineness change in these tests.

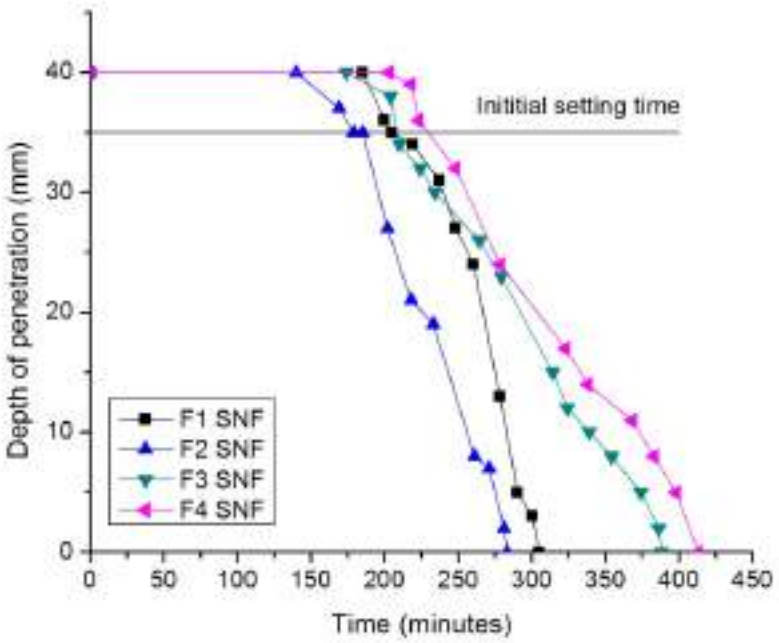


(a)



(b)

Figure 6.4 Evolution of Vicat penetration values for pastes having (a) no superplasticizer and (b) having PCE



(c)

Figure 6.4 Evolution of Vicat penetration values for pastes having (c) SNF

Table 6.4 shows the setting time values for the different cases. As indicated earlier, the initial setting times of pastes without superplasticizer decrease marginally with an increase in cement fineness, confirming previous observations such as those of Vuk et al. (2001) and Bentz et al. (1999). This can be attributed to faster hydration, as the surface area of the cement increases. Addition of superplasticizer retards the initial setting time significantly in all cases, as expected and observed earlier. The superplasticizer leads to better dispersion of the cement particles, which leads to an increase in the time to achieve set (Bentz et al. 1999). For the samples F3 (340 m^2/kg) and F4 (360 m^2/kg), the retardation is higher compared to F1 (270 m^2/kg) and F2 (290 m^2/kg) probably because of the higher amount of superplasticizer dosage. It is observed Table 6.4 that the final setting time is not affected significantly with an increase in cement fineness. Nevertheless, the addition of superplasticizer retards the final setting time, as expected and observed earlier, though not as much as the initial setting time.

Table 6.4 Setting time of cements with varying fineness

Sample	Control		PCE		SNF	
	Initial	Final	Initial	Final	Initial	Final
F1 (270 m^2/kg)	112	228	203	365	205	305
F2 (290 m^2/kg)	106	210	180	335	189	283
F3 (340 m^2/kg)	97	224	242	416	206	388
F4 (360 m^2/kg)	92	232	218	428	233	413

6.3.1.4 Effect on the Fluidity of Superplasticized Cement Mortar

In order to study the effect of cement fineness on the fluidity of mortar, flow table tests were performed as described in Section 3.3.3 of Chapter 3. The cement:sand ratio was 1:1.6 and the water/cement ratio was 0.4, in all the cases; the absorption of water by the sand was compensated by adding extra water corresponding to the coefficient of absorption (0.53%). The superplasticizer dosages correspond to the saturation dosages obtained from the Marsh cone tests on pastes (see Table 6.3). Note that the paste tests were done with w/c = 0.35 so there is a slight overdosage of the superplasticizer to be closer to site conditions where concrete is fabricated at the plant and supplied to the site. The results obtained immediately after mixing and after a delay of 60 minutes are shown in Figure 6.5.

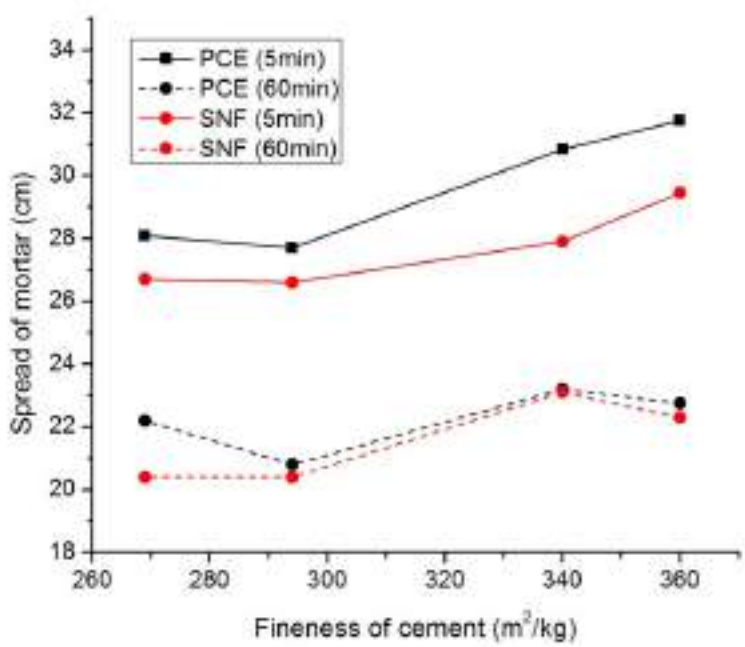


Figure 6.5 Flow table spread of cement mortar

It is observed from Figure 6.5 that the mortar fluidity immediately after mixing (i.e., at 5 minutes) increases slightly with an increase in fineness of cement. This is in accordance with the trends seen in the flow tests of pastes. The PCE based superplasticizer gave higher initial fluidity than the SNF, as expected and observed earlier. Figure 6.5 shows that mortars with cements F1 and F2, having the same superplasticizer dosages, exhibit almost same fluidity with both the PCE and SNF. However, mortars with cements having higher fineness (i.e., F3 and F4) exhibited more flow, due to the higher superplasticizer dosages.

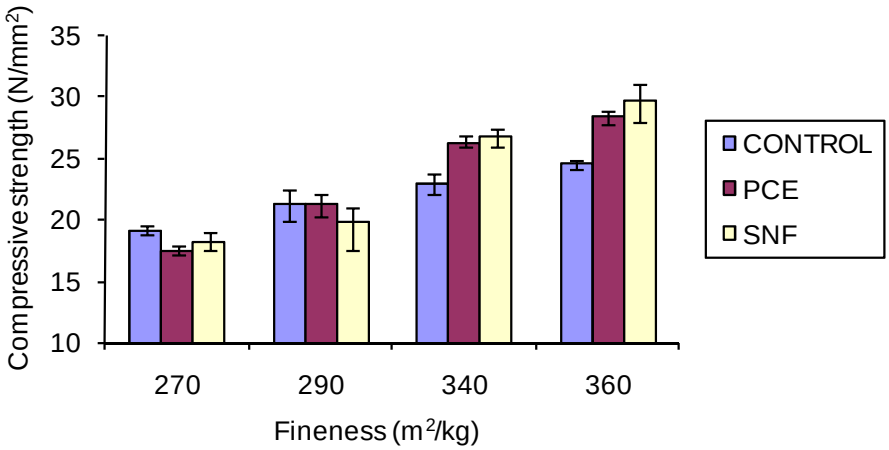
The loss in fluidity with time was also observed with the help of the flow table test. The spread of mortar after 60 minutes of adding water to cement is plotted in Figure 6.5, for all the mortars tested. The mortars have a similar loss in flow and do not seem to be as sensitive to the change in fineness as the cement pastes. It is seen that the loss in spread is about 25% with the PCE and about 20% with the SNF.

6.3.1.5 Effect on the Mechanical Properties of Mortar

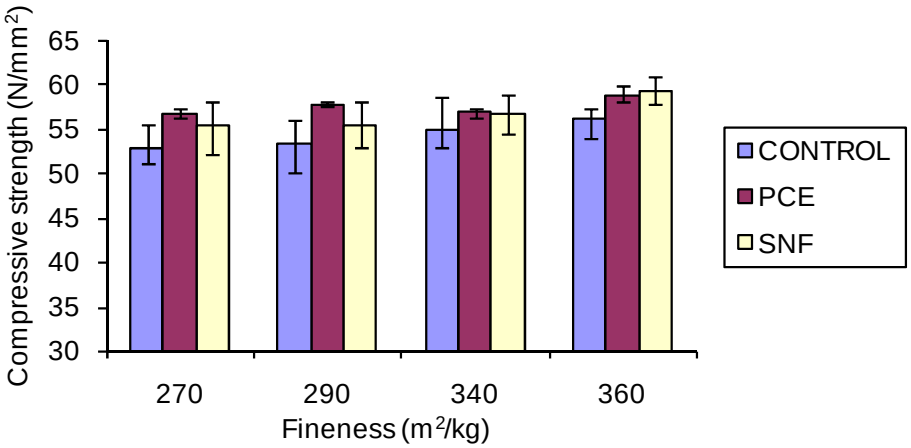
In order to study the effect of cement fineness on the mechanical properties of cement mortar, the compressive and flexural strengths were determined as explained in Section 3.3.3 of Chapter 3. The mortars were prepared with the compositions given in the previous section.

6.3.1.5.1 Effect on the Compressive Strength of Mortar

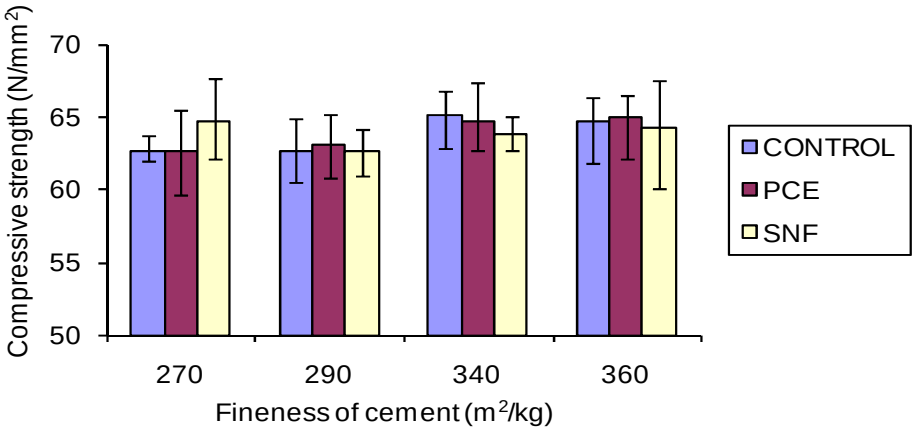
The compressive strengths were determined after 1, 7 and 28 days of curing, and the results are plotted against cement fineness in Figure 6.6 (a-c). The maximum and minimum values in each case are shown in Figure 6.6 as error bars. The evolution of the mean strengths can be better appreciated in the plots given in Figure 6.7.



(a)

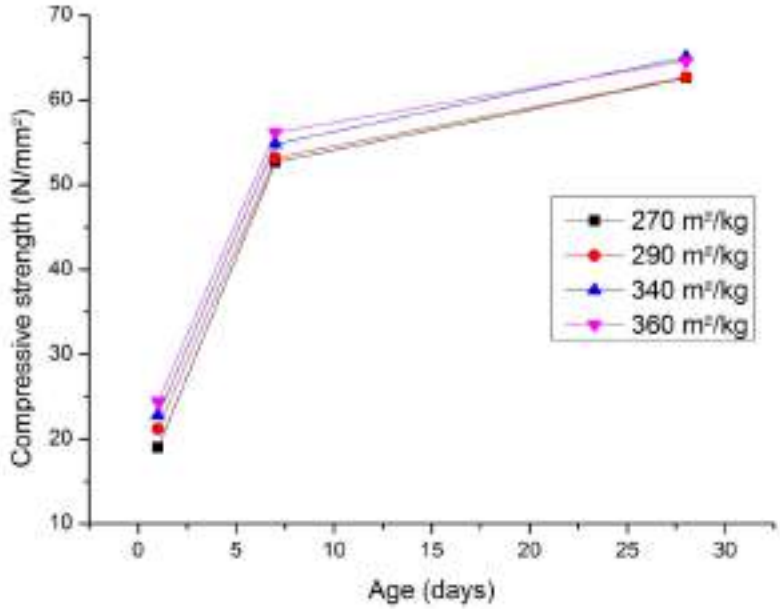


(b)

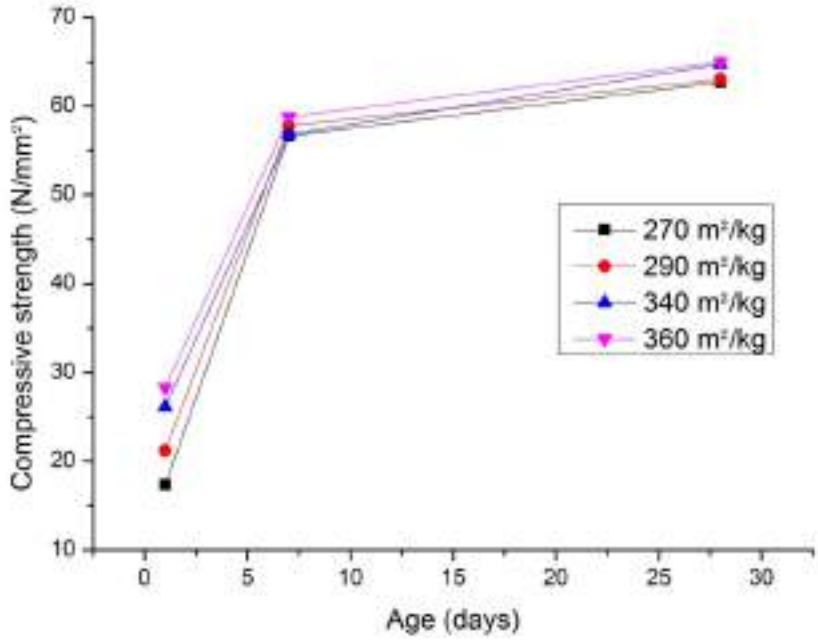


(c)

Figure 6.6 Compressive strengths of mortars at (a) 1 day, (b) 7 days, and (c) 28 days

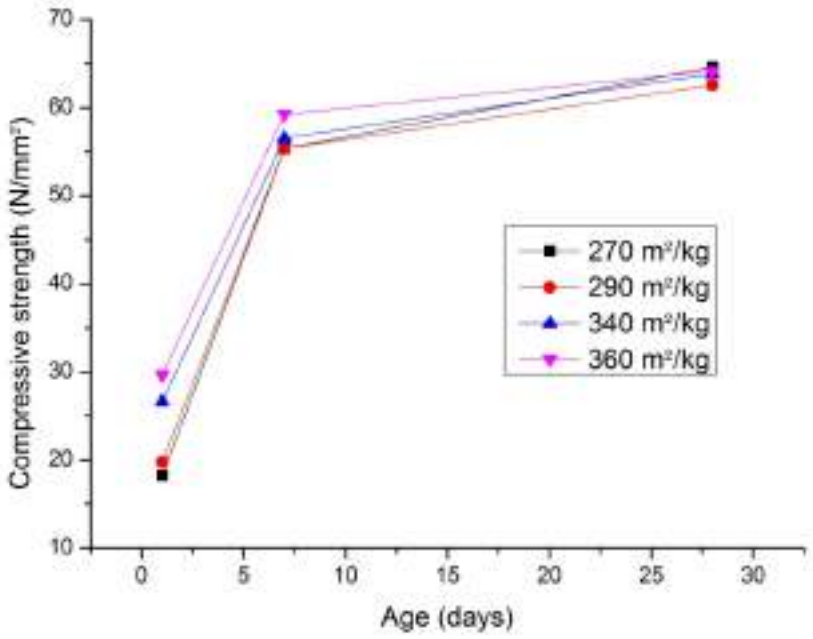


(a)



(b)

Figure 6.7 Evolution of the compressive strength of mortar with cements having varying fineness with (a) no superplasticizer (control) and (b) with PCE



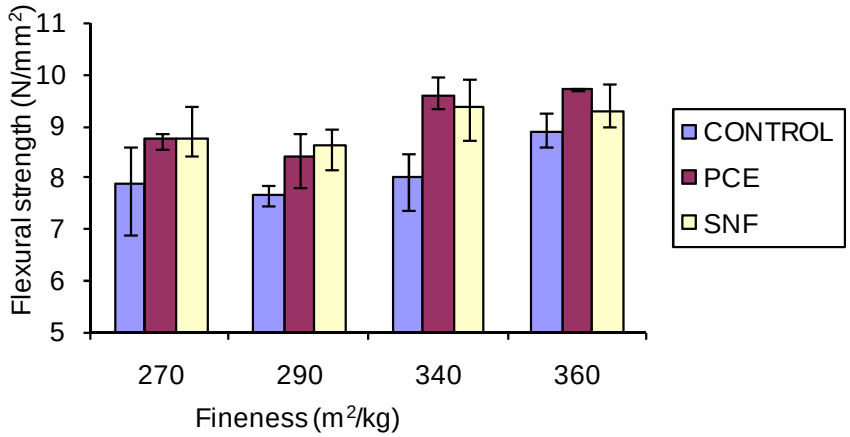
(c)

Figure 6.7 Evolution of the compressive strength of mortar with cements having varying fineness with (c) SNF

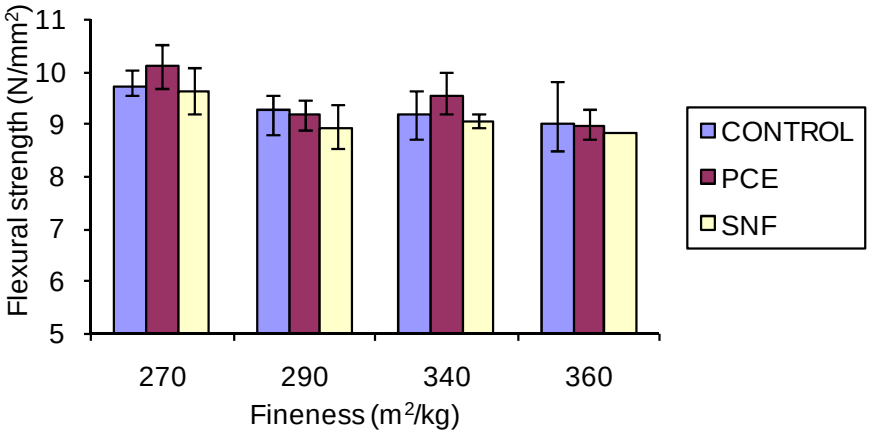
The data in Figure 6.6a and the initial part of the curves in Figure 6.7 show that the early compressive strength of cement mortar is slightly higher for finer cement, which is in accordance with the observations of Vuk et al. (2001), Öner et al. (2003), Tosun (2006), and Sajedi and Razak (2011). This can be attributed to the higher rate of hydration due to higher surface area. The 7- and 28-day compressive strengths are practically the same, indicating that the increase in fineness of cement could lead to a higher early compressive strength and that the long-term strength is not affected significantly (Bentz and Haecker, 1999; Neville, 2007). There is no significant influence of the superplasticizer on the strength values or the evolution of strength.

6.3.1.5.2 Effect on the Flexural Strength of Mortar

The flexural strength of mortar was determined at the ages of 7 and 28 days on prisms of 160×40×40 mm, and the results obtained are plotted against fineness of cement in Figure 6.8 (a and b). It can be seen that the flexural strength increases slightly with an increase in fineness of cement at 7 days. However, at 28 days, the results are similar. The mortars with superplasticizers show the same trend as that of the control mix.



(a)



(b)

Figure 6.8 Flexural strengths of mortars at (a) 7 days and (b) 28 days

6.3.1.6 Effect on the Superplasticizer Demand of Concrete

To study the effect of fineness of cement on the superplasticizer demand in concrete, mixes were prepared with a slump of 150 ± 20 mm by keeping the quantities of all the ingredients, except the superplasticizer, same; the mix proportions of the concretes used are given in Table 6.5. The water cement ratio adopted for the study was 0.40; the water in the superplasticizer is accounted for. The test conditions have been given already in Section 6.2.2. The test results, tabulated and shown in Table 6.6, indicate that the superplasticizer demand in concrete increases with an increase in fineness of cement. Both the PCE and SNF-based superplasticizers gave similar trends. This is in accordance with the observations in the paste study, where the saturation dosage was

found to increase with an increase in cement fineness. Again, the cements F1 and F2 gave almost the same superplasticizer demand in concrete as the difference in fineness is only marginal and the finer cements required slightly higher superplasticizer dosage for the same slump.

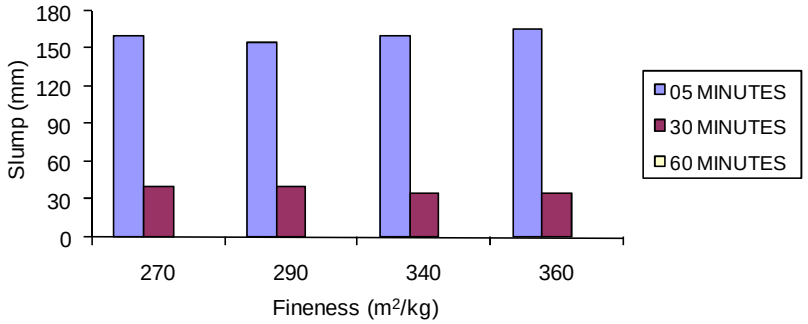
Table 6.5 Mix proportions for concrete

Description	**Quantity (kg/m^3)**
Cement	440
Water added	176
20 mm down aggregates	698
10 mm down aggregates	465
Sand	704

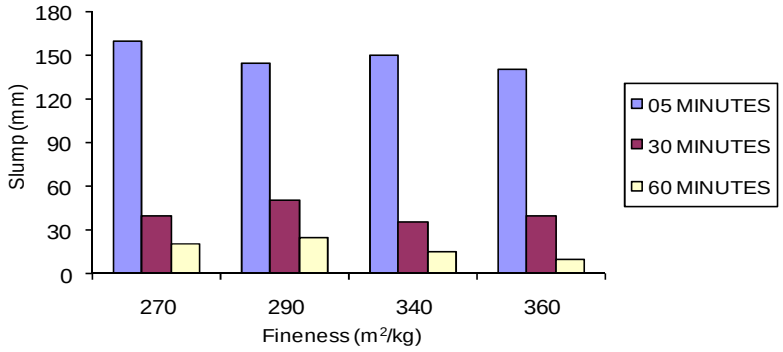
Table 6.6 Superplasticizer demand in concrete for a slump of 150 ± 20 mm

Fineness of cement (m^2/kg)	PCE		SNF	
	slump	SP dosage (%)	slump	SP dosage (%)
270	160	0.10	155	0.16
290	155	0.11	155	0.17
340	150	0.13	160	0.21
360	160	0.14	150	0.19

To study the effect of fineness of cement on the loss in slump of concrete with time, the slump was determined immediately after mixing, and subsequently after 30 and 60 minutes. It should be noted that the same mixes used to determine the superplasticizer demand were used for this part of the study. After determining the initial slump, the concrete was kept covered to avoid any evaporation of water and then mixed for one minute before the subsequent measurements. The results are plotted in Figure 6.9, and the losses in slump with time are given in Table 6.7.



(a)



(b)

Figure 6.9 Slump of concrete with cements of different fineness, having (a) PCE and (b) SNF

Table 6.7 Loss in slump of concrete with fineness of cement

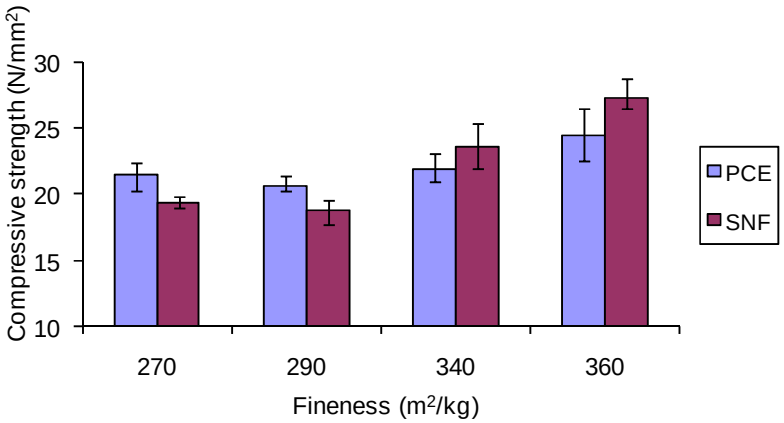
Fineness (kg/m^2)	PCE						SNF					
	sp/c (%)	Slump (mm)			Slump loss (mm)		sp/c (%)	Slump (mm)			Slump loss (mm)	
		5min	30min	60min	30min	60min		5min	30min	60min	30min	60min
270	0.10	160	45	0	115	160	0.16	160	45	20	115	140
290	0.10	155	40	0	115	155	0.17	145	50	25	95	120
340	0.15	160	35	0	125	160	0.21	150	35	15	115	135
360	0.16	165	35	0	130	165	0.19	140	40	10	100	130

It is observed from Figure 6.9 and Table 6.6 that the concretes with PCE based superplasticizer had zero slump after 60 minutes, and that the slump loss is slightly higher for cements with higher fineness. The concretes with SNF had slumps in the range of 40 mm after 30 minutes and about 15 mm at 60 minutes. The better performance of the SNF-based superplasticizer can be attributed to more retardation. In the study of cement paste, it was seen that the loss in fluidity with time was higher for the finer cements though the mortar fluidity was not influenced by the cement

fineness. It should be noted that the w/c adopted for cement paste was 0.35 while for concrete and mortar it was 0.4. As seen in the concretes, the SNF-based superplasticizer gave a slightly better flow retention compared to the PCE-based superplasticizer in the cement mortars also.

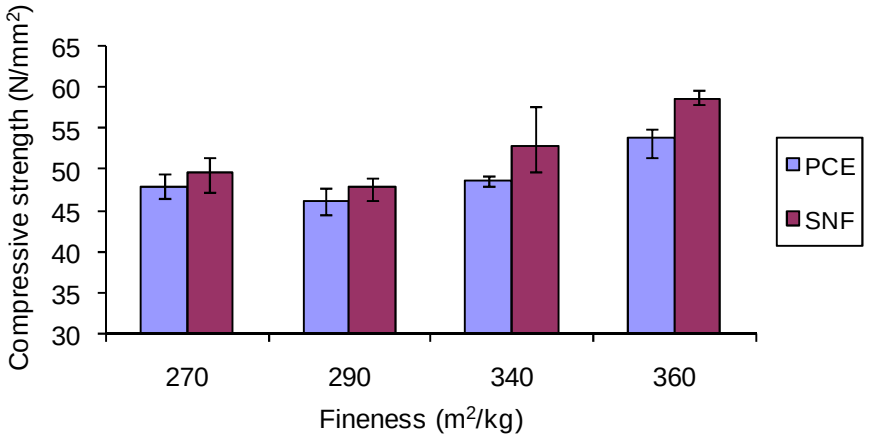
6.3.1.7 Effect on the Compressive Strength of Concrete

The influence of fineness of cement on the mechanical properties of concrete was studied with the help of compressive strength of concrete. Cube specimens of 150×150×150 mm were prepared with concrete, and tested after 1, 7 and 28 days of curing. The results plotted in Figure 6.10 (a-c) show that the compressive strength generally increases with an increase in fineness of cement. The 1- and 7-day strengths (Figure 6.10 a and b) are more significantly affected by the fineness of cement than the 28 day strengths (Figure 6.10c). The compressive strengths of cements F1 and F2 are practically the same as their fineness is only marginally different.

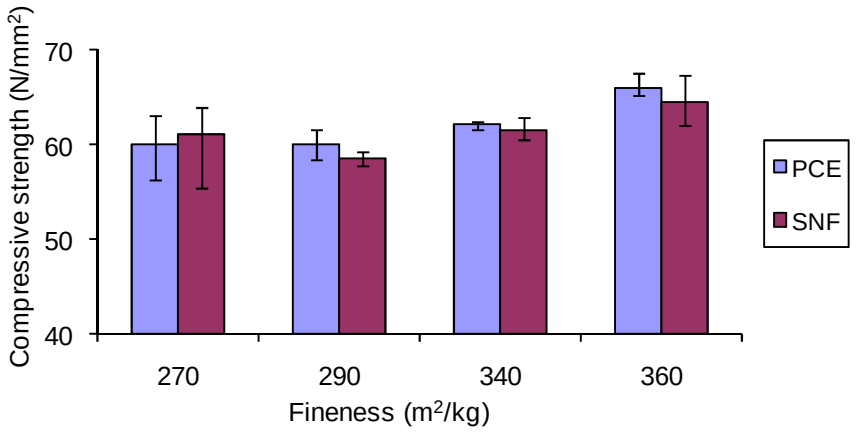


(a)

Figure 6.10 Compressive strengths of concrete with varying fineness at (a) 1 day



(b)



(c)

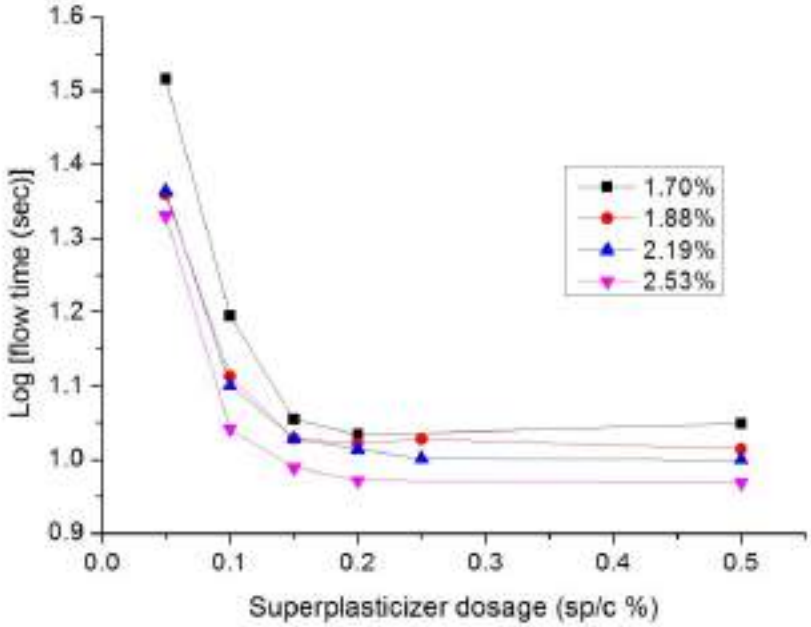
Figure 6.10 Compressive strengths of concrete with varying fineness at (b) 7 days and (c) 28 days

6.3.2 Effect of SO_3 Content of Cement on the Properties of Cement Paste, Mortar and Concrete

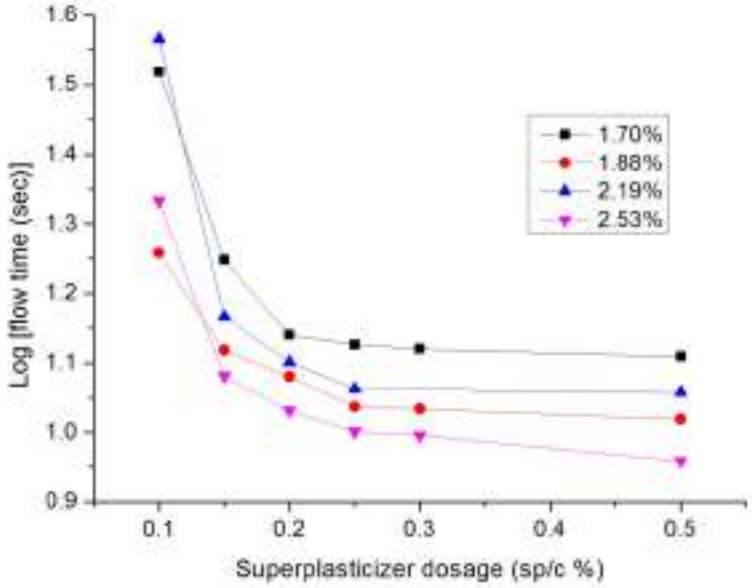
This section outlines the effect of SO_3 content of cement on the various properties of cement paste, mortar and concrete. Tailor made cements, prepared as explained in Section 6.2.1.1, were used for the study. The details of the cement samples have been given in Table 6.1. Samples S1, S2, S3 and S4 with SO_3 contents of 1.70, 1.88, 2.19 and 2.53%, respectively, were used for the study. All the tests were carried out as per the procedures given in Chapter 3.

6.3.2.1 Influence on the Fluidity of Cement Paste

The influence of the SO_3 content of cement on the fluidity of cement paste was characterized with the Marsh cone and mini-slump tests; the results obtained are plotted in Figures 6.11 and 6.12. Two trials were done for each case and the typical curves for the PCE and SNF based superplasticizers are given in the plots; the complete set of flow time curves are given in Appendix C. From Figure 6.11, it can be observed that the fluidity increases with an increase in the dosage of superplasticizer up to the saturation point, after which the fluidity does not increase considerably, for all the cement pastes, as expected and observed earlier. The flow time curves indicate that the fluidity of the pastes generally increases with an increase in SO_3 content. The saturation dosages of superplasticizers were calculated as per the procedure suggested by Gomes et al. (2001). From the results, it is observed that the sample S1 with the lowest SO_3 content (i.e., 1.70%) had a higher saturation dosage than the others; the saturation dosage of the PCE and SNF based superplasticizers with S1 cement are 0.15% and 0.2%, respectively. For the other cements, (i.e., samples S2, S3 and S4), the saturation dosages of superplasticizers were 0.1% and 0.15% for PCE and SNF based superplasticizers. The mini-slump results (Figure 6.12) also show the same trend, with flow increasing with an increase in SO_3 content of cement, over the range studied. This indicates that the effectiveness of the superplasticizer could be lower when used with cements having low SO_3 contents. Okamura et al. (1998) observed an increase in the fluidity of mortar with an increase in the SO_3 content with polycarboxylate based high-range water-reducing air entrained agents.

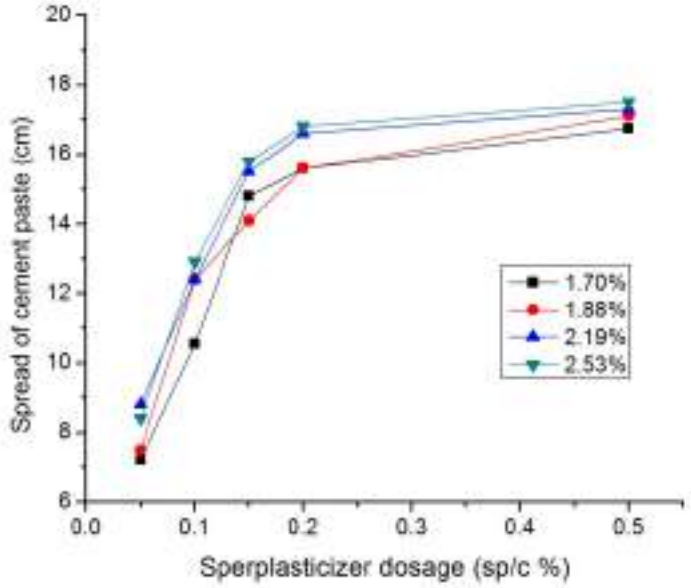


(a)

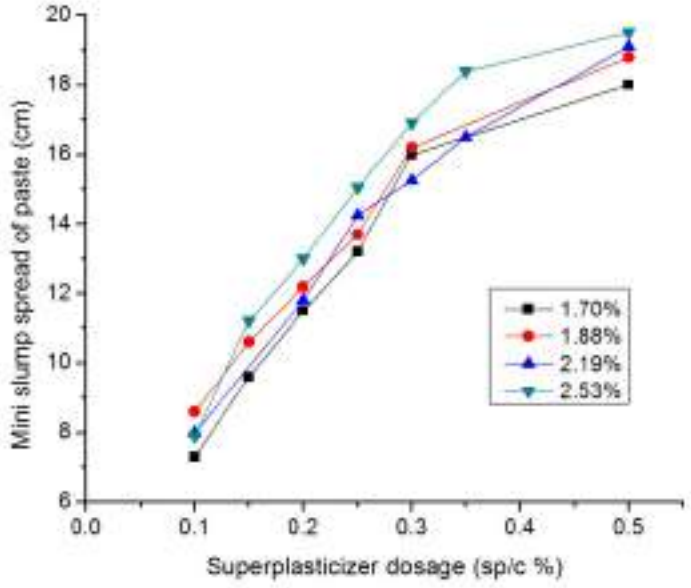


(b)

Figure 6.11 Marsh cone flow time with cements with varying SO_3 contents for (a) PCE and (b) SNF



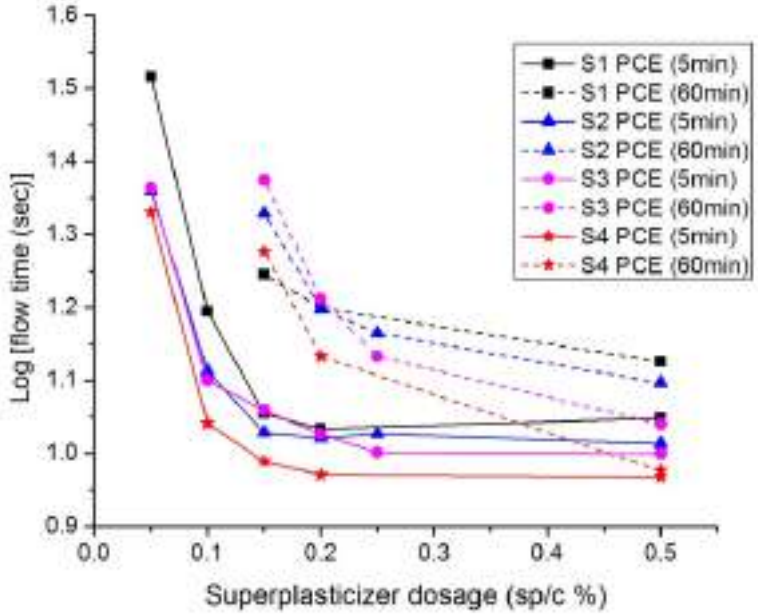
(a)



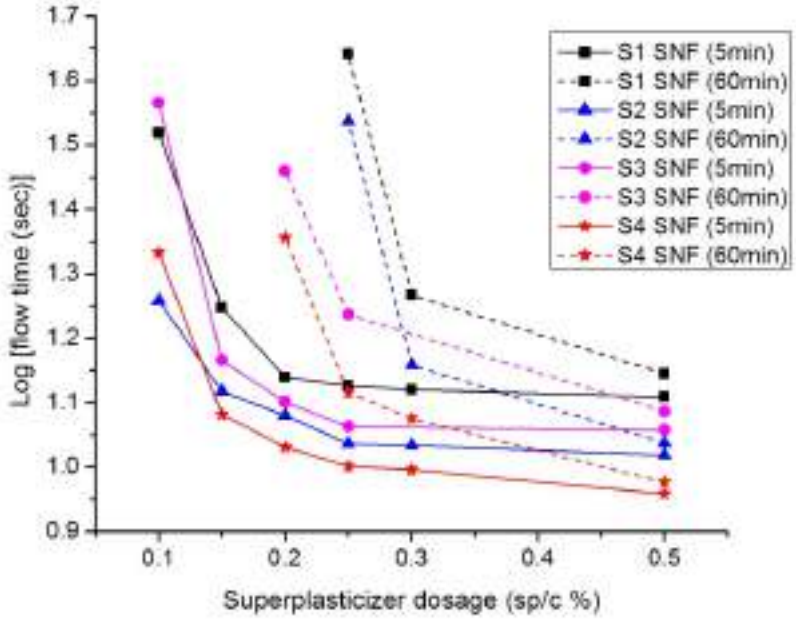
(b)

Figure 6.12 Mini-slump spread with cement having varying SO_3 contents for (a) PCE and (b) SNF

In order to study the effect of SO_3 content of cement on the loss in fluidity with time the Marsh cone flow time of cement paste was determined immediately after mixing and 60 minutes after adding water to cement. The results are plotted in Figure 6.13.



(a)



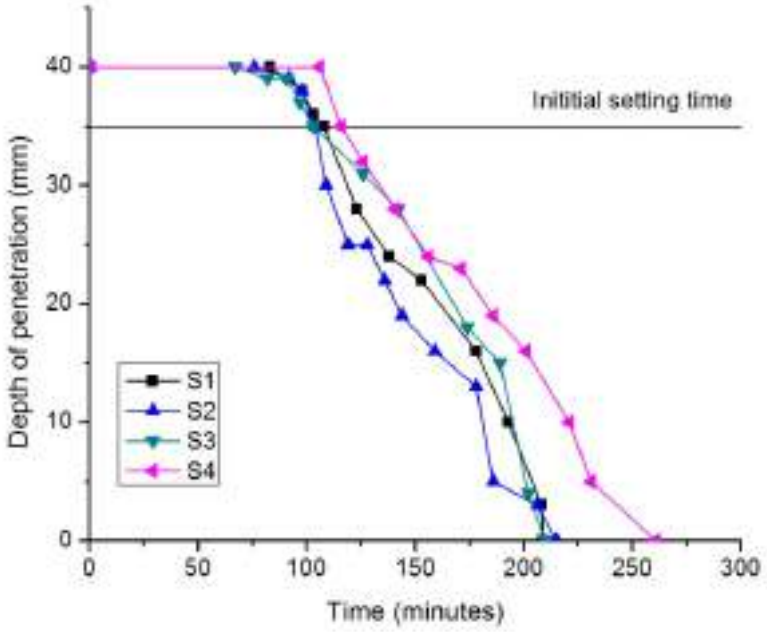
(b)

Figure 6.13 Loss in fluidity of cement pastes with varying SO_3 content of cement for (a) PCE and (b) SNF

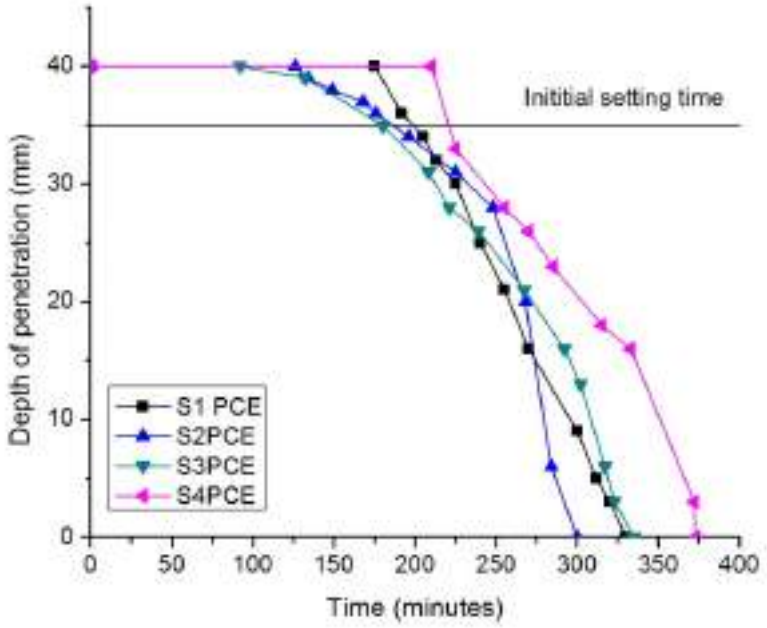
From the test results (Figure 6.13), it is observed that the loss in fluidity with time generally decreases with an increase in SO_3 content of cement at higher dosages of superplasticizer. In other words, the fluidity retention is better for cements with higher SO_3 contents. It is also observed that the loss in fluidity with time decreases with an increase in superplasticizer dosage, as expected and observed earlier. It was concluded by Nakajima and Yamada (2004) that the adsorption of a PNS based superplasticizer on the surface of the cement particles is limited when the SO_4^{2-} concentration in the solution is high and that it increases with decreasing SO_4^{2-} concentration. This could lead to the lower loss in fluidity of cement pastes having cements with higher SO_3 content.

6.3.2.2 Influence on the Setting Time of Cement Paste

The initial and final setting times of cement with various SO_3 contents were determined using the Vicat apparatus, as per the procedure explained in Section 3.3.1 of Chapter 3. The Vicat penetration for cement pastes, with and without superplasticizers, is plotted against time in Figures 6.14a-c for the cements with different SO_3 contents. The horizontal line drawn at 35 mm penetration in each plot indicates the initial setting time. For the control mix (Figure 6.14a), the sample S4 shows higher initial, as well as final setting times, whereas all the other samples shows almost same setting time. For the superplasticized cement pastes (Figure 6.14b and c), the cements with the maximum SO_3 content shows marginally higher final setting time.

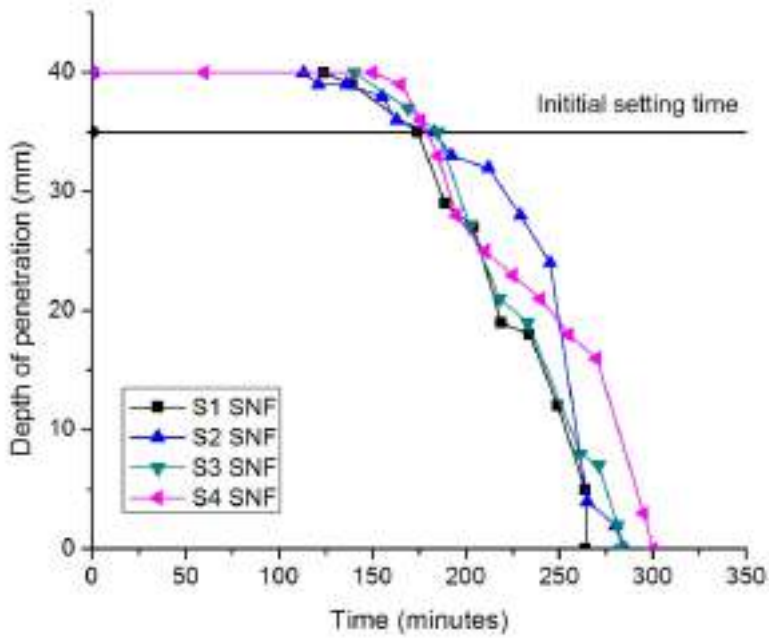


(a)



(b)

Figure 6.14 Evolution of Vicat penetration for cement pastes with cements of various SO_3 content for (a) Control and (b) PCE



(c)

Figure 6.14 Evolution of Vicat penetration for cement pastes with cements of various SO_3 content for (c) SNF

The initial and final setting times was determined for each case, and are given in Table 6.8. It is observed that the setting times do not show any specific trend with the change in SO_3 content, over the range of 1.7 to 2.53%. In all cases, the addition of superplasticizer increases the setting times.

Table 6.8 Setting times of cement with varying SO_3 content

Sample	Control		PCE		SNF	
	Initial	Final	Initial	Final	Initial	Final
S1 (1.70%)	108	209	200	330	174	264
S2 (1.88%)	104	235	190	300	183	285
S3 (2.19%)	103	210	180	335	189	283
S4 (2.53%)	116	261	215	393	180	300

6.3.2.3 Influence on the fluidity of cement mortar

The flow table test was used to study the fluidity of cement mortar. The water/cement ratio of the mortars was 0.4, and the saturation dosage of superplasticizer obtained from the Marsh cone test of pastes (with w/c = 0.35) was used as the dosage of superplasticizer. The mortar spreads were determined and plotted in Figure 6.15. In

general, the fluidity of cement mortar increases with an increase in SO_3 content, except S1, with both PCE and SNF based superplasticizers. It should be noted that the saturation dosage of sample S1 is higher compared to the other cements. Therefore, the higher fluidity of the mortar with sample S1 could be due to the higher superplasticizer dosage. It was observed earlier by Okamura et al. (1998) that the mortar flow immediately after mixing is higher for cements with higher in SO_3 content in the presence of a superplasticizer.

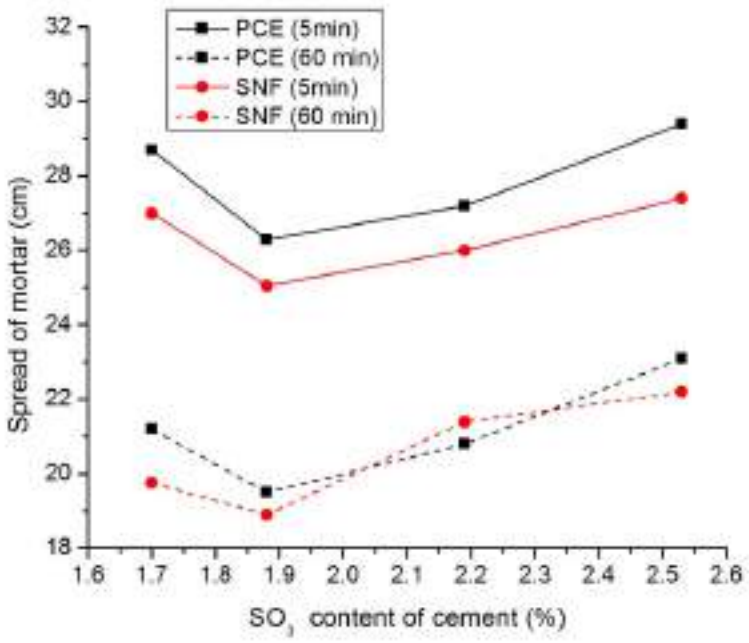
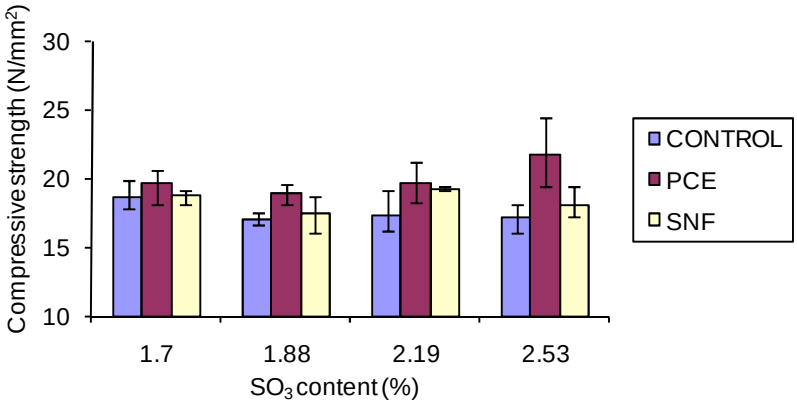


Figure 6.15 Flow table spread for mortar with varying SO_3 content

In order to study the effect of SO_3 content of cement on the loss in fluidity with time of cement mortar, the mortar spreads were determined immediately after mixing (at about 5 minutes) and after 60 minutes after adding water to cement. The plots of mortar spread versus SO_3 content of cement are shown in Figure 6.15. It is observed that the loss in fluidity with time decreases marginally (i.e., gap between the 5-minute and 60-minute curves decreases) with an increase in SO_3 content of cement, which is in accordance with the results of the paste study. Okamura et al. (1998) also observed a lower loss in spread with an increase in the SO_3 content of cement mortar.

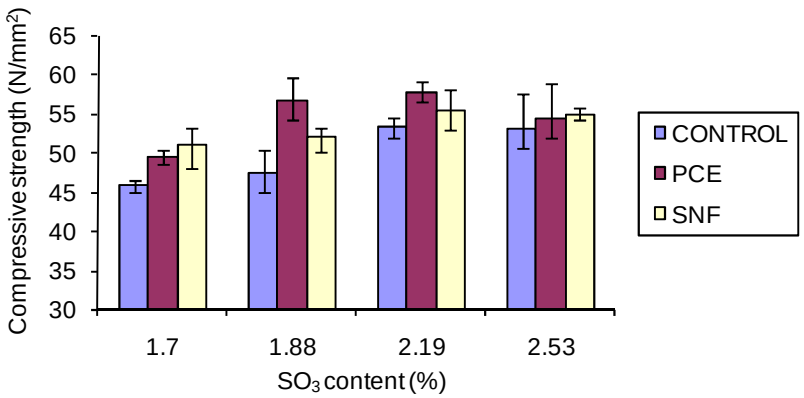
6.3.2.4 Influence on Compressive Strength of Cement Mortar

50 mm cubes of mortar, prepared as in the previous section, were tested at 1, 7 and 28 days, and the test results are shown in Figure 6.16. The 1-day compressive strength does not show any specific trend with mortar, with the PCE based superplasticizer giving a higher strength with the cement having the highest SO_3 content. At 7 days, all the mortars, the control as well as the superplasticized mortars, seem to exhibit higher compressive strengths for cements with higher SO_3 contents, with S3 and S4 giving almost the same strength. At 28 days, the compressive strength of all the mortars are practically the same. Sersale et al. (1991) also observed higher compressive strength with an increase in SO_3 content of cement up to 2.5% SO_3 content at early ages and the minimum strength after 28 days at about 2.5-3% SO_3 content. They also found that the porosity is altered by the SO_3 content. Odler and Abdul-Maula (1987) found that at any stage of hydration, the strength depends on the optimum SO_3 content, which depends on the clinker composition, and shifts to higher values with progressing cement hydration. According to Sersale et al. (1991) the influence of SO_3 content on strength development can be expressed in many ways: on one hand, the SO_3 content affects hydration at early ages and, on the other hand, it could result in the formation of tobermoritic gel with low intrinsic strength characteristics. In the present study, the range of SO_3 content selected is not wide enough to identify any optimum SO_3 content.

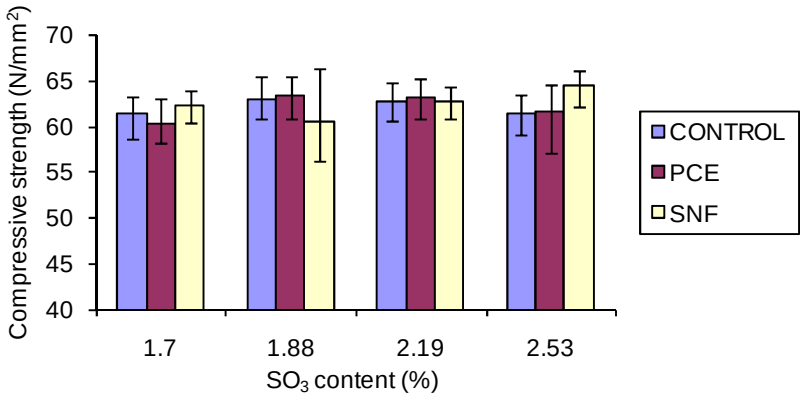


(a)

Figure 6.16 Compressive strengths of mortar with varying SO_3 contents at (a) 1 day



(b)

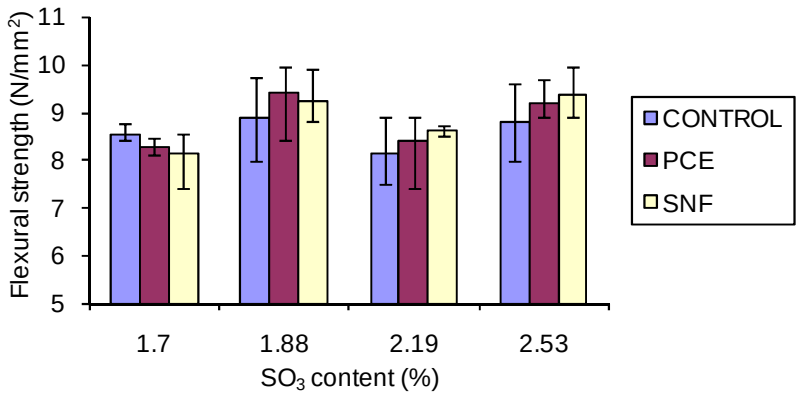


(c)

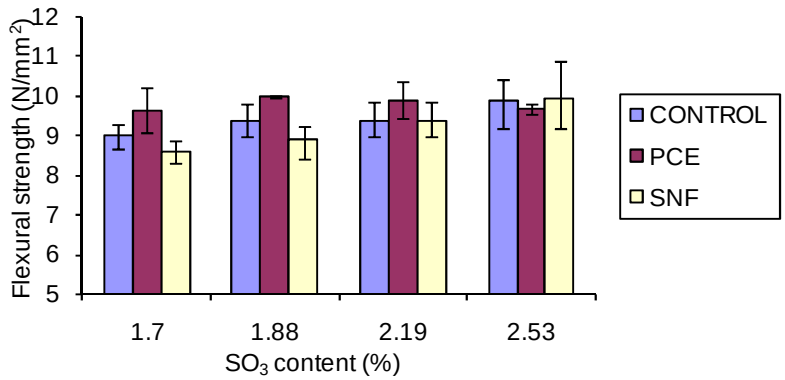
Figure 6.16 Compressive strengths of mortar with varying SO_3 contents at (b) 7 days and (c) 28 days

6.3.2.5 Influence on Flexural Strength of Cement Mortar

Mortar prisms of 160×40×40 mm were prepared and tested after 7 and 28 days; the results are plotted in Figure 6.17. The flexural strength does not yield any specific trend at 7 days. At 28 days, the control and SNF mix shows slightly higher flexural strength at higher SO_3 contents whereas the mortars with the PCE based superplasticizer have practically the same strength, for the range of SO_3 content studied here.



(a)



(b)

Figure 6.17 Flexural strength of mortar with varying SO_3 contents at (a) 7 and (b) 28 days

6.3.2.6 Influence on Superplasticizer Demand of Concrete

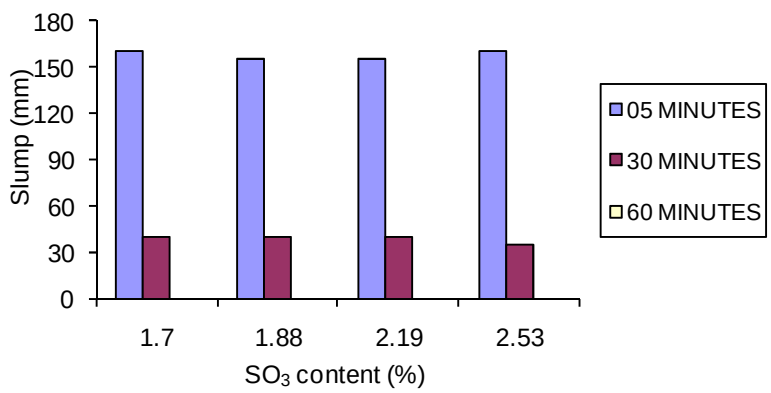
To study the effect of SO_3 content on the superplasticizer demand of concrete, concretes were prepared with slumps of 150 ± 20 mm by keeping all the ingredients constant, except the superplasticizer. The superplasticizer demand obtained in concretes with cements with different SO_3 content are given in Table 6.9, where it is observed that the superplasticizer demand for the concrete with the cement having an SO_3 content of 1.7% is marginally higher, which is in accordance with the observations from the paste study. Concretes with samples S2, S3 and S4 have almost the same superplasticizer demands for the slump of 150 ± 20 mm.

Table 6.9 Superplasticizer demand for concrete with cements of varying SO_3 content

SO_3 content (%)	PCE		SNF	
	slump	SP dosage	slump	SP dosage
1.70	160	0.12	155	0.21
1.88	155	0.09	155	0.19
2.19	155	0.10	135	0.17
2.53	160	0.11	150	0.19

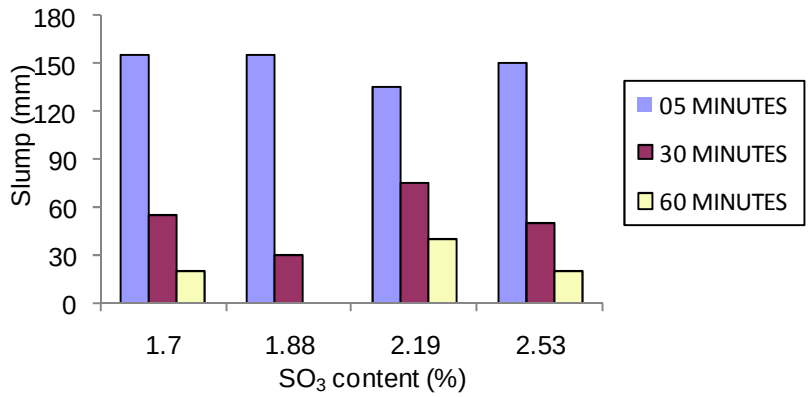
6.3.2.7 Influence on Loss in Slump of Concrete

To study the effect of SO_3 content of cement on the loss in workability of concrete with time, the slump was determined immediately after mixing, and subsequently after 30 and 60 minutes. The results are plotted in Figure 6.18, and the loss in slump is calculated and presented in Table 6.10 for each case. It is observed that the concrete with the PCE based superplasticizer had a slump loss of about 115-125 mm within the first half hour and had a zero slump after an hour. The SNF based superplasticizer gave a slump loss of 95-125 mm within the first half hour and 120-155 mm after an hour.



(a)

Figure 6.18 Slump of concrete with SO_3 content (a) PCE



(b)

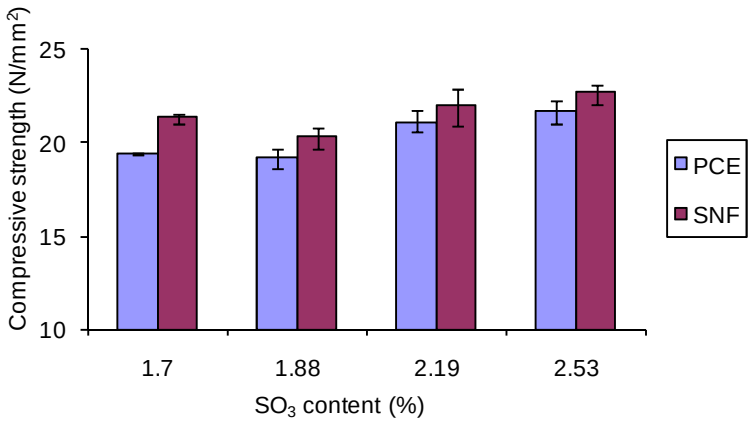
Figure 6.18 Slump of concrete with SO_3 content (b) SNF

Table 6.10 Loss of slump with time for concrete with varying SO_3 content of cement

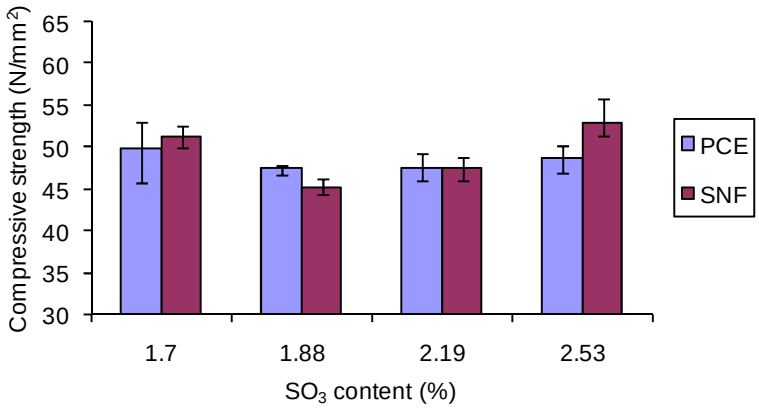
SO_3 content of cement (%)	PCE						SNF					
	sp/c (%)	Slump			Slump loss (mm)		sp/c (%)	Slump			Slump loss (mm)	
		5min	30min	60min	30min	60min		5min	30min	60min	60min	30min
1.70	0.12	160	40	0	120	160	0.21	155	55	20	100	135
1.88	0.09	155	40	0	115	155	0.19	155	30	0	125	155
2.19	0.10	155	40	0	115	155	0.21	160	50	40	95	120
2.53	0.11	160	35	0	125	160	0.19	150	50	20	100	130

6.3.2.8 Influence on Compressive Strength of Concrete

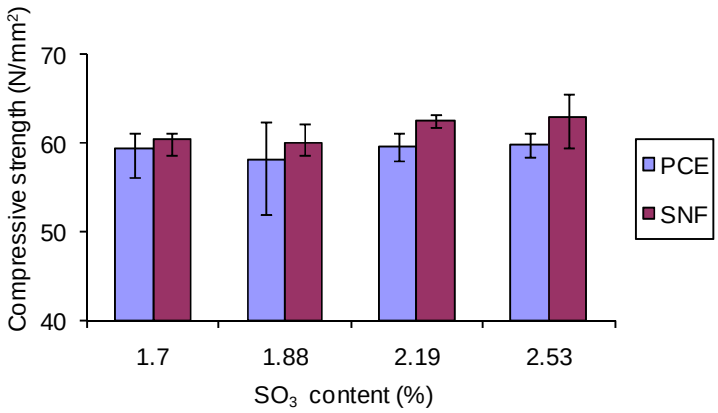
The compressive strength of concrete was determined after 1, 7 and 28 days. The test results are plotted against SO_3 content of cement in Figure 6.19. The results show that the concretes with cements S3 and S4 had slightly higher compressive strength after one day. However, after 28 days of curing, all the samples show almost the same compressive strength, except that the concretes with the PCE based superplasticizer has slightly lower strengths. The SNF based superplasticized concretes had marginally higher compressive strengths at all ages, especially for the cements with higher SO_3 content.



(a)



(b)



(c)

Figure 6.19 Compressive strength of concrete with varying SO_3 contents at (a) 1 day (b) 7 days and (c) 28 days

6.4 CONCLUSIONS

The influence of fineness and SO_3 content of cement on different properties of cement paste, mortar and concrete has been studied. Tailor made cements were prepared in a cement manufacturing plant by varying the fineness and SO_3 content of cement. Two types of commercially available superplasticizers (PCE and SNF) were incorporated. The following conclusions can be drawn:

- The saturation dosage of superplasticizer increases with an increase in cement fineness for cement paste, which indicates a higher superplasticizer demand at higher fineness. This can be attributed to higher surface area of the finer cements, which leads to higher adsorption and hydration reactions. The fluidity of cement paste decreases with an increase in fineness of cement at lower dosages of superplasticizer, and increases marginally or remains constant at higher dosages of superplasticizer.

- The loss in fluidity of cement paste with time increases with an increase in fineness of cement for the same dosage of superplasticizer. The higher loss in fluidity for finer cements can be attributed to the higher adsorption of the superplasticizer and the increase in hydration rate for the finer cements. The loss in fluidity with time decreases with an increase in the dosage of superplasticizer. Therefore, the dosage of superplasticizer should be selected in such a way that the loss in fluidity after the required time should be within the permissible limit, for workability retention.

- The initial setting time decreases with an increase in cement fineness. This can be attributed to faster hydration, as the surface area of the cement is higher. The addition of a superplasticizer retards both the initial and final setting times significantly.

- The early compressive strength of cement mortar increases with an increase in the cement fineness, for the control as well as superplasticized mortars. However, the later age strengths are practically the same. This indicates that the increase in cement fineness could lead to higher early compressive strength without affecting the long-term strength significantly. The flexural

strength of cement mortar also increases slightly with an increase in fineness of cement at 7 days while the 28 day strengths are not affected significantly.

- The superplasticizer demand for the concrete to get a slump of 150 ± 20 mm increases slightly with an increase in the fineness of cement. This is in accordance with the paste study, which showed that the saturation dosage of superplasticizer increases with an increase in the fineness of cement.

- The compressive strength of concrete generally increases with an increase in fineness of cement. The initial strengths are more significantly affected by the cement fineness than the 28 day strength.

- The fluidity of cement paste generally increases with an increase in SO_3 content of cement. The saturation dosage of superplasticizer is not significantly affected by the SO_3 content of cement over the range studied, except for the lowest SO_3 content. The cement with the lowest SO_3 content required a higher superplasticizer dosage. The loss in fluidity with time generally decreases with an increase in SO_3 content of cement.

- The fluidity of cement mortar increases with an increase in SO_3 content, except for the sample with the lowest SO_3 content. The cement with the lowest SO_3 content resulted in higher fluidity, which can be due to the higher superplasticizer dosage. The loss in fluidity of mortar with time generally decreases with an increase in SO_3 content, which is in accordance with the paste study.

- The compressive strengths are marginally improved with an increase in SO_3 content of cement at 7 days. At 28 days, the compressive and flexural strengths are practically the same.

- The superplasticizer demand of concrete to obtain a slump of 150 ± 20 mm is almost same for the cements with varying SO_3 content, except for the sample with the lowest SO_3 content, which is accordance with the paste study.

- The early compressive strength of concrete is slightly higher for cements with higher SO_3 content but the 28 day strengths are almost the same.

CHAPTER 7

EFFECT OF CASTING TEMPERATURE ON THE MICROSTRUCTURE OF HARDENED CEMENT PASTE

7.1 INTRODUCTION

The influence of temperature on the fresh properties of cement paste was discussed in Chapter 4 whereas Chapter 5 presented the effects of temperature on the fresh and hardened properties of cement mortar and concrete. The study of the flow behaviour of superplasticized cement pastes showed that the fluidity and loss in fluidity with time depend on the type and dosage of superplasticizer and the ambient temperature to which the pastes are exposed. It is seen that the fluidity of cement paste decreases and the loss in fluidity with time increases with an increase in temperature. At higher temperatures, the cement pastes exhibit higher saturation superplasticizer dosages compared to those at lower temperatures. The setting times of cement paste decrease with an increase in exposure temperature whereas the water demand increases. The fluidity of cement mortar and concrete also decreases significantly with an increase in the exposure temperature. The mechanical properties of mortar and concrete are also affected by the temperature; the early strength of cement mortar and concrete is higher when the materials are exposed to higher temperatures during casting and during the first 24 hours but the later age strengths are lower. Literature shows that the change in ambient temperature alters various properties of concrete, which can be due to the change in the rate of hydration and the nature of the hydrated products (Jolicoeur and Simard, 1998; Agarwal et al., 2000; Prince et al., 2002; Nkinamubanzi and Aitcin, 2004; Bedard and Mailvaganam, 2005; Hanehara and Yamada, 2008).

In this chapter, an attempt is made to understand the influence of the initial exposure temperature on the microstructure of hardened superplasticized cement paste in order to understand better the hydration processes and the microstructural development of hardened cement paste. The details of the sample preparation and experimental procedure for various techniques used in the microstructure study have been given in Section 3.3.5 of Chapter 3. Scanning electron microscopy (SEM) provides

information about the different components of hydrated cement paste and how they are arranged in the microstructure (Scrivener, 1989; Ramachandran and Beaudoin, 2001). Indirect techniques like thermogravimetric (TG) analysis and X-ray diffraction study (XRD) give information about the average characteristics of the microstructure. The complementary use of various methods is expected to provide a better picture of the hydration processes, with respect to the formation of new phases, as well as the consumption of the anhydrous phases.

7.2 SCANNING ELECTRON MICROSCOPY (SEM)

7.2.1 Background

The development of the microstructure of hardened cement paste can be studied by using SEM images of cement paste. The technique consists of generating and focusing an electron beam over the surface of the specimen. The electron beam impinges on the surface and produces signals that can be detected as back scattered (BSE), secondary electrons (SE) and X-rays. The SEs are originated at the near surface of the specimen and are low energy electrons emitted from the sample whereas back scattered electrons are high energy electrons scattered by the atom nuclei (Balendran et al. 1998). These electrons are captured by detectors and the resultant information is converted to images.

The sample preparation and test procedures have been given in Section 3.3.5 of Chapter 3. To study the effect of ambient temperature on the microstructure development of cement paste, samples were prepared at 5, 15, 25, 35 and 40˚C. To study the effect of age on the microstructure development of cement paste with and without superplasticizer, the SEM investigations were conducted on specimens cured until half setting (i.e., the age when the Vicat penetration is 20 mm for a paste of normal consistency), and at the ages of 1, 3, 7 and 28 days. The results of secondary electron (SE) imaging on the fractured surface and back scattered electron (BSE) imaging on the polished surface are presented in the following sub-sections.

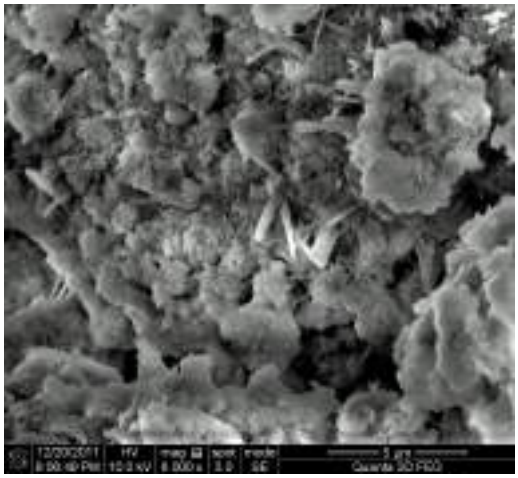
7.2.2 Secondary Electron Imaging (SE)

Secondary electron imaging involves the evaluation of the topographical features on the surface of the specimen. The detection of the SEs from all the directions allows

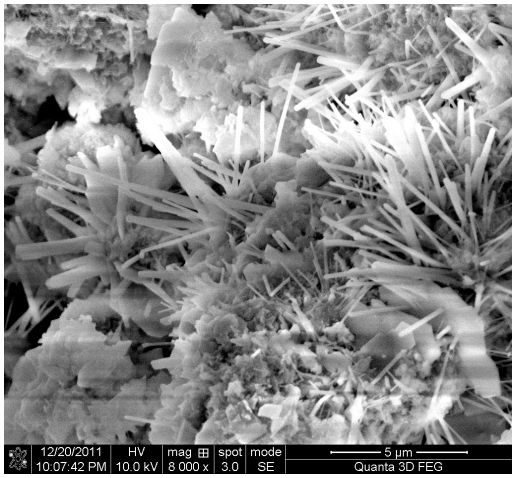
the formation of a three-dimensional image of the specimen (Balendran et al. 1998). The samples used here for the imaging were fragments of fractured cement paste that had been cast at the prescribed temperature and cured till the desired age. The images and interpretations from the images are given in the following sub-sections.

7.2.2.1 Development of Microstructure at Half-setting

The samples were tested at half setting to understand the influence of temperature on the early age and to study the retarding effect of superplasticizer on the setting of cement (Roncero et al. 2002), where half setting time is taken as that corresponding to a Vicat needle penetration of 20 mm. (Note that the total depth of the Vicat mould is 40 mm.) Also, most of the water in the paste is expected to be in the form of free water. The actual age of the sample can differ from one paste to another but all are expected to have the same degree of setting at the half-setting time. Secondary electron images at half setting are shown in Figure 7.1 (a-e). For imaging, the sample needs to be dried, the process of which can affect the microstructure. Here, solvent replacement method at room temperature, as explained in Chapter 3, was used to dry the specimens. Further, the lower integrity of the hardened paste makes the examination of the microstructure difficult at this age, as the adherence of the gold coating may not be proper, which can lead to the charging effect that is reflected in Figure 7.1.

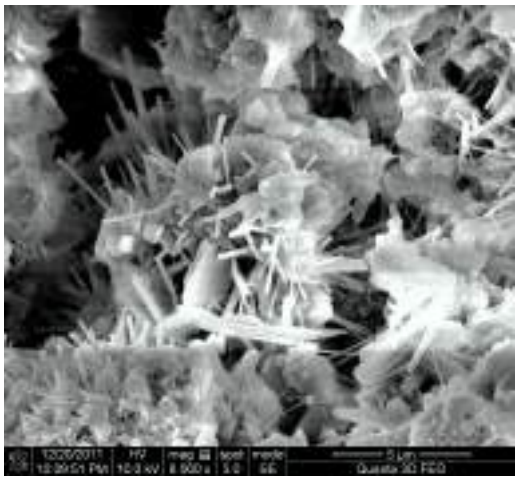


(a) 5°C-Control-Half setting

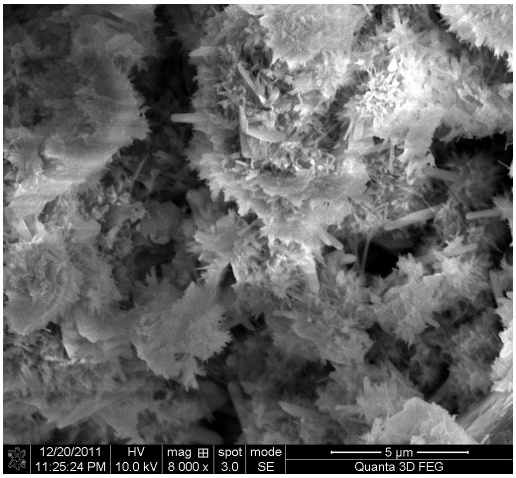


(b) 15°C-Control-Half setting

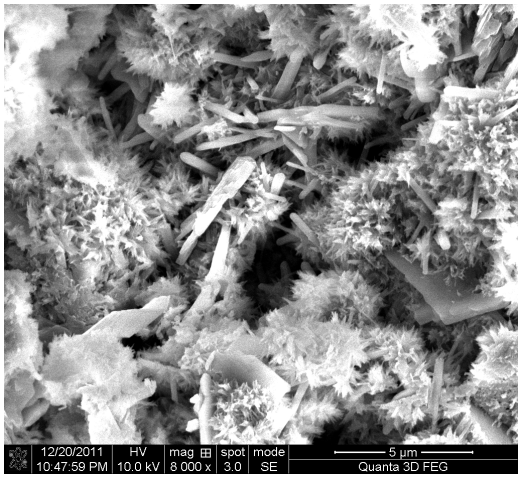
Figure 7.1 SE micrographs of cement paste at half setting for control paste



(c) 25°C-Control-Half setting



(d) 35°C-Control-Half setting



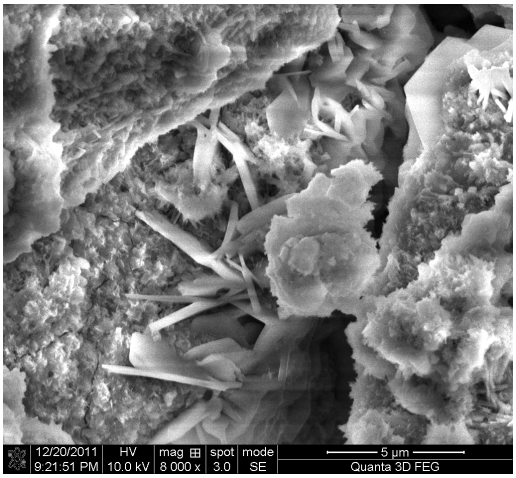
(e) 40°C-Control-Half setting

Figure 7.1 SE micrographs of cement paste at half setting for control paste

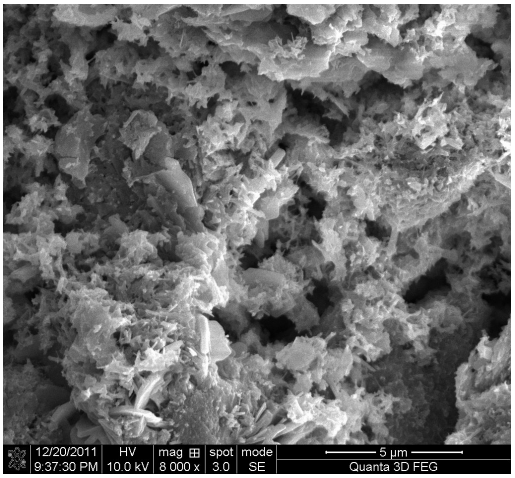
Figure 7.1 a, it can be seen that, at 5˚C, in the paste without superplasticizer (i.e., the control paste), the cement particles are surrounded by a gel-type material, which is probably an amorphous colloidal product that is rich in alumina and silica (Roncero 2000). Only a few ettringite crystals are seen, which confirms the observation of Scrivener (1989). The needles seem to be thick and distinct but fewer in numbers. At 15˚C, more ettringite needles and gel are visible. The long and distinct crystals of ettringite are clearly observed at this stage for the control paste (Figure 7.1b). The clusters of ettringite needles can be seen at half-setting at 15°C. At 25°C, larger amounts of gel can be observed. At higher temperatures (i.e., at 35°C and 40°C), more

hydration products are observed (Figures 7.1 c and d). Hexagonal crystals of calcium hydroxide are observed at half setting only at 40°C; see Figure 7.1 e. It is seen that the morphology of the hydration products is significantly different at higher temperatures and that the slower formation of the ettringite at lower temperature leads to larger crystals. The presence of ettringite needles at higher temperatures seems to be less prominent compared to that at lower temperatures, probably due to the burial of the ettringite needles under the newly formed hydration products as the amount of hydration products is more at higher temperature. Lothenbach et al. (2007) also observed that the ettringite needles formed at higher temperatures are significantly smaller compared to those formed at lower temperatures. It was also reported that the stability of ettringite decreases with an increase in temperature.

In order to study the influence of superplasticizer at half setting (i.e., corresponding to 20 mm Vicat penetration) on the development of microstructure, cement pastes were prepared at different temperatures with the PCE-based superplasticizer at the saturation dosage corresponding to 25°C. The images obtained on the fractures surfaces from secondary imaging are shown in Figure 7.2.

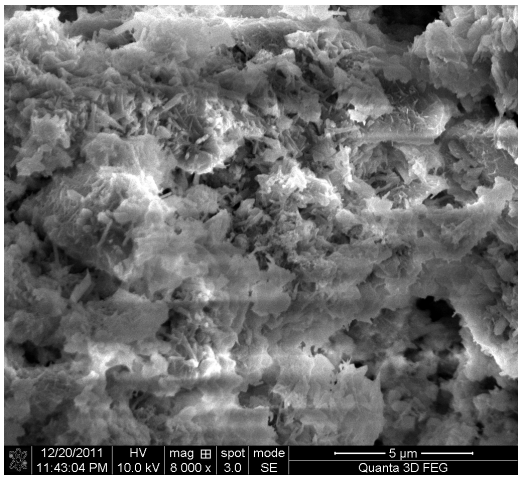


(a) 5°C-PCE-Half setting

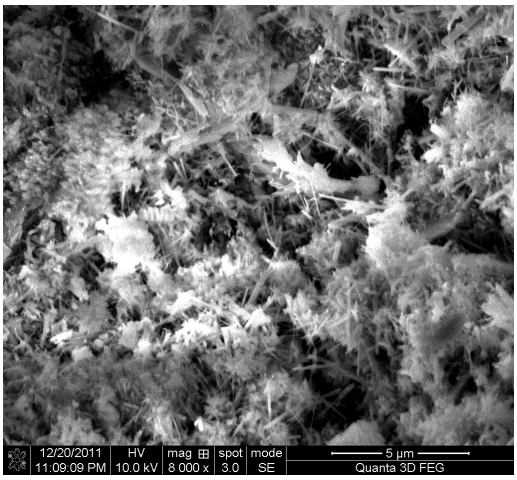


(b) 15°C-PCE-Half setting

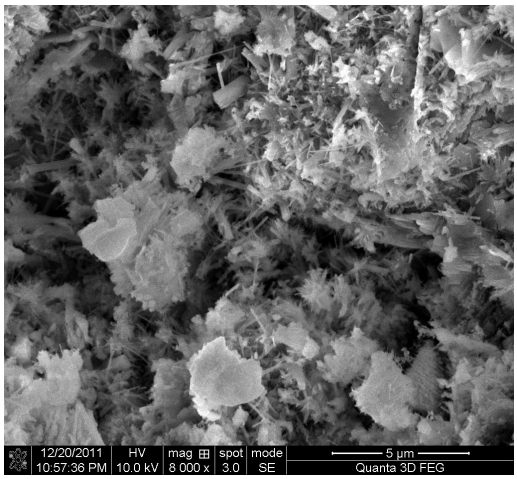
Figure 7.2 SE micrographs of cement paste at half setting for Superplasticized cement paste



(c) 25°C-PCE-Half setting



(d) 35°C-PCE-Half setting



(e) 40°C-PCE-Half setting

Figure 7.2 SE micrographs of cement paste at half setting for Superplasticized cement paste

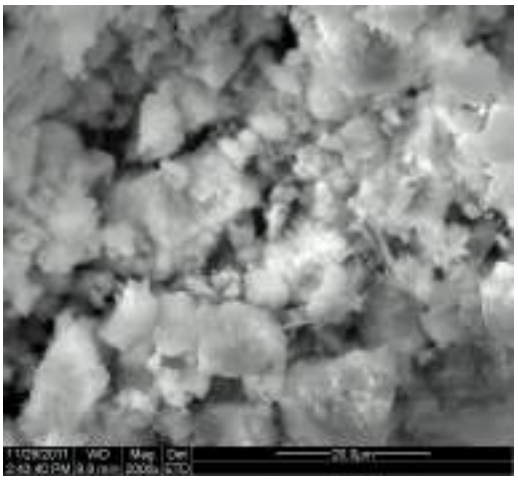
From the comparison of Figures 7.1 and 7.2, it can be generally observed that the hydration is retarded with the addition of superplasticizer at half setting, which is evident from lesser hydration products compared those in the control paste, especially at lower temperatures. At 5°C, for the superplasticized cement paste, the cement grains are clearly visible with their boundaries. The formation of ettringite seems to be considerably lower at this age; however, the formation of plate-like crystals is observed. The formation of gel is significantly lower when compared to pastes without superplasticizer at 5°C. At 15°C, more gel is formed compared to 5°C; however, it is less when compared to that in the control paste. At 25°C, as well as at 35°C and 40°C, the formation of gel is more compared to that at lower temperatures.

The cement grains are fully surrounded by the hydration products and it is difficult to distinguish the cement grains at this temperature. The formation of more ettringite needles are observed at higher temperatures. At 40°C, the maximum hydration products and substantial increase in formation of ettrigite are observed. The formation of gel and hydration products is more dense in the superplasticized cement paste compared to the control paste, at all temperatures. The denser packing can be due to better dispersion of the cement particles in the presence of superplasticizer (van Breugel 1997).

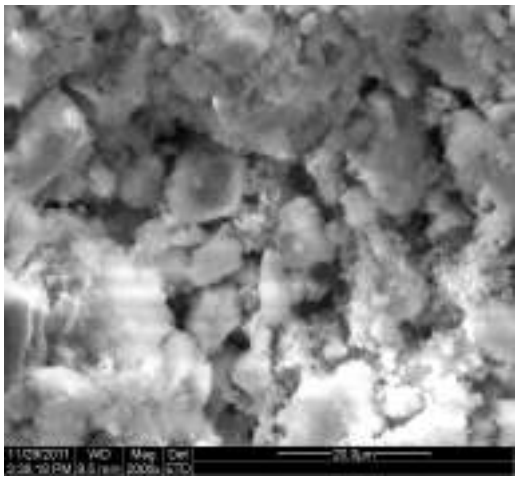
In general, it can be concluded that the rate of hydration increases with an increase in exposure temperature. The microstructure seems more dense in the case of superplasticized cement pastes. The incorporation of the superplasticizer leads to the lower gel and hydration product formation at early ages, which reflects the retardation in the hydration due to the incorporation of the superplasticizer.

7.2.2.2 Development of Microstructure at 1 day

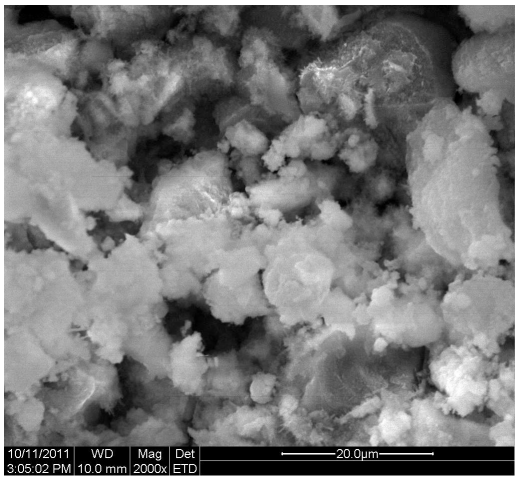
The secondary electron images at one day are shown in Figure 7.3 (a-k) for the control and superplasticized cement pastes. An increase in hydration products can be seen at higher temperatures. At 5°C (Figure 7.3 a and b), the formation of hydration products is comparatively less; hydration products are visible around the cement grains. At 15°C (Figure 7.3 c and d), the hydration products are more and the cement particles are covered by the hydration products. In the case of superplasticized paste, more dense microstructure is observed, along with the presence of ettringite needles. More hydration products are seen at 25°C and the cement particles are bridged by the hydration products. At 35°C, the cement paste seems to be more dense and in the control paste, thin ettringite crystals are also present. At 40°C, the paste becomes a more compact mass after one day.



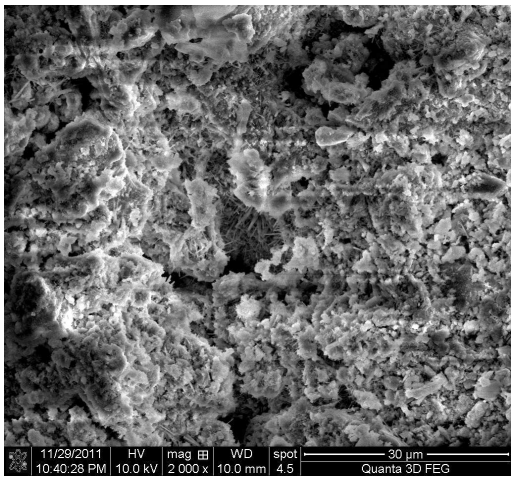
(a) 05℃-Control-1 day



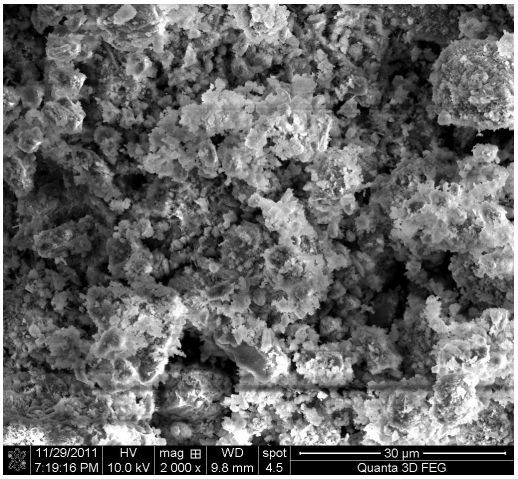
(b) 05℃-PCE-1 day



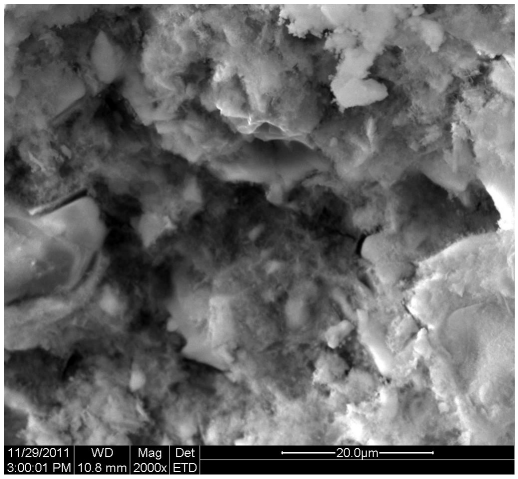
(c) 15℃-Control-1 day



(d) 15℃-PCE-1 day

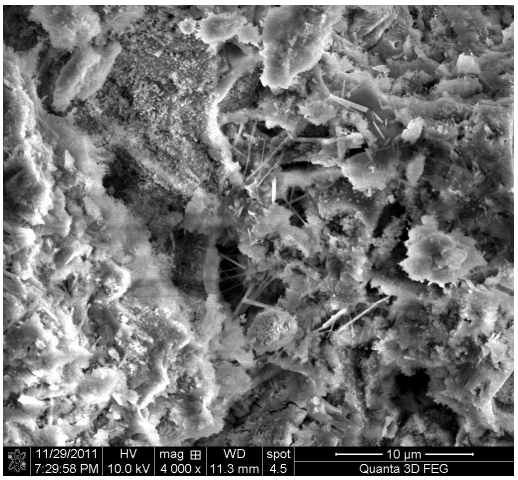


(e) 25℃-Control-1 day

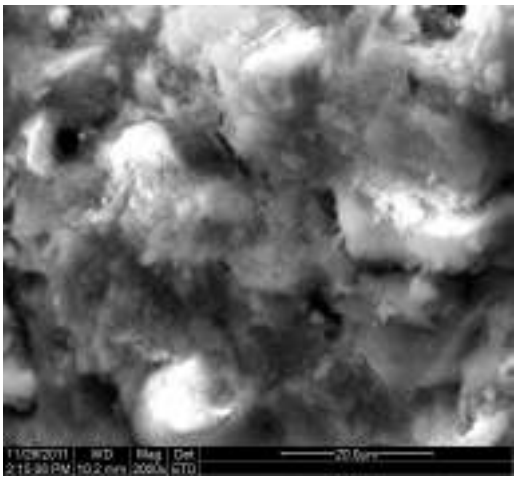


(f) 25℃-PCE-1 day

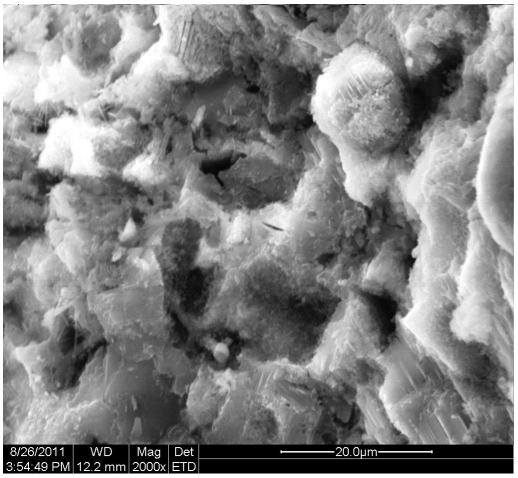
Figure 7.3 SE micrographs of cement paste after 1 day curing



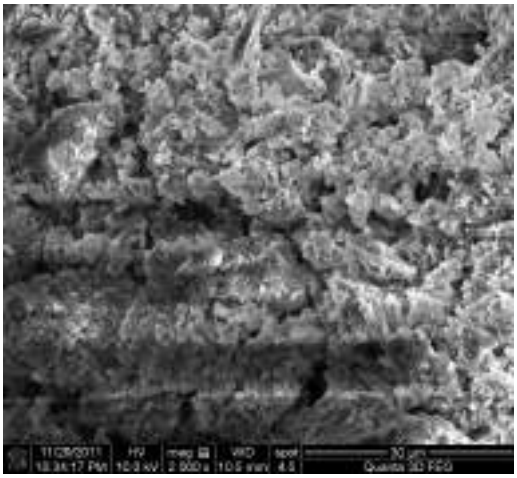
(g) 35℃-Control-1 day



(h) 35℃-PCE-1 day



(j) 40℃-Control-1 day



(k) 40℃-PCE-1 day

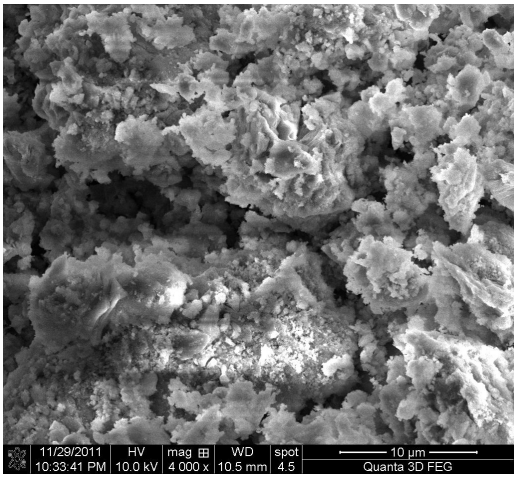
Figure 7.3 SE micrographs of cement paste after 1 day curing

It is clearly observed from Figure 7.3 that the hydration is affected by the temperature at early ages with more hydration products forming at higher exposure temperatures. This can be the reason for the higher strength in the mortar and concrete at early ages and at higher temperatures, as in the results presented in Chapter 5. The incorporation of superplasticizer generally leads to a denser microstructure, which can be the reason for the better mechanical properties of the superplasticized cement mortar and concrete, as reported in Chapter 5.

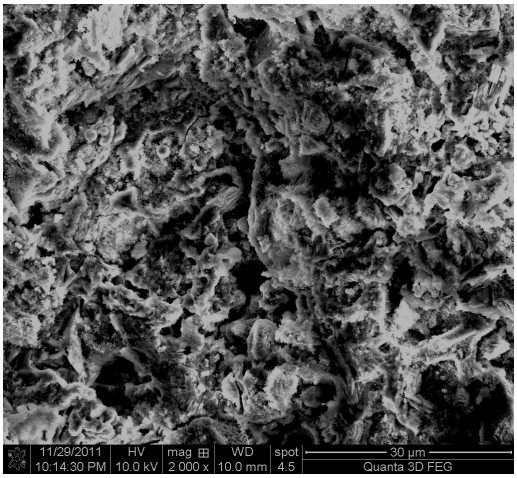
7.2.2.3 Development of Microstructure at 3 days

The microstructure of cement paste prepared with and without superplasticizer at three days is shown in Figure 7.4. It can be observed that the microstructure is more

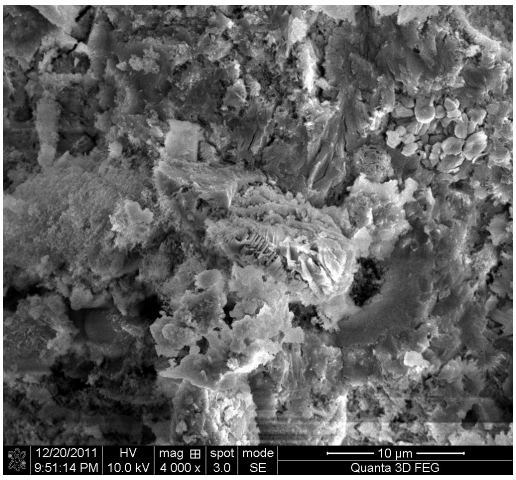
compact compared to that at one day. The pores in the microstructure are filled with hydration products and there is less porosity at higher temperatures, for both types of paste.



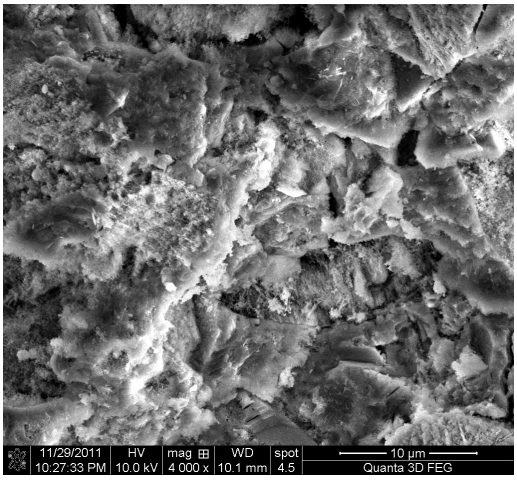
(a) 5°C-Control-3 day



(b) 5°C-PCE-3 day

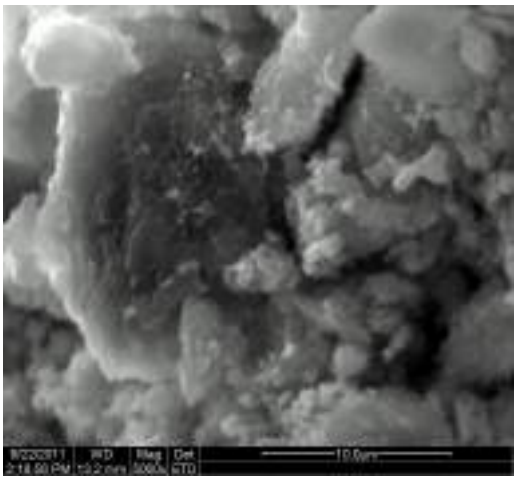


(c) 15°C-Control-3 day

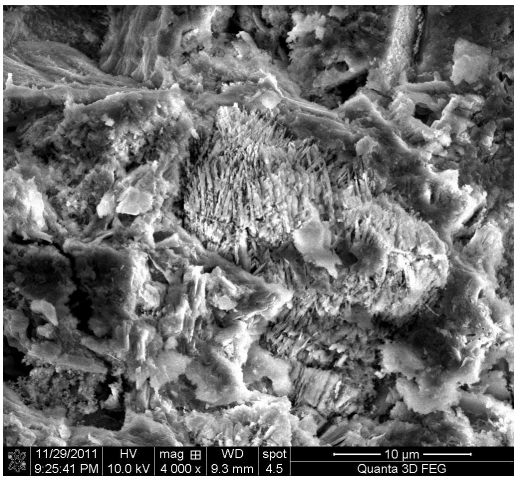


(d) 15°C-PCE-3 day

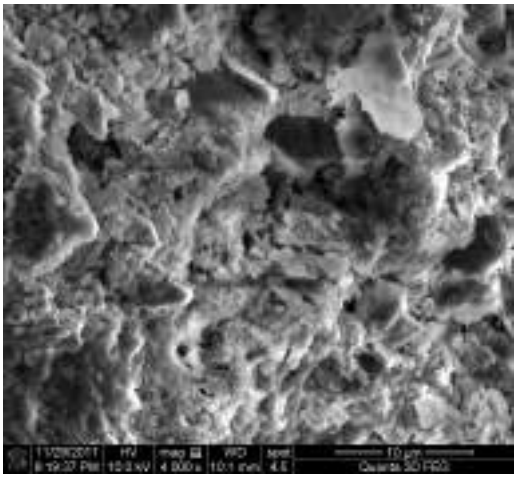
Figure 7.4 SE micrographs of cement paste after 3 day curing



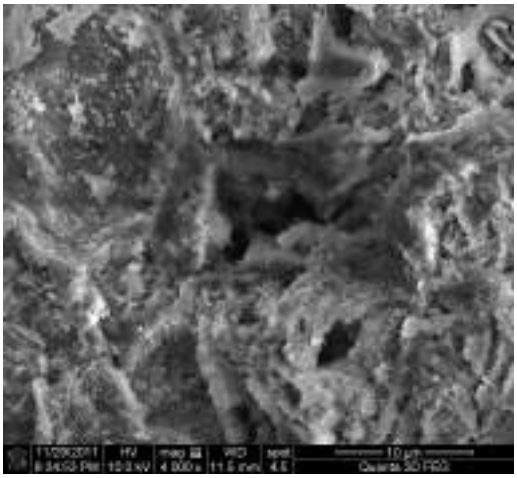
(e) 25°C-Control-3 day



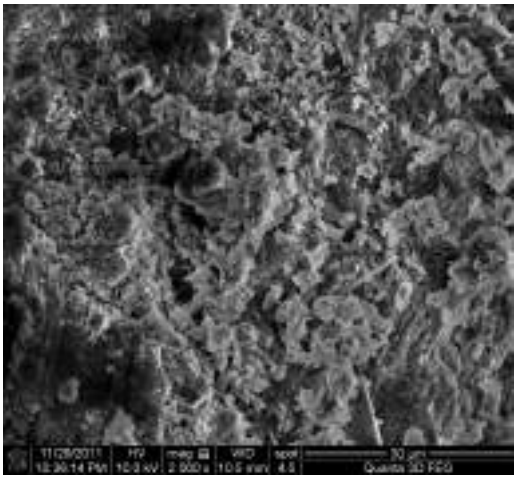
(f) 25°C-PCE-3 day



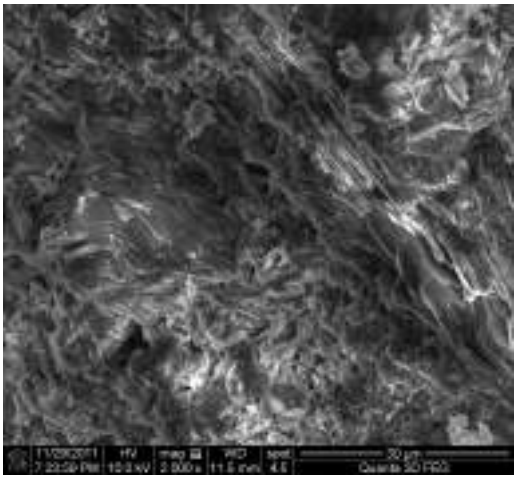
(g) 35°C-Control-3 day



(h) 35°C-PCE-3 day



(i) 40°C-Control-3 day

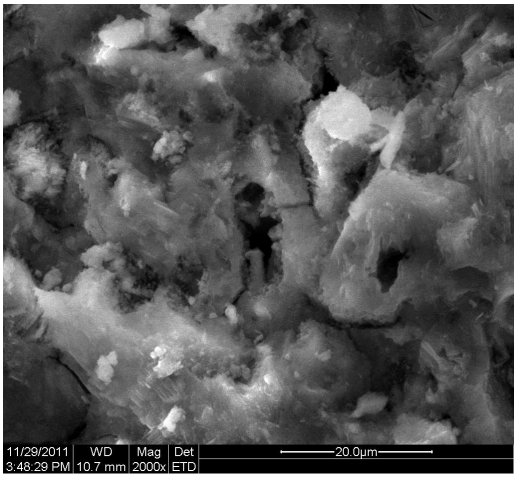


(j) 40°C-PCE-3 day

Figure 7.4 SE micrographs of cement paste after 3 day curing

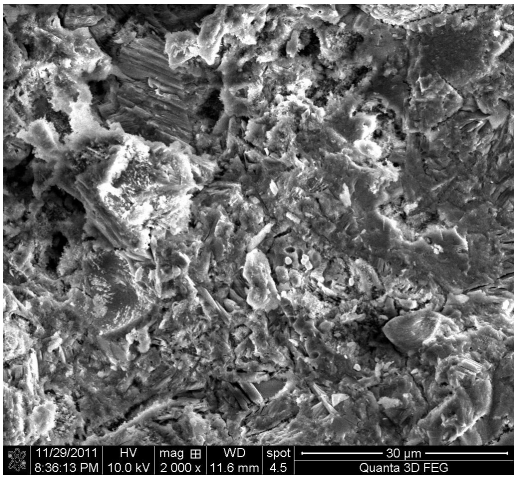
(e) 25°C-Control-7 day

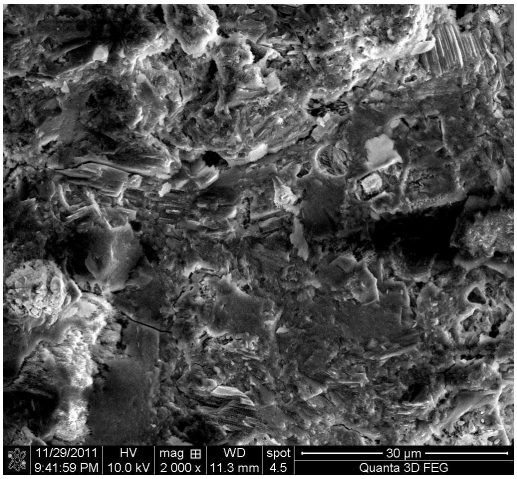
(f) 25°C-PCE-7 day



(g) 35°C-Control-7 day

(h) 35°C-PCE-7 day





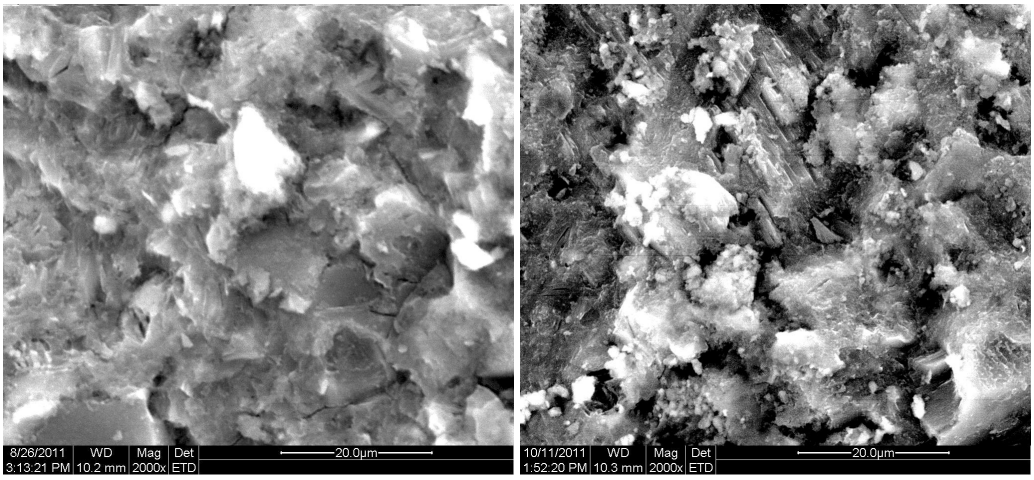
(i) 40°C-Control-7 day

(j) 40°C-PCE-7 day

Figure 7.5 SE micrographs of cement paste after 7 day curing

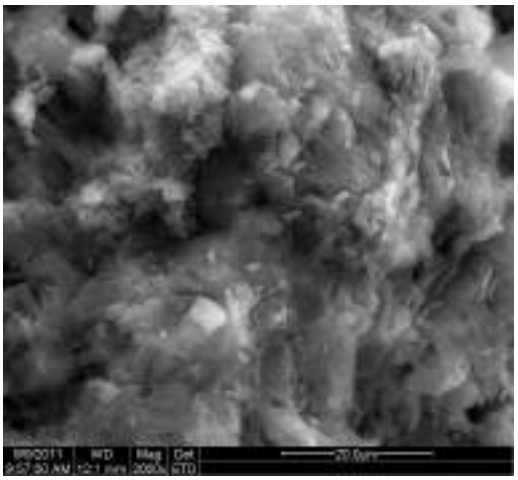
7.2.2.5 Development of Microstructure at 28 days

The microstructure of cement pastes prepared with and without superplasticizer, after 28 days of curing, is shown in Figure 7.6. The microstructure is further developed, and seems to be compact after 28 days. At higher temperatures, especially at 35 and 40°C, the pores are very clear and distinct. It is clearly observed that the microstructure is denser and more uniform at lower temperatures, confirming the observations of Kjellsen et al. (1991). Lothenbach et al. (2007) also observed a decrease in coarser pores at lower temperatures compared to higher temperature. Cao and Detwiler (1995) also observed a more scattered distribution of hydration products and an extremely porous microstructure for specimens cured at higher temperature. They showed that the pores are more evenly distributed at lower temperatures compared to higher temperatures. This can be the reason for the lower strength of mortar and concrete exposed to higher temperature initially, as observed in Chapter 5.

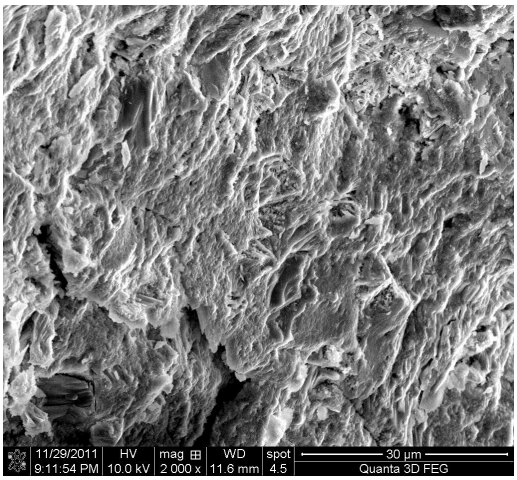


(a) 5°C-Control-28 day (b) 5°C-PCE-28 day

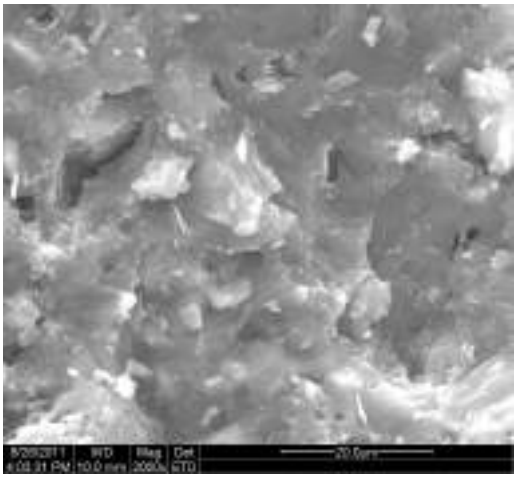
Figure 7.6 SE micrographs of cement paste after 1 day curing



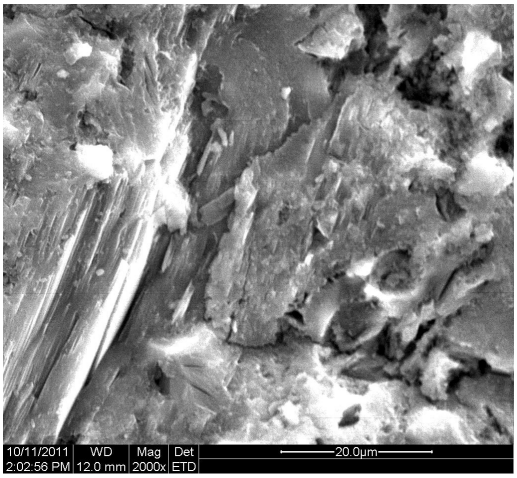
(c) 15℃-Control-28 day



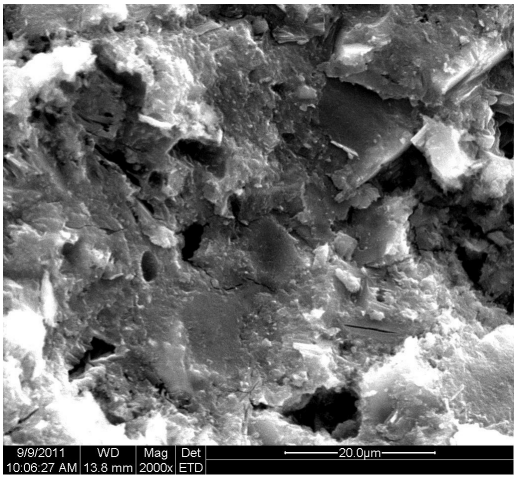
(d) 15℃-PCE-28 day



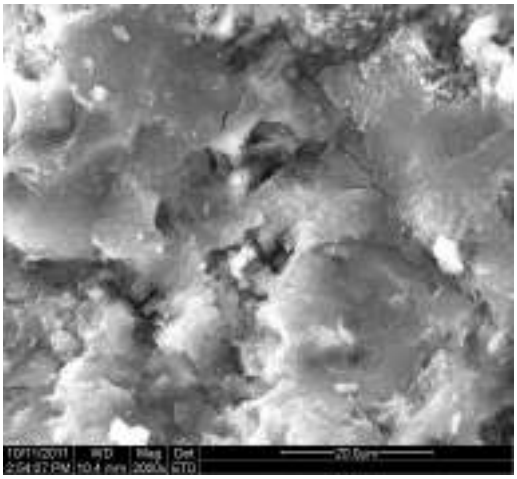
(e) 25℃-Control-28 day



(f) 25℃-PCE-28 day

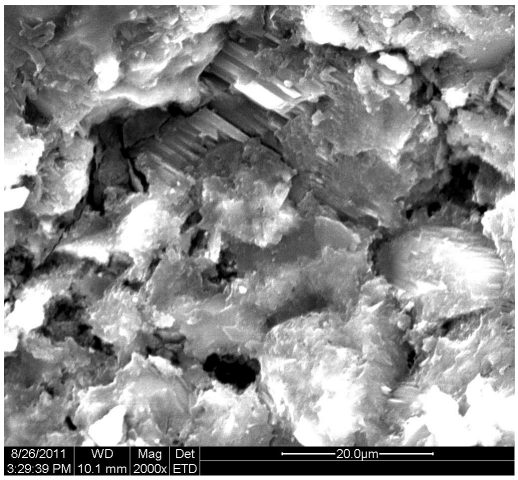


(g) 35℃-Control-28 day

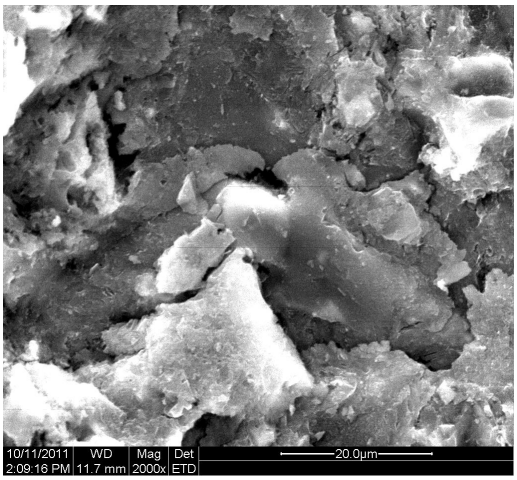


(h) 35℃-PCE-28 day

Figure 7.6 SE micrographs of cement paste after 1 day curing



(i) 40°C-Control-28 day



(j) 40°C-PCE-28 day

Figure 7.6 SE micrographs of cement paste after 1 day curing

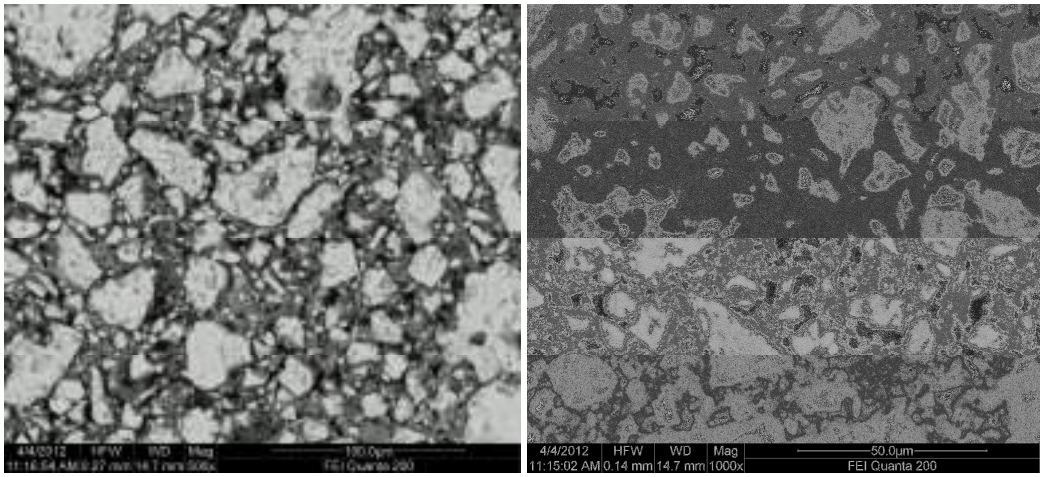
In general, it can be observed from the secondary electron images that the hydration increases with an increase in temperature at early ages, which can seen from the presence of more hydration products (Figures 7.1 and 7.2). As the age increases, the hydration also progresses, and the microstructure becomes denser and uniform. The pores are filled with hydration products as the hydration progresses, and the porosity decreases (Bentz and Stutzman 1994). However, after 28 days, the microstructure seems to be more compact for the specimens exposed to lower initial temperatures (Figure 7.6). This is in accordance with earlier observations that curing at higher temperatures can result in an increase in porosity for the same degree of hydration (Kjellsen et al. 1990; Mouret et al. 1999). As cited by Kjellsen et al. (1990), Verbeck and Helmuth observed that at higher temperatures, the cement hydration products would not be able to diffuse through a significant distance in the cement grain due to lower solubility and diffusibility. Again at higher temperature, as the hydration is rapid, there will not be sufficient time for the precipitation of the hydration products away from the cement grains. This results in a highly non-uniform distribution of the solid phases of the hydration products. They state that the denser layer of hydration products formed around the cement grain at higher temperatures prevents or slows down further hydration. At lower temperatures, the hydration products will get sufficient time to diffuse and precipitate relatively more uniformly throughout the interstitial space between the cement grains. Again, the incorporation of

superplasticizer retards hydration in the initial stages. At later ages, the microstructure seems to be more uniform with the addition of the superplasticizer probably due to better dispersion of the cement particles and the consequent increase in hydration and pore-filling.

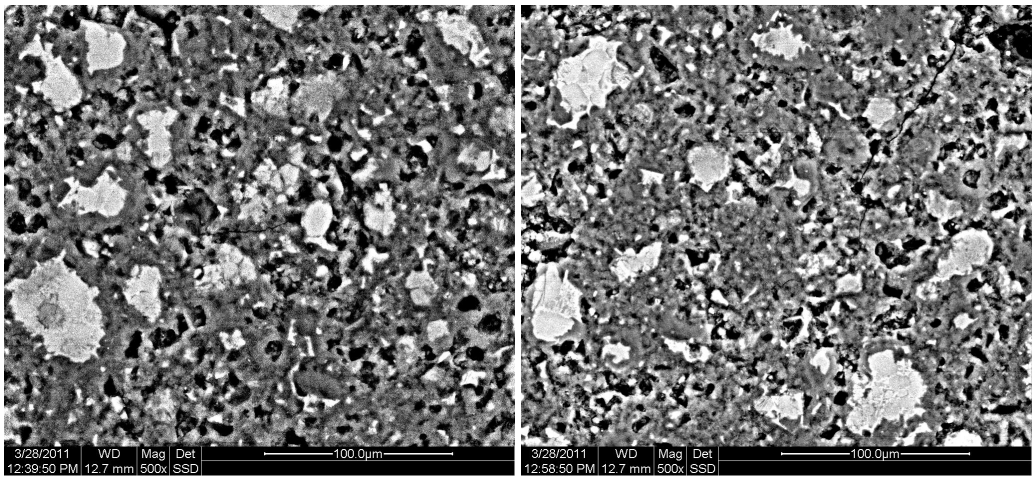
7.2.3 Backscattered Electron Imaging (BSE)

Backscattering electron (BSE) imaging is generally used to understand the development of the microstructure of cement paste and to identify the different phases of hardened cement paste. Backscattered electrons have higher energy than secondary electrons, and so can be detected from greater depths. However, the resolution of the BSE images is less compared to that of secondary electron images (Scrivener 2004). This technique has been used to study the hydration of cement and microstructure of cement paste by many researchers (e.g., Scrivener 1989; Kjellsen et al. 1990; Zhao and Darwin, 1992; Bentz and Stutzman, 1994; Escalante-Garía and Sharp 2001; Famy et al., 2002; Puertas et al., 2005). The basic principle of this technique is that the electrons of the incident beam rebound from the surface atoms of the specimen, depending on the composition of the phases. The intensity of the BSE signal is a function of the average atomic number of the phase and the contrast observed is based on the atomic number of phases (Kjellsen et al. 1990; Bentz and Stutzman, 1994; Famy et al., 2002). The unhydrated cement particles have higher molecular weight with higher backscattering intensity than hydrated particles (Zhao and Darwin, 1992; Puertas et al., 2005). It has been observed that C_4AF has the highest intensity. In hydrated cement paste, the major phases from brightest to darkest are unhydrated cement, calcium hydroxide, calcium silicate hydrate gel and the pores (Bentz and Stutzman, 1994). In addition to the grey scale, the physical shape can also be used to identify the different phases in the microstructure (Escalante-García and Sharp 2001).

A comparative study of the microstructure of cement pastes prepared at different temperatures has been conducted to understand the influence of the initial temperature on the hydration process and microstructure development. Cement pastes were prepared with PCE based superplasticizer at the saturation dosage of superplasticizer at 25°C (as determined by Marsh cone test). The BSE images of cement paste at one day are presented in Figure 7.7.



(a) 5°C -Control-1 day (b) 5°C-PCE-1 day

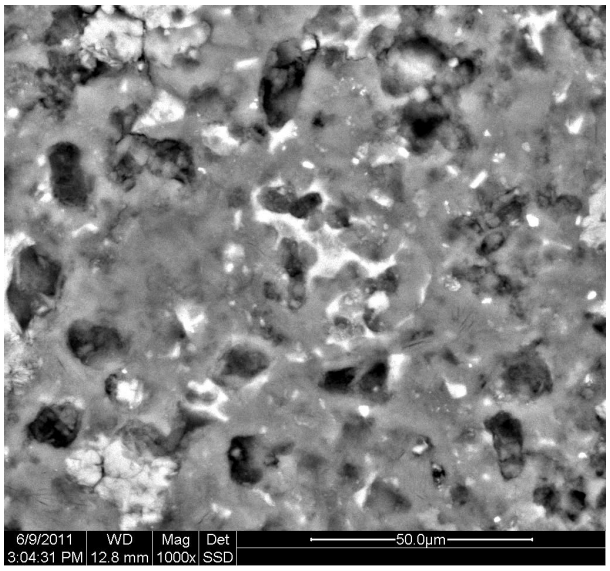


(c) 40°C-Control-1 day (d) 40°C-PCE-1 day

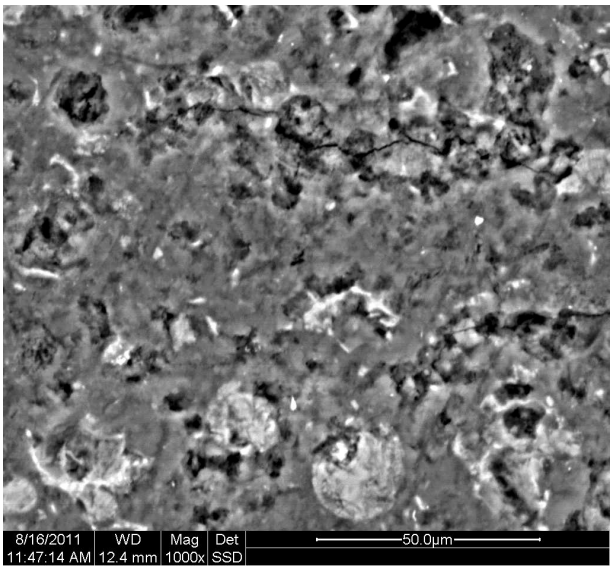
Figure 7.7 BSE images of cement paste after one day: (a) 5°C-Control (b) 5°C-PCE (c) 40°C-Control and (d) 40°C-PCE

The unhydrated cement particles can be seen as bright areas and pores appear dark in Figure 7.7. It can be observed that there are fewer unhydrated particles at higher temperature, implying more hydration. This could be the reason for the higher initial strength for mortar and concrete exposed to higher temperatures initially, as observed in Chapter 5. In Figure 7.7, at 5°C, the unhydrated cement particles are clearly visible. When comparing the images of 5°C and 40°C, it can be observed that the amount of unhydrated cement particles is significantly less at 40°C.

The BSE images of cement paste prepared at 5, 25 and 40°C, and cured for three days are shown in Figure 7.8(a-c). It can be observed from the figure that the porosity (dark areas) decreases with an increase in age. This is due to the formation and distribution of the hydration products in the pores between the cement particles. It can also be seen from the figure that the porosity is higher for the specimens exposed to higher temperature (i.e., at 40°C).

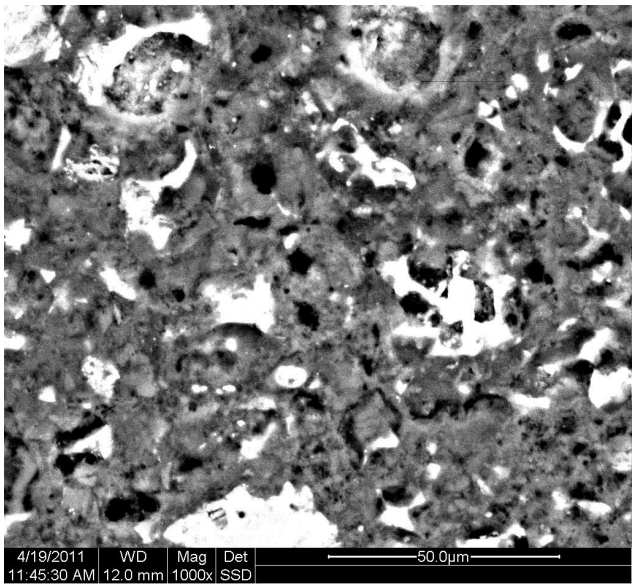


(a) 5°C -Control-3 day



(b) 25°C -PCE-3 day

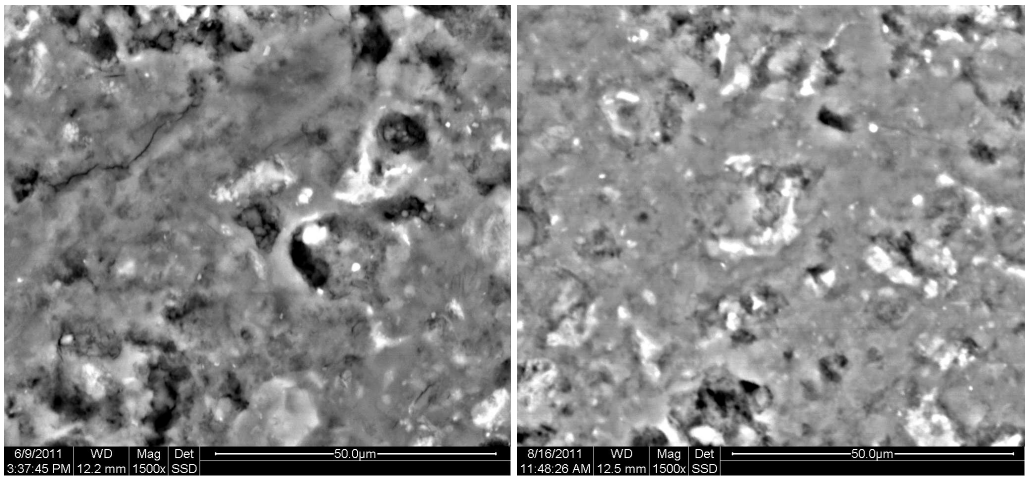
Figure 7.8 BSE images of superplasticized cement paste after 3 days when exposed to initial temperatures of (a) 5°C, (b) 25°C



(c) 40°C -PCE-3 day

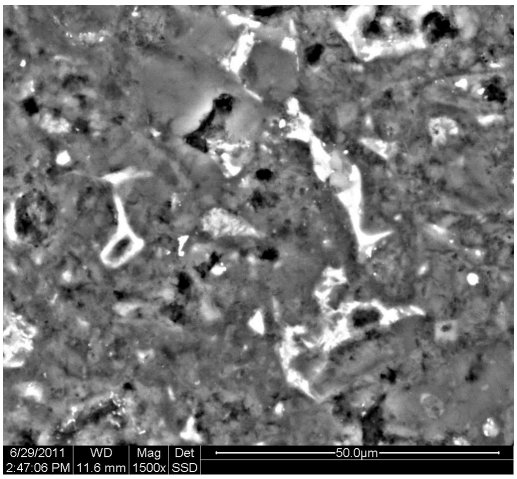
Figure 7.8 BSE images of superplasticized cement paste after 3 days when exposed to initial temperatures of (c) 40°C

The BSE images of cement paste cured for 7 days after the initial exposure to 5, 25 and 40°C are shown in Figure 7.9. It can be observed that the microstructure is denser compared to that at 3 days, as expected. It is also seen that the microstructure is more uniform for the specimen initially exposed to lower temperatures. In all the cases, the incorporation of superplasticizer makes the microstructure more compact.

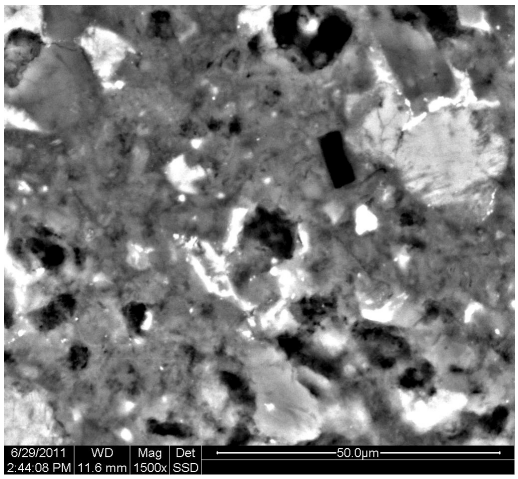


(a) 5°C -Control-7 day (b) 5°C -PCE-7 day

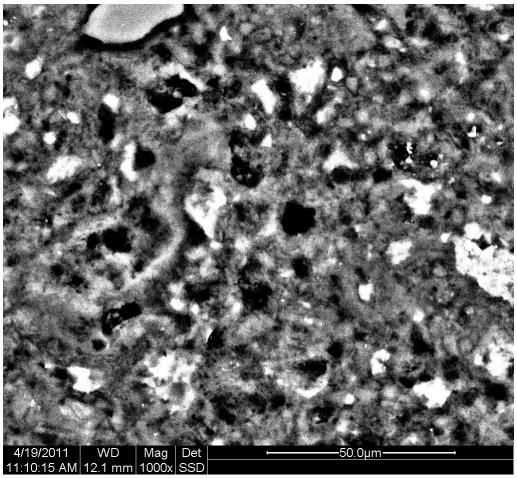
Figure 7.9 BSE images of superplasticized cement paste after 7 days, when exposed to various initial temperatures with and without superplasticizer



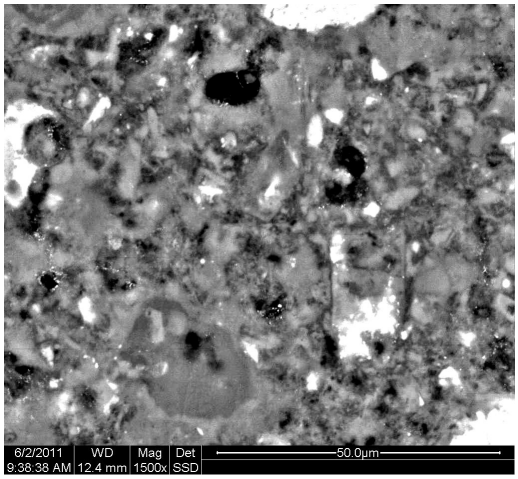
(c) 25°C -Control-7 day



(d) 25°C -PCE-7 day



(e) 40°C -Control-7 day

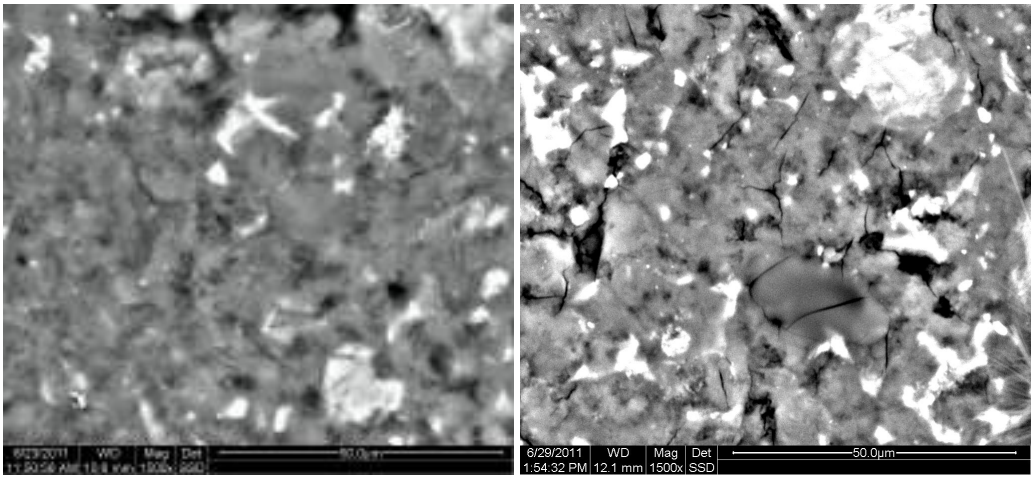


(f) 40°C -PCE-7 day

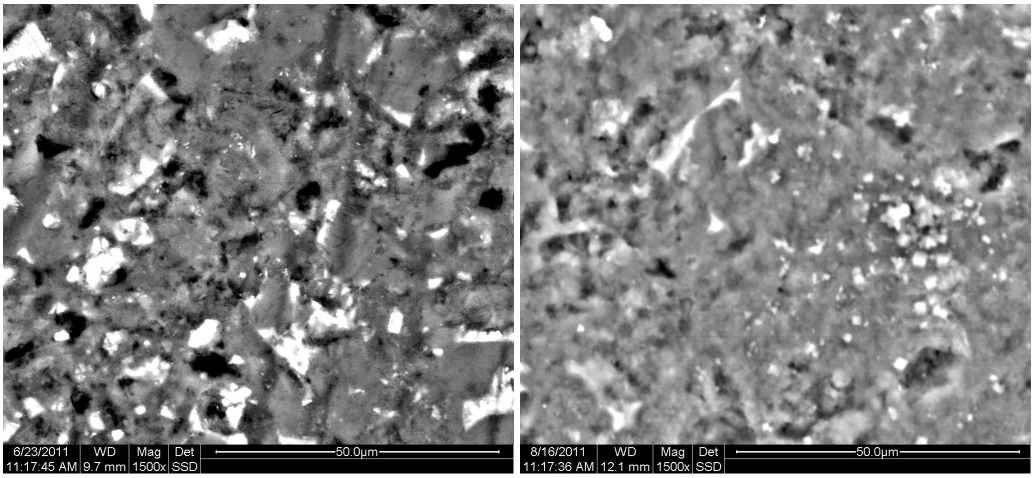
Figure 7.9 BSE images of superplasticized cement paste after 7 days, when exposed to various initial temperatures with and without superplasticizer

The BSE images of cement paste exposed to 5, 25 and 40°C initially and cured for 28 days are shown in Figure 7.9. The microstructure is more developed and the pores are fewer compared to those at earlier ages. This can be due to the decrease in the capillary pore volume as the capillary space is filled with hydration products and the gel porosity increases, causing a net reduction in total porosity (Mellas et al. 2003). It can be observed that the microstructure developed is more porous at higher temperature, which can be the reason for the lower strength of the specimen exposed to higher initial temperature, as observed in Chapter 5. At 5°C, the microstructure

seems to be more uniform; however, at higher temperatures, a more porous microstructure can be seen after 28 days. The enhanced hydration rate and the formation of denser hydration rims lead to more heterogeneous and porous distribution of hydration products at higher temperatures. However, at lower temperatures, the hydration products are more uniformly distributed, which results in smaller pores and better interlocking of different phases (Lothenbach et al. 2007). Kjellsen et al. (1990) also observed a more homogeneous distribution of hydration products for the specimens hydrated at lower temperatures.

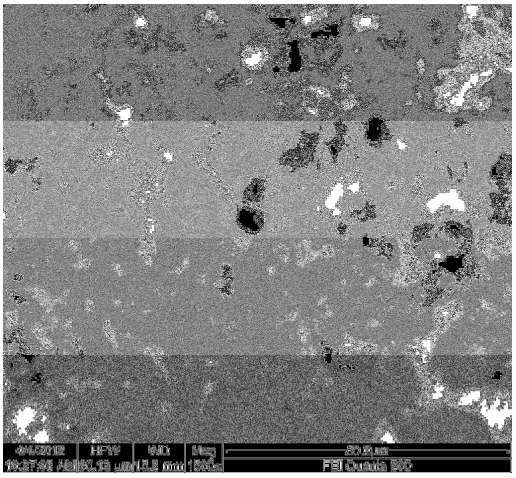


(a) 5℃ -Control-28 day (b) 5℃ -PCE-28 day

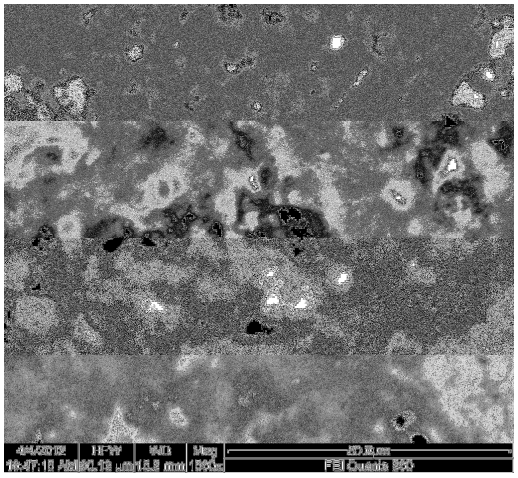


(c) 25℃ -Control-28 day (d) 25℃ -PCE-28 day

Figure 7.10 BSE images of superplasticized cement paste after 28 days exposed to various initial temperatures with and without superplasticizers



(e) 40°C -Control-28 day



(f) 40°C -PCE-28 day

Figure 7.10 BSE images of superplasticized cement paste after 28 days exposed to various initial temperatures with and without superplasticizers

7.3 THERMAL ANALYSIS

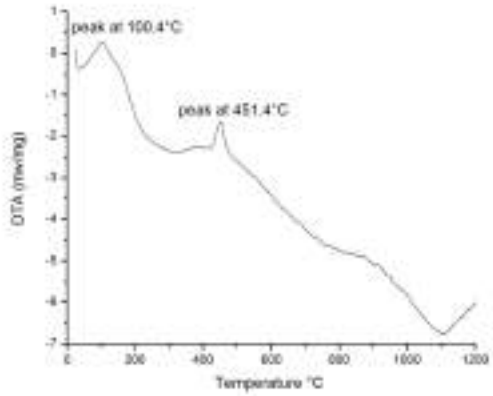
7.3.1 Background

Thermogravimetric analysis has been used here to study the hydration reactions of cement paste with and without superplasticizer. In this method, the material is heated at a constant rate and the consequent change in mass, due to the reactions taking place, is obtained. The constituents of the sample causing the loss in weight at a particular temperature can be identified if the reactions occurring at specific temperatures are known. For example, calcium hydroxide decomposes at about 450-550°C, which can help identify the presence of the calcium hydroxide in a sample, when there is a loss in mass at that temperature range.

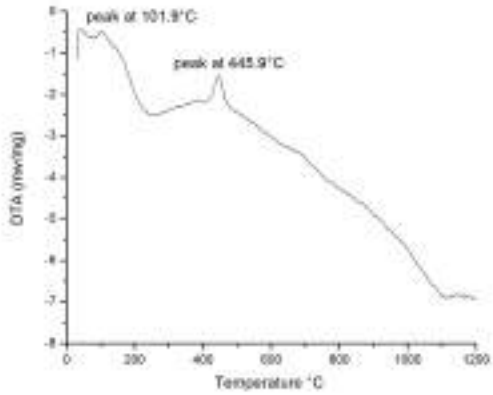
7.3.2 Results and Discussions

The tests were conducted in a nitrogen atmosphere with a NETZSCH STA 409 C/CD instrument. A uniform rate of increase in temperature of 20K/min was used in the study. The samples were obtained by powdering the hardened cement paste and sieving through a 75μ sieve, as explained in Section 3.3.5 of Chapter 3. The DTA results of cement pastes prepared at 5, 25 and 40°C, and cured for 28 days are shown in Figure 7.10. In all the cases, there is a small endothermic peak at around 100°C, which corresponds to the decomposition of monosulphate and evaporation of the gel

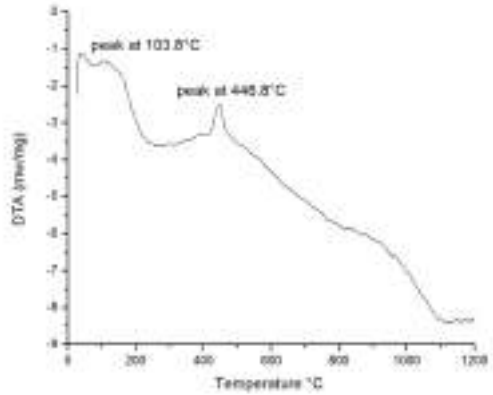
water. The endothermic peak at 440-450°C range, in all the three cases, corresponds to the decomposition of C-H (Prince et al. 2003).



(a)



(b)



(c)

Figure 7.11 DTA analysis of cement pates without superplasticizer after curing for 28 days and prepared at (a) 5°C (b) 25°C and (c) 40°C.

Thermogravimetric studies were conducted on cement pastes prepared at 5, 25 and 40°C for ages corresponding to half setting, one day and 28 days. A typical TG curve is shown in Figure 7.11 and all the individual curves are given in Appendix D. The loss in mass corresponding to the decomposition of the C-H was calculated and the results are tabulated in Table 7.1. The quantity of C-H is calculated from the weight loss corresponding to the temperature range of 450-550°C. Earlier researchers had also used this range of temperature to calculate the C-H content in the cement paste (Franke and Sisomphon 2004; Jayasree 2008). Franke and Sisomphon (2004) observed that the values obtained from the TGA method is comparable with that of the results obtained from titration.

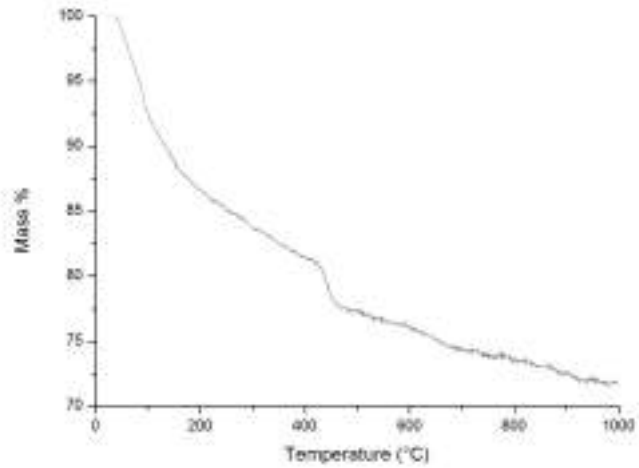


Figure 7.12 TG curve of cement paste at the age of one day after exposure to 5°C

Table 7.1 Losses in mass corresponding to decomposition of CH

Paste	Time	Mass loss (%) corresponding to decomposition of CH		
		5˚C	25˚C	40˚C
Control	Half setting	1.38	1.84	3.06
	1 Day	9.10	9.61	9.51
	28 Day	11.88	10.27	9.47
PCE	Half setting	1.37	1.82	1.77
	1 Day	6.66	7.89	11.39
	28 Day	17.09	15.73	14.35

From Table 7.1, it can be observed that the loss in mass corresponding to the decomposition of C-H increases with age, in all the cases. This indicates that the hydration increases with an increase in age, as expected. It is observed that at early ages, i.e., at half setting, the loss corresponding to the decomposition of the C-H increases with increase in temperatures. This implies the presence of more C-H reflecting a higher rate of hydration for the specimen initially exposed to higher temperature. It can be observed that the loss increases marginally after one day for the control paste at higher temperatures. This higher rate of hydration could be the reason for the increase in strength observed for the mortar and concrete exposed initially to higher temperatures, as reported in Chapter 5. However, after 28 days, the pastes exposed to lower temperature had higher loss in mass (Table 7.1) or, in other words, more amount of C-H possibly due to higher degree of hydration or different nature of the products, which could be the reason for the observed higher strength for the mortar and concrete exposed initially to lower temperature, as seen in Chapter 5.

The trends are similar in pastes without and with superplasticizer. It is observed from Table 7.1, that the superplasticizer retards the hydration initially. It can be seen that the loss in mass corresponding to the decomposition of C-H is almost same at 5°C, for both control and superplasticized cement paste, especially at lower temperatures. After one day, the superplasticized paste specimen exposed to 5°C seems to have significantly lower hydration compared to control mix while the difference at 25°C is only marginal. At 40°C, the superplasticized cement paste seems to have undergone more hydration, compared to the control mix, which could imply that the retarding effect of the superplasticizer will cease earlier at higher temperatures. It should be noted that the setting time increased significantly in the presence of the superplasticizer at 5°C, which could be the reason for less hydration at lower temperature. However, at 25 and 40°C, the loss in mass corresponding to the composition of C-H was 7.89 and 11.39%, respectively, i.e., hydration increases with an increase in temperature. At higher temperature (i.e., at 40˚C), the retardation is compensated earlier and higher mass loss is observed. The better dispersion of the

cement particles in the presence of superplasticizer and the increased rate of hydration at higher temperature could be the reasons for this. However, at higher temperature, this trend is reversed for both the control as well as for the superplasticized cement paste. The decomposition corresponding to the C-H decreases with an increase in temperature after 28 days. This indicates that the increase in hydration due to higher in initial exposure temperatures occurs only at the early ages and the total amount of hydration is negatively affected with this increase in temperature. This could be the reason for the increased strength at early ages for the mortar and concrete exposed to higher initial exposure temperature and the reduction in strength after 28 days, as observed in Chapter 5.

Again, it is also observed that the superplasticized cement paste shows significantly higher loss in mass compared to the control mix after 28 days, indicating a higher amount of hydration or different nature of the hydration products for the superplasticized paste. This could be due to the better dispersion of cement particles in the presence of superplasticizer and the consequent increase in the area of reaction sites. More loss in mass corresponding to the decomposition of C-H was observed in the case of cement paste with superplasticizer, at all temperatures, which implies more or different hydration of the cement paste with superplasticizer. However, the loss in mass also decreases with an increase in temperature for the superplasticized cement paste. The higher mass loss at lower temperatures could be due to better dispersion of the cement particles in the presence of superplasticizer.

7.4 XRD Analysis

7.4.1 Background

X-ray diffraction studies help understand the hydration process of cement paste by identifying the crystalline products of hydration and studying the consumption of the anhydrous phases of cement (Roncero et al. 2002). The formation of the amorphous C-S-H is indicated by an upward shift or hump in the diffractogram between 2θ of 25-35°. Using this technique, the polycrystalline phases of hardened cement paste (i.e., ettringite, monosulphate and portlandite) can be identified from the X-ray spectra,

which are unique for each of them. The sample preparation and experimental procedures have been explained in Section 3.3.5.3.

7.4.2 Results and Discussions

The XRD patterns of cement paste cured at 1, 3, 7 and 28 days, for the samples prepared at 25°C are shown in Figure 7.12. The relative evolution of cement paste with age can be identified by comparing the intensity of crystalline phases like C_3S and portlandite. The intensity of peaks corresponding to the anhydrous phases of cement (i.e., C_3S) decreases with an increase in age and the C-H increases. In the TGA analysis, it was observed that the formation of C-H increases with an increase in age, which is in accordance with the present observations of higher peaks for C-H.

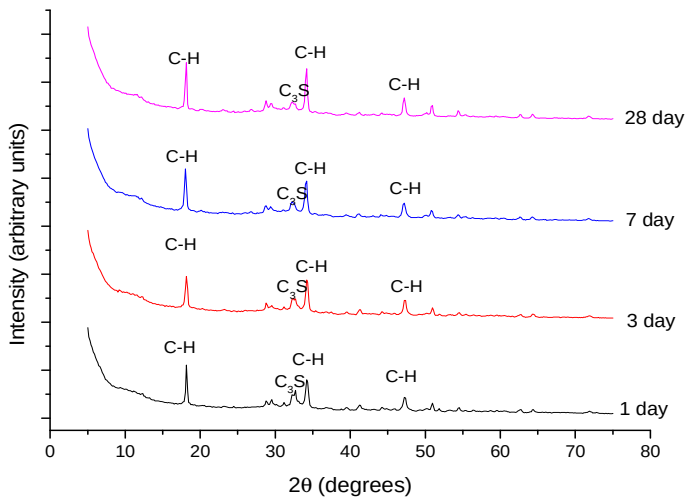
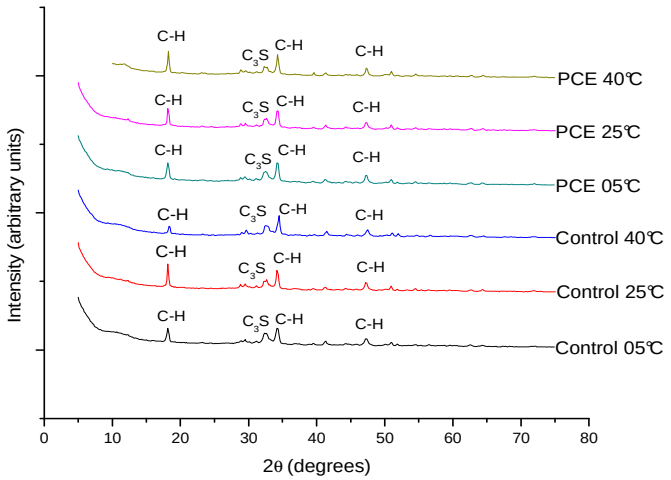


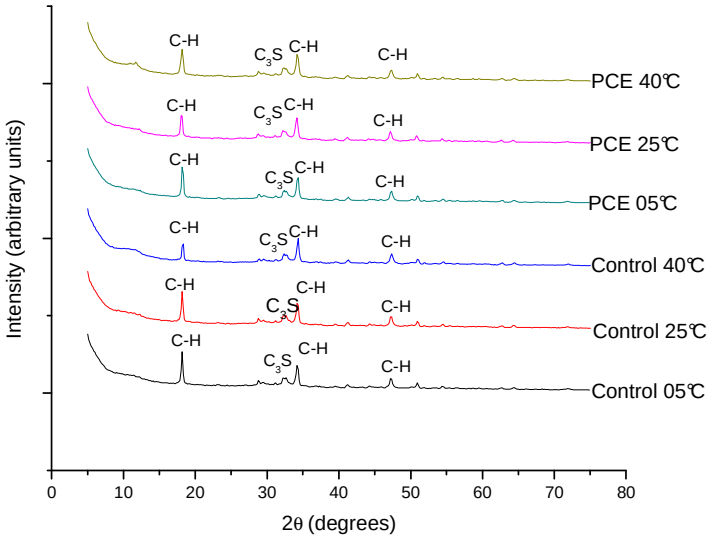
Figure 7.13 X-ray diffractogram of cement paste prepared at 25°C with age

X-ray diffractograms for the cement pastes prepared at 5, 25 and 40°C and cured for 1, 3, 7 and 28 days are shown in Figure 7.13 a-d and all the individual curves are given in Appendix E. The different phases of the hydration products can be identified with the help of the XRD patterns. It appears that after one day, the intensity of peak corresponding to C_3S decreases whereas the calcium hydroxide generally increases with an increase in initial exposure temperature. This is in accordance with the observations from the TG analysis, where the amount of C-H was seen to increase

with initial exposure temperature. After one day, there is no significant qualitative difference in the case of C_3S. It is generally observed that the calcium hydroxide increases with an increase in the initial ambient exposure temperature except at 28 days. At 28 days, it is observed that the peaks corresponding to the calcium hydroxide decrease compared to the lower temperatures at 40°C, for the both control and superplasticized cement paste.

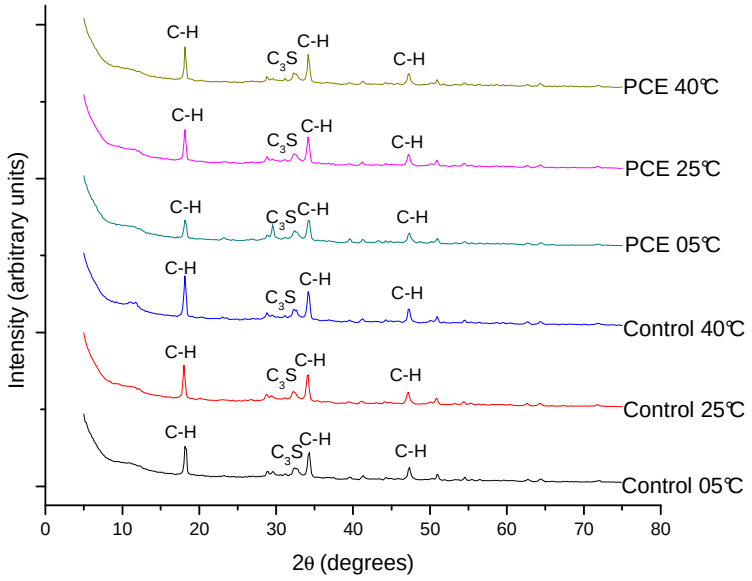


(a)

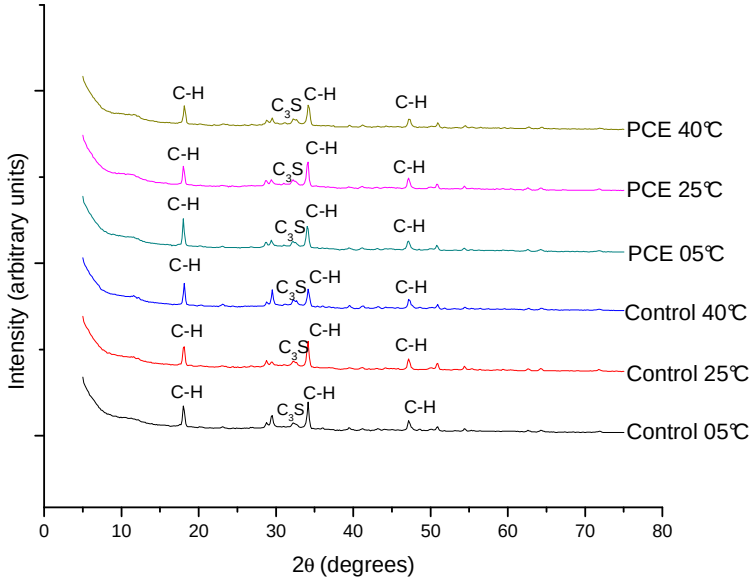


(b)

Figure 7.14 X-ray diffractogram of cement pastes prepared at various temperatures and cured for (a) one day and (b) 3 days



(c)



(d)

Figure 7.14 X-ray diffractogram of cement pastes prepared at various temperatures and cured for (c) 7 days and (d) 28 days

7.5 CONCLUSIONS

The microstructure of superplasticized cement paste was studied to understand the influence of temperature on the hydration behaviour. From the analysis of the cement pastes prepared at various temperatures, with and without superplasticizer, the following conclusions can be made.

- The initial rate of hydration increases with an increase in the initial exposure temperature of the cement paste. In the SEM analysis, more hydration products are observed at higher temperature initially and the TG analysis shows higher mass loss corresponding to decomposition of C-H. This could be the reason for the higher early strength in mortar and concrete.

- Even though the initial hydration increases with an increase in temperature, the later age microstructure is adversely affected. A more porous microstructure is observed in the SEM images for the pastes exposed to higher initial temperature. In the TG analysis, there is less mass loss corresponding to the decomposition of C-H decreases in pastes exposed to initial higher temperatures. This could be the reason for lower later age strengths seen in specimens exposed to higher initial temperature.

- The addition of superplasticizer decreases the formation of hydration products initially, especially at lower temperature; i.e., the incorporation of superplasticizer retards the hydration, as expected. This is evident from the TG analysis that there is a lower degree of hydration for the superplasticized cement paste compared to control mix after one day; however, at 40 °C, the retardation is compensated early and a higher degree of hydration is observed. This could be due to the better dispersion of the cement particles due to the presence of superplasticizer and the consequent increase in hydration. SEM images also show that less hydration products are formed in the superplasticized cement paste compared to the control paste.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

The study helps understand the influence of ambient temperature, cement fineness and SO_3 content of cement on the cement-superplasticizer interaction and on the properties of superplasticized cement paste, mortar and concrete. The salient findings that lead to the fulfilment of the main objectives of the work are given below.

8.1 GENERAL CONCLUSIONS

- Simple methods like the Marsh cone, mini-slump and Vicat penetration were used to characterise the influence of temperature on the properties of cement paste. It is observed that the ambient temperature influences the properties of cement paste significantly. The water demand of cement paste increases with an increase in temperature, whereas, the setting time decreases with an increase in temperature. The efficiency of superplasticizer in decreasing the water demand increases with increase in temperature. The fluidity of cement paste with and without superplasticizer decreases with an increase in temperature at lower dosages of superplasticizer; however, the fluidity increases or remains almost constant at higher dosages of superplasticizer. The saturation dosage of superplasticizer increases with an increase in temperature. The loss in fluidity of cement paste with time increases with an increase in ambient temperature. The PCE based superplasticizer is least susceptible to changes in temperature and the LS based superplasticizer is the most.

- The influence of temperature on the properties of cement mortar and concrete were studied, and can be concluded that the fresh properties of cement mortar and concrete are negatively influenced by the increase in temperature. The mechanical properties of cement mortar and concrete are also severely affected by the temperature. The early age strength increases with an increase in the exposure temperature whereas the long term strength is decreased significantly.

- The saturation dosage of superplasticizer increases with an increase in cement fineness. This can be attributed to the higher surface area of the finer cements, which leads to higher

adsorption and hydration reactions. The fluidity of cement paste decreases with an increase in fineness of cement at lower dosages of superplasticizer, and increases marginally or remains constant at higher dosages of superplasticizer. The loss in fluidity of cement paste with time increases with an increase in fineness of cement. The initial compressive strength of cement mortar and concrete increases with an increase in cement fineness, whereas the later age strengths are not significantly affected.

- The fluidity of cement paste increases marginally with an increase in SO_3 content of cement. The loss in fluidity with time generally decreases with an increase in SO_3 content of cement. The mechanical properties of mortar and concrete are not significantly affected by the variation of SO_3 content of cement studied.

- Different characterization techniques have been used to study the influence of temperature on the hydration processes as well as on the microstructure development. The complementary use of SEM, TGA and XRD has given an insight into the properties of hardened cement paste. The lower later age strength for the specimen exposed to higher temperature can be due to the heterogeneous nature and more porous microstructure developed at higher temperatures. It is observed that the initial hydration is higher for the samples exposed to higher initial temperatures. The initial increase in the hydration rate can be the reason for the improved strength in the early ages. The addition of superplasticizer retards the hydration especially at the lower temperature and the microstructure seems to be more uniform in the presence of superplasticizer.

The major findings of the thesis in terms of the trends observed are summarised in Table 8.1.

Table 8.1 The major findings of the thesis in terms of the trends observed

Parameter	*Effect of an increase in*		
	Temperature	*Fineness of cement*	*SO_3 content of cement*
Cement Paste			
Water demand	Increases (0-23%)	Not significant (0-3.5%)	Not affected
Initial setting time	Decreases (80-90%)	Decreases (0-18%)	Not significant (0-10%)
Final setting time	Decreases (70-80%)	Not significant (0-2%)	No trend could be identified
Superplasticizer demand	Increases (55-200%)	Increases (110-130%)	Not affected
Loss in fluidity with time	Increases (23-100%)	Increases	Decreases
Mortar			
Initial spread	Decreases (30%)	Increasing (17%)	Increases (12-14%)
Loss in spread	Increases (0-15%)	Not clear	Decreases (5-10%)
Initial compressive strength	Increases (8-22%)	Increases (28-63%)	Increases (0-15%)
28-day compressive strength	Decreases (9-14%)	Not affected (0-3%)	Not affected (0-3%)
28-day Flexural strength	Decreases (5-7%)	Not affected (8-10%)	No trend could be identified
Concrete			
Superplasticizer demand	Not assessed	Increases (30-40%)	Not significant (10-20%)
Initial slump	Decreases (75%)	Not assessed	Not assessed
Initial compressive strength	Increases (21-31%)	Increases (14-41%)	Increases (6-12%)
28-day compressive strength	Decrease (8-13%)	Increase (6-10%)	Not affected (1-5)

8.2 SPECIFIC CONCLUSIONS

The specific conclusions obtained from the experimental investigations conducted on the cement paste, mortar and concrete are classified under the following topics: (i) influence of temperature on the properties of cement paste (ii) influence of temperature on the properties of cement mortar and concrete (iii) influence of fineness of cement on the properties of cement paste, mortar and concrete (iv) influence of SO_3 content of cement on the properties of cement paste, mortar and concrete (v) influence of temperature on hardening and hardened state properties of superplasticized cement paste. Simple and already proven techniques were used to bring out the influence of the ambient temperature, cement fineness and SO_3 content of cement on various properties of cement paste, mortar and concrete. The complementary use of multiple techniques was used to understand the effect of ambient temperature on the hardened properties of superplasticized paste.

8.2.1 Influence of Temperature on the Properties of Cement Paste

- The fluidity of cement paste decreases with an increase in temperature at lower dosages of superplasticizer; however, the fluidity increases with an increase in temperature at higher dosages of superplasticizer. This may be due to two compensating mechanisms, the increase in water demand with an increase in temperature and the decrease in viscosity of the cement paste at higher temperature (or the increase in the efficiency of the superplasticizer with an increase in temperature).

- The saturation dosage of superplasticizer obtained from the Marsh cone test increases with an increase in temperature, for all the superplasticizers studied here. The PCE based superplasticizer had the least temperature sensitivity and LS based superplasticizer exhibited the most. The results emphasize that, the saturation dosage of superplasticizer needs to be determined over the range of ambient temperatures to which the ingredients and fresh concrete are exposed to for obtaining the required fluidity for concrete.

- The loss in fluidity with time increases as the temperature increases and decreases with an increase in the dosage of superplasticizer. Therefore, in order to get better flow retention, a slightly higher dosage of superplasticizer than the saturation dosage obtained from Marsh cone test can be used. Nevertheless, proper care has to be taken for deciding on the higher dosage to avoid adverse effects on concrete like segregation, delay in setting, etc.

- Water demand increases with increase in temperature, both with and without superplasticizer. The increase in water demand can be attributed to the increased rate of hydration at higher temperature. Nevertheless, there is a larger decrease in water demand due to the incorporation of a superplasticizer with an increase in temperature.

- The initial and final setting times decrease as the temperature increases, both with and without superplasticizer. However, the setting time increases with the addition of superplasticizer and varies with the type of superplasticizer.

8.2.2 Influence of Temperature on the Properties of Cement Mortar and Concrete

- The temperature has a significant influence on the initial fluidity and loss in fluidity with time of cement mortar. The fluidity decreases with increase in temperature with and

without superplasticizer. Therefore the ambient temperature should be taken into consideration while finalising the proportion of the mix to get the required fluidity for cement mortar.

- Higher superplasticizer dosage can increase the fluidity of cement mortar. A higher dosage of superplasticizer can be adopted if necessary for obtaining the required fluidity for cement mortar; however, care should be taken to avoid problems like segregation and retardation due to over dosage.

- The compressive strength of cement mortar increases initially with an increase in temperature, however, the long term strength decreases with an increase in initial exposure temperature. The higher rate of hydration due to higher temperature at early ages can be the reason for the higher early strength, however, at later ages this effect is neutralised and the detrimental effects of higher temperature exposure become more predominant. Therefore proper study has to be done to make sure that the required strength will be obtained at the actual exposure conditions. The flexural strength of mortar also decreases with increase in temperature.

- The slump of concrete decreases rapidly with increase in temperature. The higher hydration of cement, increased absorption of the aggregates and the increased evaporation of water from the mix at higher temperature can be the reason for the decreased slump at higher temperature.

- The compressive strength of concrete increases initially with an increase in ambient temperature to which the concrete is exposed, however, the long term strength reduces with increase in initial temperature. Therefore the ambient temperature to which the concrete is subjected should be considered in the determination of the proportioning of the ingredients of concrete. The splitting tensile strength of concrete was also found to decrease with an increase in ambient temperature to which the concrete is exposed initially.

- There exists a good correlation between the initial fluidity of cement paste, mortar and concrete. Studies on fluidity of cement paste give a guideline for the superplasticizer demand for the mortar and concrete at varying temperatures, however, lower temperatures compared to the temperature at which the saturation dosage of cement paste is determined

does not exhibit any loss in flow for cement paste, whereas the cement mortar and concrete exhibited a decrease in fluidity.

- The influence of temperature on the 28 day compressive strength of cement mortar and concrete can be generally comparable even though the development of strength is varying marginally. The advantage of initial increased rate of hydration due to higher temperature disappears early in the case of cement mortar, whereas the increased strength is observed for longer time for concrete.

8.2.3 Influence of Fineness of Cement on the Properties of Cement Paste, Mortar and Concrete

- The saturation dosage of superplasticizer increases with an increase in cement fineness for cement paste, which indicates a higher superplasticizer demand at higher fineness. This can be attributed to higher surface area of the finer cements, which leads to higher adsorption and hydration reactions. The fluidity of cement paste decreases with an increase in fineness of cement at lower dosages of superplasticizer, and increases marginally or remains constant at higher dosages of superplasticizer.

- The loss in fluidity of cement paste with time increases with an increase in fineness of cement for the same dosage of superplasticizer. The higher loss in fluidity for finer cements can be attributed to the higher adsorption of the superplasticizer and the increase in hydration rate for the finer cements. The loss in fluidity with time decreases with an increase in the dosage of superplasticizer. Therefore, the dosage of superplasticizer should be selected in such a way that the loss in fluidity after the required time should be within the permissible limit, for workability retention.

- The initial setting time decreases with an increase in cement fineness. This can be attributed to faster hydration, as the surface area of the cement is higher. The addition of a superplasticizer retards both the initial and final setting times significantly.
- The initial compressive strength of cement mortar increases with an increase in the cement fineness, for the control as well as superplasticized mortars. However, the later age strengths are practically the same. This indicates that the increase in cement fineness could lead to higher early compressive strength without affecting the long-term strength

significantly. The flexural strength of cement mortar also increases slightly with an increase in fineness of cement at 7 days while the 28 day strengths are not affected significantly.

- The superplasticizer demand for the concrete to get a slump of 150 ± 20 mm increases slightly with an increase in the fineness of cement. This is in accordance with the paste study which showed that the saturation dosage of superplasticizer increases with an increase in the fineness of cement.

- The compressive strength of concrete generally increases with increase in fineness of cement. The initial strengths are more significantly affected by the cement fineness than the 28 day strength.

8.2.4 Influence of SO_3 Content of Cement on the Properties of Cement Paste, Mortar and Concrete

- The fluidity of cement paste generally increases with an increase in SO_3 content of cement. The saturation dosage of superplasticizer is not significantly affected by the SO_3 content of cement over the range studied, except for the lowest SO_3 content. The cement with the lowest SO_3 content required a higher superplasticizer dosage. The loss in fluidity with time generally decreases with an increase in SO_3 content of cement.

- The fluidity of cement mortar increases with an increase in SO_3 content, except for the sample with the lowest SO_3 content. The cement with the lowest SO_3 content resulted in higher fluidity, which can be due to the higher superplasticizer dosage. The loss in fluidity of mortar with time generally decreases with an increase in SO_3 content, which is in accordance with the paste study.

- The compressive strengths are marginally improved with an increase in SO_3 content of cement at 7 days. At 28 days, the compressive and flexural strengths are practically the same.

- The superplasticizer demand of concrete to obtain a slump of 150 ± 20 mm is almost same for the cements with varying SO_3 content over the range studied, except for the sample with the lowest SO_3 content, which is accordance with the paste study.

- The early compressive strength of concrete is slightly higher for cements with higher SO_3 content but the 28 day strengths are almost the same.

8.2.5 Influence of Temperature and Superplasticizer on Hardening and Hardened State Properties of Concrete.

- The initial rate of hydration increases with an increase in the initial exposure temperature of the cement paste. In the SEM analysis, more hydration products are observed at higher temperature initially and the TG analysis shows higher mass loss corresponding to decomposition of C-H. This could be the reason for the higher early strength in mortar and concrete.

- Even though the initial hydration increases with an increase in temperature, the later age microstructure is adversely affected. A more porous microstructure is observed in the SEM images for the pastes exposed to higher initial temperature. In the TG analysis, there is less mass loss corresponding to decomposition of C-H decreases in pastes exposed to initial higher temperatures. This could be the reason for lower later age strengths seen in specimens exposed to higher initial temperature.

- The addition of superplasticizer decreases the formation of hydration products initially, especially at lower temperature; i.e., the incorporation of superplasticizer retards the hydration, as expected. This is evident from the TG analysis that there is a lower degree of hydration for the superplasticized cement paste compared to control mix after one day; however, at 40 °C, the retardation is compensated early and a higher degree of hydration is observed. This could be due to the better dispersion of the cement particles due to the presence of superplasticizer and the consequent increase in hydration. SEM images also show that less hydration products are formed in the superplasticized cement paste compared to the control paste.

8.3 Recommendations for Further Research

The present study helps clarify many of the conflicting views and real time issues related to the construction sites, like the variation in fluidity, loss in fluidity with time, variation in strength etc. Continued research on the following aspects can give better understanding and be of more use to the construction industry:

- The effect of coupled effect of temperature and ambient humidity on different properties of concrete could be studied, as the humidity may affect the rate of evaporation and hence the loss in fluidity with time.

- Regarding the microstructure and hydration processes, further studies could be conducted by incorporating quantitative measurements of the different phases involved in the hydration through various techniques.

- The determination of the Ca/Si ratio of the C-S-H and image analysis of more samples can give a clearer picture of the effect of superplasticizers and temperature on the composition of C-S-H and pores in the microstructure. An extensive study on the pore structure of the superplasticized paste is essential for understanding the effect of superplasticizers on the shrinkage of concrete.

- The influence of different parameters on the performance of superplasticizer in the presence of mineral admixtures has to be checked.

- The influence of other admixtures like shrinkage reducing admixtures, corrosion inhibiting admixtures, accelerators, viscosity modifying admixtures etc., on the cement-superplasticizer interaction needs further attention.

- A wide range of variation of SO_3 content of cement is required to understand completely the influence of SO_3 content of cement on the properties of concrete.

- A rheological investigation can be done to quantify the influence of ambient temperature, fineness of cement and SO_3 content of cement, in terms of the parameters of the Bingham model, to substantiate the conclusions drawn from tests such as the Marsh cone and mini-slump tests.

- The results can be compared with those from trials with larger scale mixing (i.e., on the industrial- or site-scale) with correlations to "real time measurements", such as mixer power consumption, which could be used for on-site adjustment of mix proportions as well as for the development of protocols of good practice.

REFERENCES

Abbasi, A.F., and A.J. Ai-Tayyib (1985) Effect of hot weather on modulus of rupture and splitting tensile strength of concrete. *Cement and Concrete Research*, **15**, 233-244.

Abd-El.Aziz, M.A., S. Abd.El.Aleem, and H. Mohamed (2012) Physico-chemical and mechanical characteristics of pozzolanic cement pastes and mortars hydrated at different curing temperatures. *Construction and Building Materials*, **26**, 310–316.

ACI 116 R (2000) *Cement and Concrete Terminology*. American Concrete Institute, Detroit, USA.

ACI Committee 308 (1998) Recommended Practice for Hot Weather Concreting. ACI 305R-77, *ACI Manual of Concrete Practice*, American Concrete Institute, Detroit, Part 2.

ACI Committee Report 305 (1991) Hot Weather Concreting. *ACI Materials Journal*, **88**, 417–436.

Agarwal, S.K., I. Masood, and S.K. Malhotra (2000) Compatibility of superplasticizers with different cements. *Construction and Building Materials*, **14**, 253-259.

Agullo, L., Toralles-Carbonari, R. Gettu, and A. Aguado (1999) Fluidity of Cement Pastes with Mineral Admixtures and Superplasticizer - A Study Based on the Marsh Cone Test. *Materials and Structures*, **32**, 479-485.

Ahmadi, B. H. (2000) Initial and final setting time of concrete in hot weather. *Materials and Structures/Matériaux et Constructions*, **33**, 511-514.

Aiad, I., S. Abd El-Aleem, and H. El-Didamony (2002) Effect of delaying addition of some concrete admixtures on the rheological properties of cement pastes. *Cement and Concrete Research*, **32,** 1839–1843.

Aïtcin, P.C., S. Jiang, B.G. Kim, P.C. Nkinamubanzi, and N. Petrov (2001) Cement/superplasticizer interaction: The case of polysulphonates. *Bulletin Des Laboratories Ponts et Chausses*, July-August, 89-99.

Aïtcin, P. C. *High Performance Concrete*, E& FN Spon., London, 1998.

Aïtcin, P.C., C. Jolicoeur, and J.G. Macgregor (1994) Superplasticizers: How they work and why they occasionally don't. *Concrete International*, **16**, 45-52.

Aïtcin, P.C. (2000) Cements of yesterday and today - Concrete of tomorrow. *Cement and Concrete Research*, **30**, 1349-1359.

Akman, M.S., and Z. Cavdar (1999) Efflorescence problem in superplasticized concretes. *Proceedings of International Symposium on the Role of Admixtures in High Performance Concrete*, Mexico, RILEM, 316-329.

Al-Martini, S., and M. Nehdi (2007) Effect of chemical admixtures on rheology of cement paste at high temperature. *Journal of ASTM International*, **4**, 1-17.

Alshamsi, A. M. (1994) Temperature rise inside pastes during hydration in hot climates. *Cement and Concrete Research*, **24**, 353-360.

Alshamsi, A.M., A.R. Sabouni, and A.H. **Bushlaibi** (1993) Influence of set-retarding superplasticizers and microsilica on settting times of pastes at various temperatures. *Cement and Concrete Research*, **23**, 592-598.

Andersen, P.J., D.M. Roy, and J.M. Gaidis (1987) The effects of adsorption of superplasticizers on the surface of cement. *Cement and Concrete Research*, **17**, 805-813.

Asaga, K., and D.M. Roy (1980) Rheological properties of cement mixes: 1V. Effects of superplasticizers on viscosity and yield stress. *Cement and Concrete Research*, **10**, 287-295.

ASTM C109/109M (1998) Standard test method for compressive strength of hydraulic cement mortars. Annual book of ASTM standards, *American Society of Testing and Materials*, USA.

ASTM C187 (2011) Standard Test Method for Normal Consistency of Hydraulic Cement. Annual book of ASTM standards, *American Society of Testing and Materials*, USA.

ASTM C191-08 (2008) Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle. Annual book of ASTM standards, *American Society of Testing and Materials*, USA.

ASTM C204 (2007) Standard Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus. Annual book of ASTM standards, *American Society of Testing and Materials*, USA.

ASTM C230/C230M (2008) Standard Specification for Flow Table for Use in Tests of Hydraulic Cement. Annual book of ASTM standards, *American Society of Testing and Materials*, USA.

ASTM C348 (2008) Standard Test Method for Flexural Strength of Hydraulic-cement Mortars. Annual book of ASTM standards, *American Society of Testing and Materials*, USA.

ASTM C939 (1987) Standard Test Method for Flow of Grout for Preplaced-aggregate Concrete (flow cone method). Annual book of ASTM standards, American *Society for Testing and Materials*, USA.

ASTM C1437 (2007) Standard Test Method for Flow of Hydraulic Cement Mortar. Annual book of ASTM standards, *American Society for Testing and Materials*, USA.

Aydın, S., A.H. Aytaç, K. Ramyar (2009) Effects of fineness of cement on polynaphthalene sulfonate based superplasticizer–cement interaction. *Construction and Building Materials*, **23**, 2402–2408.

Balendran, R.V., H.W. Pang, and H.X. Wen (1998) Use of scanning electron microscopy in concrete studies. *Structural Survey*, **16**, 146–153.

Banfill, P.F.G. (2003) The rheology of fresh cement and concrete - A review. *Proceedings of 11th International Congress on Cement Chemistry*, Durban, South Africa, 50-62.

Basile, F., S. Biagini, G. Ferrari, and M. Collepardi (1989) Influence of different sulphonated naphthalene polymers on the fluidity of cement paste. *Third International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*. V.M Malhotra (ed.) American Concrete Institute, Detroit, USA, 209-220.

Bedard, C.P.E., and N.P. Mailvaganam (2005) The use of chemical admixtures in concrete: Part1: Admixture –Cement compatibility. *ASCE Journal of Performance of Constructed Facilities*, **19**, 263-266.

Bentur, A. (2002) Cementitious materials-Nine millennia and a new century: Past, present and future. *Journal of Materials in Civil Engineering*, January/February, 2-22.

Bensted, J. (1982) Effects of the clinker – Gypsum grinding temperature upon early hydration of Portland cement. *Cement and Concrete Research*, **12**, 341-348.

Bentz, P. D., E. J. Garboczi, C. J. Haecker, and O. M. Jensen (1999) Effect of cement particle size distribution on the performance properties of portland cement-based materials. *Cement and Concrete Research*, **29**, 1663-1673.

Bentz, P. D., and C. J. Haecker (1999) An argument for using coarse cement in high-performance concretes. *Cement and Concrete Research*, **29**, 615-618.

Bentz, P. D., and P. E. Stutzman (1994) Evolution of porosity and calcium hydroxide in labouratory concretes containing silica fume. *Cement and Concrete Research*, **24**, 1044-1050.

Bonen, D., and S.L. Sarkar (1995) The superplasticizers adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss. *Cement and Concrete Research*, **25**, 1423-1434.

Cao, Y., and R. J. Detwiler (1995) Backscattered electron imaging of cement pastes cured at elevated temperatures. *Cement and Concrete Research*, **25,** 627-638.

Chandra, S., and J. Bjornstrom (2002) Influence of Cement and Superplasticizers Type and Dosage on the Fluidity of Cement Mortars - Part 1. *Cement and Concrete Research*, **32**, 1605-1611.

Celik, I. B. (2009) The effects of particle size distribution and surface area upon cement strength development. *Powder Technology*, **188**, 272-276.

Collepardi, M. (2005) Admixtures enhancing concrete performance. *Proceedings of International Conference on Admixtures-Enhancing Concrete Performance*, R.K. Dhir, P.C. Hewlett and M.D Newlands (eds.) Thomas Telford, Dundee, UK, 217-230.

Corradi, M., R. Khurana, and R. Magarotto (2005). New superplasticizers for the total control of performances of fresh and hardened concrete. *Proceedings of International Conference on Admixtures-Enhancing Concrete Performance*, R.K. Dhir, P.C. Hewlett and M.D. Newlands (eds),Thomas Telford, London, 1-10.

de Larrard, F. (1990) A method for proportioning high strength concrete mixtures. *Cement, Concrete and Aggregates*, **12**, 47-52.

Dhir, R.K., and A.W.F. Yap (1983) Superplasticized high workability concrete: some properties in the fresh and hardened states. *Magazine of Concrete Research*, **35**, 215-228.

Dodson, V. H., and T. D. Hayden (1989) Another Look at the Portland Cement/Chemical Admixture Incompatibility Problem. *Cement Concrete and Aggregates*, **11**, 52-56.

Elkhadiri, I., M. Palacios, and F. Puertas (2009) Effect of curing temperature on cement hydration. *Ceramics – Silikáty*, **53**, 65-75.

Erdogdu, S. (2000) Compatibility of superplasticizers with cements different in composition. *Cement and Concrete Research*, **30**, 767-773.

Escalante-García, J.I., and J.H. Sharp (1998) Effect of temperature on the hydration of the main clinker phases in Portland cements: Part II, blended cements. *Cement and Concrete Research*, **28**, 1259–1274.

Escalante-García, J.I., and J. H. Sharp (2001) The microstructure and mechanical properties of blended cements hydrated at various temperatures. *Cement and Concrete Research*, **31**,695-702.

Falikman, V.R., Y.V Sorokin, A.Y.Vainer, and N.F Bashlykov (2005) New high performance polycarboxylate superplasticizers based on derivative copolymers of maleinic acid. *Proceedings of International Conference on Admixtures-Enhancing Concrete Performance*. R.K. Dhir, P.C. Hewlett and M.D Newlands (eds.) Thomas Telford, Dundee, UK, 41-46.

Famy, C., K.L. Scrivener, A. Atkinson, and A.R. Brough (2002) Effects of an early or late heat treatment on the microstructure and composition of inner C-S-H products of portland cement mortars. *Cement and Concrete Research*, **32**, 269-278.

Felekoglu, B., and H. Sarikahya (2008) Effect of chemical structure of polycarboxylate-based superplasticizers on workability retention of self-compacting concrete. *Construction and Building Materials*, **22**, 1972-1980.

Fernàndez-Altable, V., and I. Casanova (2006) Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures. *Cement and Concrete Research*, **36**, 1222–1230.

Fernon, V., A. Vichot, N. Le Goanvic, P. Colombet, F. Corazza, and U. Costa (1997) Interaction between Portland cement hydrates and polynaphthalene sulfonates. *Proceedings of the 5th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, Rome, 225-248.

Flatt, R.J., and Y.F. Houst (2001) A Simplified view on Chemical Effects Perturbing the Action of Superplasticizers. *Cement and Concrete Research*, **31**, 1169-1176.

Flatt, R.J., Y.F. Houst, P. Bowen, H. Hofmann, J. Widmer, U. Sulser, U. Maeder, and T.A. Bürge (1998) Analysis of superplasticizers used in concrete. *Analysis Magazine*, **26**, 28-34.

Franke, L., and K. Sisomphon (2004) A new chemical method for analyzing free calcium hydroxide content in cementing material. *Cement and Concrete Research*, **34**, 1161–1165.

Gaidis, J.M., and E.M. Gartner (1991) Hydration Mechanisms II. *Materials Science of Concrete II*, J. Skalny and S. Mindess (eds)The American Ceramic Society, USA, 9-39.

Gettu, R., A. Aguado, L. Agullo, B. Toralles-Carbonari, and Roncero J. (1997) Characterization of cement pastes with silica fume and superplasticizer as components of high performance concretes. *Mario Collepardi Symposium on Advances in Concrete Science and Technology*, P.K Mehta (ed.), 331-344.

Gettu, R., J. Roncero, and M.A. Martin (2002) Long term behaviour of concrete incorporating a shrinkage-reducing admixture. *The Indian Concrete Journal*, February, 1-7.

Ghafoori, N., and H. Diawara (2010) Influence of temperature on fresh performance of self-consolidating concrete. *Construction and Building Materials*, **24**, 946–955.

Gołaszewski, J., and **J. Szwabowski** (2004) Influence of superplasticizers on rheological behavior of fresh cement mortars. *Cement and Concrete Research*, **34,** 235-248.

Gomes, P.C.C., R. Gettu, L. Agullo, and C. Bernad (2001) Experimental optimization of high strength self compacting concrete. *Proceedings of Second International Symposium on SCC*, K. Ozawa, and M. Ouchi (eds.) Kochi, Japan, 377-386.

Grabiec, A.M., and Z. Piasta (2004) Study on compatibility of cement – superplasticizer assisted by multicriteria statistical optimization. *Journal of Materials Processing Technology*, **152**, 197-203.

Griesser, A. (2002) Cement-superplasticizer interactions at ambient temperatures, *Doctoral thesis*, Swiss Federal Institute of Technology, Zurich.

Grzeszczyk, S., and M. Sudol (2005) The influence of temperature on the fluidity of fresh self compacting concrete. Proceedings of the *International Conference on Admixtures-Enhancing Concrete Performance*, R.K. Dhir, P.C. Hewlett and M.D Newlands (eds.) Thomas Telford, Dundee, UK, 165-170.

Gu, P., P. Xie, J.J. Beaudoin, and C. Jolicoeur (1994) Investigation of the retarding effect of superplasticizers on cement hydration by impedance spectroscopy and other methods. *Cement and Concrete Research*, **24**, 433-342.

Hanehara, S., and K. Yamada (2008) Rheology and early age properties of cement systems. *Cement and Concrete Research*, **21**, 175-195.

Hanehara, S., and K. Yamada (1999) Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture and paste rheology. *Cement and Concrete Research*, **29**, 1159-1165.

Hanna, E., M. Ostiguy, K. Khalifé, O. Stoica, B.-G. Kim, C. Bédard, M. Saric-Coric, M. Baalbaki, S. Jiang, P.C. Nkinamubanzi, P.C. Aïtcin, and N. Petrov (2000) The importance of superplasticizers in modern concrete technology. *CANMET/ACI International conference* on *superplasticizers and other chemical admixtures in concrete*, ACI SP, *Nice*.

Hewlett, P.C. (ed.) (2004) *Lea's chemistry of cement and concrete*. Elsevier Ltd, Burlington, UK.

Houst, Y.F., R.J. Flatt, H. Hofmann, U. Mader, J. Widmer, U. Sulser, and T.A. Burge (1999a) Influence of superplasticizer adsorption on the rheology of cement paste. *Proceedings of International Symposium on the Role of Admixtures in High Performance Concrete*, J.G. Cabrera and R.R. Villarreal (eds.) Mexico, 71-78.

Houst, Y.F., R.J. Flatt, P. Bowen, and H. Hofmann (1999b) Optimization of superplasticizers: From research to application. *Proceedings of International Symposium on the Role of Admixtures in High Performance Concrete*, J.G. Cabrera, and R.R. Villarreal (eds.) Mexico, 121-134.

Houst, Y.F., P. Bowen, and F. Perche (2005) Towards tailored superplasticizers. Proceedings of *International Conference on Admixtures-Enhancing Concrete Performance*, R.K. Dhir, P.C. Hewlett and M.D. Newlands (eds.) Thomas Telford, London, 11-20.

IS 383 (2002) Indian standard specification for coarse and fine aggregates from natural sources for concrete. *Bureau of Indian Standards*, New Delhi.

IS 516 (2004) Indian standard specification for Methods of tests for strength of concrete. *Bureau of Indian Standards*, New Delhi.

IS 650 (2004) Indian standard specification for Standard sand for testing cement – specification. *Bureau of Indian Standards*, New Delhi.

IS 1199 (2004) Indian standard specification for methods of sampling and analysis of concrete. *Bureau of Indian Standards*, New Delhi.

IS 2386 (2007) Indian standard specification for methods of test for aggregates of concrete. *Bureau of Indian Standards*, New Delhi.

IS 4031 – Parts 2, 4 and 5 (2005) Indian standard specification for method of physical tests for hydraulic cement. *Bureau of Indian Standards*, New Delhi.

IS 9103 (2004) Indian standard specification for Concrete Admixtures. *Bureau of Indian Standards*, New Delhi.

IS 10078 (2004) Indian standard specification for jolting apparatus used for testing cement. *Bureau of Indian Standards*, New Delhi.

IS 12269 (2004) Indian standard specification for 53 grade ordinary Portland cement. *Bureau of Indian Standards*, New Delhi.

Jayasree, C. (2008) Study of cement-superplasticizer interactions and its implications for concrete performance. *Ph D thesis*, IIT Madras**.**

Jayasree, C., and R. Gettu (2006) Influence of Mixing Method on the Fluidity of Superplasticized Cement Paste. Proceedings of the *Fifth Asian Symposium on Polymers in Concrete*, Chennai, India, September, 665-670.

Jayasree, C., and R. Gettu (2008) Experimental Study of the Flow Behaviour of Superplasticized Cement Paste. M*aterials and Structures*, RILEM, **41**, 1581-1593.

Jayasree, C., and R. Gettu (2010) Correlating properties of cement paste, mortar and concrete. *The Indian Concrete Journal*, **84**, 7-18.

Jayasree, C., M. Santhanam, and R. Gettu (2011a) Cement-superplasticizer Compatibility-issues and Challenges. *Indian Concrete Journal*, **85**, 48-60.

Jayasree, C., M. J. Krishnan, and R. Gettu (2011b) Influence of Superplasticizer on the Non-Newtonian Characteristics of Cement Paste. *Materials and Structures*, **44**, 929–942.

Jayasree, C., and R. Gettu (2012) Choice of compatible cement-superplasticizer combinations. *The Indian Concrete Journal*, January-March, 14-31.

Jiang, S., B.G. Kim, and P.C. Aïtcin (1999) Importance of adequate soluble alkali content to ensure cement/superplasticizer compatibility. *Cement and Concrete Research*, **29**, 71-78.

Jolicoeur, C., and M.A. Simard (1998) Chemical admixture–cement interactions: Phenomenology and physico-chemical concepts. *Cement and Concrete Composites*, **20**, 87-101.

Jolicoeur, C., P.C. Nkinamubanzi, M.A. Simard, and M. Piotte (1994) Progress in understanding the functional properties of superplasticizer in fresh concrete. *ACI SP-148*, 63 – 88.

Justnes, H., M.V. Dooren, and D.V. Gemert (2003) Reasons for workability loss in cementitious binders. *Seventh CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, V.M. Malhotra (ed.) Berlin, Germany, 53-65.

Kantro, D.L. (1980) Influence of water-reducing admixtures on properties of cement paste-A miniature slump test. *Cement, Concrete and Aggregates*, **2**, 95- 102.

Khatib, J.M. and P.S. Mangat (1999) Influence of superplasticizer and curing on porosity and pore structure of cement paste. *Cement and Concrete Composites*, **21**, 431-437.

Khayat, K.H. and A. Yahia (1998) Simple field tests to characterize fluidity and washout resistance of structural cement grout. *Cement, Concrete and Aggregates*, **20**, 145-156.

Kim, J.K., Y.H. Moon, and S.H. Eo (1998) Compressive strength development of concrete with curing time and temperature. *Cement and Concrete Research*, **28**, 1761–1773.

Kim, B.G., S. Jiang, and P.C. Aïtcin (1999) Influence of molecular weight of PNS superplasticizers on the properties of cement pastes containing different alkali contents. *Proceedings of International Symposium on the Role of Admixtures in High Performance Concrete*, J.G. Cabrera, and R.R. Villarreal (eds.) Mexico, 111-127.

Kim B., S. Jiang, C. Jolicoeur, P.C. Aitcin (2000) The adsorption behavior of PNS superplasticizer and its relation to fluidity of cement paste. *Cement and Concrete Research*, **30**, 887-893.

Kim, B.G., and P.C. Aïtcin (2003) Dispersing mechanism of PNS superplasticizers in high performance concrete. *Proceedings of 11th international congress on the chemistry of cement*, G. Grieve and G. Owens (eds.) Durban, South Africa.

Kim, J. J., M.K. Rahman, and M.M.R. Taha (2012) Examining microstructural composition of hardened cement paste cured under high temperature and pressure using nanoindentation and Si MAS NMR. *Appl Nanosci*, **2**, 445-456.

Kjellsen, K.O., R.J. Detwiler, and O.E. Gjorv (1991) Backscattered Electron image analysis of cement paste specimens: specimen preparation and analytical methods. *Cement and Concrete Research*, **21**, 388-390.

Kjellsen, K.O., and R.J. Detwiler (1992) Reaction kinetics of Portland cement mortars hydrated at different temperatures. *Cement and Concrete Research*, **22**, 112-120.

Kjellsen, K.O., R.J. Detwiler, and O.E. Gjørv (1990) Backscattered electron imaging of cement paste hydrated at different temperatures. *Cement and Concrete Research*, **20**, 308-311.

Kjellscn, K.O., R.J. Detwiler, and O.E. Gjørv (1990) Pore structure of plane cement paste hydrated at different temperatures. *Cement and Concrete Research*, **20**, 927-933.

Li, G., A. Tagnit-Hamou, and P.C. Aïtcin, (2003) Improving cement-superplasticizer compatibility by using soluble alkalis as a chemical additive in concrete. *Proceedings of 11th international congress on the chemistry of cement*, G. Grieve and G. Owens (eds.) South Africa, Durban, South Africa, 655-665.

Lim, G.G., S.S. Hong, D.S. Kim, B.J. Lee, and J.S. Rho (1999) Slump loss control of cement paste by adding polycarboxylic type slump-Releasing dispersant. *Cement and Concrete Research*, **29**, 223–229.

Lothenbach, B., F. Winnefeld, C. Alder, E. Wieland, and P. Lunk (2007) Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes. *Cement and Concrete Research*, **37**, 483–491.

Magarotto, R., I. Torresan, and N. Zeminian (2003) Influence of molecular weight of polycarboxylate ether superplasticizers on the rheological properties of fresh cement pastes, mortar and concrete. *Proceedings of 11th international congress on the chemistry of cement*, G. Grieve and G. Owens (eds.) Durban, South Africa, 514-526.

Maltais, Y. and J. Marchand (1997) Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars. *Cement and Concrete Research*, **27**, 1009-1020.

Matschei, T., and F. P. Glasser (2010) Temperature dependence, 0 to 40 °C, of the mineralogy of Portland cement paste in the presence of calcium carbonate. *Cement and Concrete Research*, **40**, 763–777.

Mehta, P.K., and P.J.M. Monteiro *Concrete - Microstructure, properties and materials*, Indian Concrete Institute, Chennai, India, 2005.

Mellas, M., B. Mezghiche, and J.E. Ash (2003) Estimation of the porosity of Portland cement pastes using backscattered electron image. *Courrier du Savoir*, N°04, 47-51.

Mirza, W.H., S.I. A1-Noury, and W.H. A1-Bedawi (1991) Temperature effect on strength of mortars and concrete containing blended cements. *Cement & Concrete Composites*, 13, 197-202.

Mollah, M.Y.A., P. Palta, and T.R. Hess, R.K. Vempati, and D.L. Cocke (1995) Chemical and physical effects of sodium lignosulphonate superplasticizer on the hydration of portland cement and solidification/stabilization consequences. *Cement and Concrete Research*, **25**, 671-682.

Mounanga, P., V. Baroghel-Bouny, A. Loukili, and A. Khelid (2006) Autogenous deformations of cement pastes: Part I. Temperature effects at early age and micro–macro correlations. *Cement and Concrete Research*, **36**, 110– 122.

Mounanga P., A. Khelidj, A. Loukili, and V. Baroghel-Bouny (2004) Predicting Ca(OH)2 content and chemical shrinkage of hydrating cement pastes using analytical approach. *Cement and Concrete Research*, **34**, 255–265.

Mouret M., A. Bascoul, and G. Escadeillas (1999) Microstructural features of concrete in relation to initial temperature - EM and ESEM characterization. *Cement and Concrete Research*, **29**, 369–375.

Mouret M., Bascoul A., and Escadeillas G. (1999) Microstructural features of concrete in relation to initial temperature—SEM and ESEM characterization. *Cement and Concrete Research*, **29**, 369–375.

Nakajima, Y., and K. Yamada (2004) The effect of the kind of calcium sulphate in cements on the dispersing ability of poly β naphthalene sulphonate condensate superplasticizer. *Cement and Concrete Research*, **34**, 839-844.

Nawa, T., H. Ichiboji, and M. Kinoshita (2000) Influence of temperature on fluidity of cement paste containing superplasticizer with polyethylene oxide graft chains. *Sixth CANMET/ ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete*, V.M Malhotra (ed) Ottawa, Canada, 195-210.

Nehdi, M., and S. Al-Martini (2007) Effect of Temperature on Oscillatory Shear Behavior of Portland Cement Paste Incorporating Chemical Admixtures. *Journal of Materials in Civil Engineering*, **19**, 1090-1100.

Neville, A.M. *Properties of concrete*, ELBS with Longman, Harlow, UK, 2000.

Nkinamubanzi, P.C., B.G. Kim, and P.C. Aïtcin (2000) Some key cement factors that control the compatibility between naphthalene-based superplasticizers and ordinary Portland cements. *6th CANMET/ACI International Conference on superplasticizers and other chemical admixtures in concrete*, V.M. Malhotra (ed.) Paris, 33-54.

Nkinamubanzi, P.C., and P.C. Aïtcin (2004) Cement and superplasticizer combinations: Compatibility and Robustness. *Cement, Concrete and Aggregates*, **26**, 1-8.

Nmai C. K. (1998) Cold weather concreting admixtures. *Cement and Concrete Composites*, **20**, 121 - 128.

Odler, I., and S. Abdul-Maula (1987) Investigations on the relationship between porosity structure and strength of hydrated cement paste III. Effect of clinker composition and gypsum addition. *Cement and Concrete Research*, **17**, 22-30.

Okamura T., H. Harada, and M. Daimon (1998) Influence of calcium sulfate in belite-richn cement on the change in fluidity of mortar with time. *Cement and Concrete Research*, **28**, 1297–1308.

Öner M., K. Erdoğdu, and A. Günlü (2003) Effect of components fineness on strength of blast furnace slag cement. *Cement and Concrete Research*, **33**, 463–469.

Ortiz, J., A. Aguado, L. Agullo, and T. Garcia (2005) Influence of environmental temperatures on the concrete compressive strength: Simulation of hot and cold weather conditions. *Cement and Concrete Research*, **35**, 1970 – 197.

Ortiz, J., A. Aguado, L. Agulló, T. García, and M. Zermeño (2009) Influence of environmental temperature and moisture content of aggregates on the workability of cement mortar. *Construction and Building Materials*, **23**, 1808–1814.

Page, M., P.C Nkinamubanzi, and P.C. Aïtcin (1999) The cement/superplasticizer compatibility: A headache for superplasticizer manufacturers. *Proceedings of International Symposium on the Role of Admixtures in High Performance Concrete*, J.G. Cabrera, and R.R. Villarreal (eds.) Mexico.

Petit, J.Y., E. Wirquin, and K.H. Khayat (2010) Effect of temperature on the rheology of flowable mortars. *Cement & Concrete Composites*, **32**, 43-53.

Petit, J.Y., K.H. Khayat, and E. Wirquin (2009) Coupled effect of time and temperature on variations of plastic viscosity of highly flowable mortar. *Cement and Concrete Research*, **39**, 165–170.

Petit, J.Y., K.H. Khayat, and E. Wirquin (2006) Coupled effect of time and temperature on variations of yield value of highly flowable mortar. *Cement and Concrete Research*, **36**, 832 – 841.

Plank J., B. Sachsenhauser, and J.d. Reese (2010) Experimental determination of the thermodynamic parameters affecting the adsorption behaviour and dispersion effectiveness of PCE superplasticizers. *Cement and Concrete Research*, **40**, 699-709.

Plank, J., and C. Hirsch (2007) Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cement and Concrete Research*, **37**, 537-542.

Porter, M.R. *Handbook of surfactants*. Blackie Academic and Professional, United Kingdom, 1994.

Prince W., and M. Espagne, P.-C. (2003) Aïtcin Ettringite formation: A crucial step in cement superplasticizer compatibility. *Cement and Concrete Research*, **33**, 635-641.

Prince, W., M. Edwards-Lajnef, and P.C. Aïtcin (2002) Interaction between ettringite and polynaphthalene sulphonate superplasticizer in cementitious paste. *Cement and Concrete Research*, **32**, 79-85.

Puertas, F., H. Santos, M. Palacios, and S. Martinez-Ramirez (2005) Polycarboxylate Superplasticizer admixtures: effects on hydration, microstructure and rheological behaviour in cement pastes. *Advances in Cement Research*, **17**, 77- 89.

Ramachandran, V.S. *Concrete Admixtures Handbook*, 2nd Edition, Standard Publishers Distributors, New Delhi, India, 2002.

Ramachandran, V.S., V.M Malhotra, C. Jolicoeur, and N. Spiratos, *Superplasticizers: Properties and Applications in Concrete*. Materials Technology Laboratory, CANMET, Canada, 1998.

Ramachandran, V.S., and J.J. Beaudoin, *Handbook of analytical techniques in concrete science and technology*. Noyes and William Andrew Publications, USA, 2001.

Ramezanianpour, A.A., V. Sivasundaram, and V.M. Malhotra (1995) Superplasticizers: Their effect on the strength properties of concrete. *Concrete International*, April, 30-35.

Ravina, D., and I. Soroka (1994) Slump loss and compressive strength of concrete made with WRR and HRWR admixtures and subjected to prolonged mixing. *Cement and Concrete Research*, **24**, 1455-1462.

Rixom, R., and N. Mailvaganam *Chemical Admixtures for Concrete*, 3rd Edition, E & FN SPON, London, UK, 1999.

Roberts, L.R. (1995) Dealing with cement-admixture interactions. *23rd Annual convention of the Institute of concrete technology*, April, Telford.

Roncero, J., R. Gettu, E. Vázquez, and J.M. Torrents (1999) Effect of Superplasticizer Content and Temperature on the Fluidity and Setting of Cement Pastes. *Proceedings of International Symposium on the Role of Admixtures in High Performance Concrete*, J.G. Cabrera, and R.R. Villarreal (eds.) RILEM Publications, Mexico, 343-356.

Roncero, J. (2000) Effect of Superplasticizers on the Behaviour of Concrete in the Fresh and Hardened States: Implications for High Performance Concretes. *Doctoral thesis*, Universitat Politecnica de Catalunya, Barcelona, Spain.

Roncero, J., S. Valls, and R. Gettu (2002) Study of the influence of superplasticizers on the hydration of cement paste using nuclear magnetic resonance and X-ray diffraction techniques. *Cement and concrete Research*, **22**, 103-108.

Roussel, N., and R.L. Roy (2005) The Marsh cone: a test or a rheological apparatus? *Cement and Concrete Research*, **35**, 823-830.

Sajedi, F., and H.A. Razak (2011) Effects of curing regimes and cement fineness on the compressive strength of ordinary Portland cement mortars. *Construction and Building Materials*, **25**, 2036–2045.

Sakai, E., K. Yamada, and A. Ohta (2003) Molecular structure and dispersion-adsorption mechanisms of comb-type superplasticizers used in Japan. *Journal of Advanced Concrete Technology*, **1**, 16-25.

Scrivener K.L. (2004) Backscattered electron imaging of cementitious microstructures: understanding and quantification. *Cement & Concrete Composites*, **26,** 935-945.

Scrivener, K.L. *The microstructure of Concrete*. pp. 127-157. *In* **J.P. Skalny** (ed.) *Materials science of concrete I*. The American ceramic society publication, Westerville, 1989.

Sereda, P.J., R.F. Feldman, and V.S. Ramachandran (1980) Physical factors controlling structure and strength development. Proceedings of *7th International Congress on the Cement pastes*, Paris, IV-1/22 - VI-1/31.

Sersale, R., R. Cioffi, G. Frigione, and F. Zenone (1991) Relationship between gypsum content, porosity and strength in cement. *Cement and Concrete Research*, **21**, 120-126.

Shoukry, S.N., G.W. William, B. Downie, and M.Y. Riad (2011) Effect of moisture and temperature on the mechanical properties of concrete. *Construction and Building Materials*, **25**, 688-696.

Škvára, F., K. Kolář, J. Novotný, and Z. Zadák (1981) The effect of cement particle size distribution upon properties of pastes and mortars with low water-to-cement ratio. *Cement and Concrete Research*, **11**, 247-255.

Soroka, I., and D. Ravina (1998) Hot Weather Concreting with Admixtures. *Cement and Concrete Composites*, **20**, 129–136.

Spiratos, N., M. Page, N.P. Mailvaganam, V.M. Malhotra, and C. Jolicouer (2003) Superplasticizers for Concrete- Fundamentals, Technology and Practice. Supplementary Cementing materials for Sustainable Development, Ottawa, Canada.

Singh, N.B., R. Sarvahi, and N.P Singh (1992) Effect of superplasticizers on the hydration of cement. *Cement and Concrete Research*, **22,** 725-735.

Sugiyama, T., A. Ohta and T. Uomota (2003) The dispersive Mechanism and applications of polycarboxylate based superplasticizers. *Proceedings of 11th international congress on the chemistry of cement*, G. Grieve and G. Owens (eds.) Durban, South Africa, 560-568.

Tanaka, Y., A. Ohta, and T. Sugiyama (1999) Polycarboxylate based advanced superplasticizers for high performance concrete. *Proceedings of the International Symposium on the Role of Admixtures in High Performance Concrete*, J.G. Cabrera, and R.R. Villarreal (eds.) Mexico, 135-142.

Tattersall G.H., and P.F.G Banfill, *The rheology of fresh concrete*. Pitman Books Limited, London, 1983.

Taylor, H.F.W. *Cement Chemistry*, Thomas Telford, London UK, 1997.

Termkhajornkit, P., and R. Barbarulo (2012) Modelling the coupled effects of temperature and fineness of Portland cement on the hydration kinetics in cement paste. *Cement and Concrete Research*, **42**, 526–538.

Thomas, J.J., D. Rothstein, H.M. Jennings, and B. J. Christensen (2003) Effect of hydration temperature on the solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pastes. *Cement and Concrete Research*, **33**, 2037–2047.

Topçu, İ.B., and M. U. Toprak (2005) Fine aggregate and curing temperature effect on concrete maturity. *Cement and Concrete Research*, **35**, 758 - 762.

Torrents, J.M., J. Roncero, and R. Gettu (1998) Utilization of impedence spectroscopy for studying the retarding effect of a superplasticizer on the setting of the cement. *Cement and Concrete Research*, **28**, 1325-1333.

Torresan, I., and R. Khurana (1998) New superplasticizers based on modified melamine polymer. *Proceedings of Fourth CANMET/ACI/JCI International Conference on Recent Advances in Concrete Technology*, V.M Malhotra (ed) ACI International, Tokushima, Japan, 235-253.

Tosun, K. (2006) Effect of SO3 content and fineness on the rate of delayed ettringite formation in heat cured Portland cement mortars. *Cement & Concrete Composites*, **28**, 761–772.

Uchikawa, H., S. Hanehara, T. Shirasaka and D. Sawaki 1992). Effect of admixture on hydration of cement, adsorptive behaviour of admixtures and fluidity and setting of fresh cement. *Cement and Concrete Research,* Vol. 22, 1115-1129.

Uchikawa, H., S. Hanehara, and D. Sawaki (1997) The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture. *Cement and Concrete Research,* **27**, 37-50.

Uchikawa H., D. Sawaki and S. Hanehara (1995) Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement. *Cement and Concrete Research,* **25**, 353-364.

Uchikawa H., S. Hanehara, T. Shirasaka and D. Sawaki (1992) Sawaki Effect of admixture on hydration of cement, adsorptivebehaviour of admixture and fluidity and setting of fresh cement paste. *Cement and Concrete Rsearch,* **22**, 1115-1129.

Valenza J. J., and J.J. Thomas (2012) Thomas Permeability and elastic modulus of cement paste as a function of curing temperature. *Cement and Concrete Research,* **42**, 440-446.

Vikan, H., H. Justnes, F. Winnefeld, and R. **Figi** (2007) Correlating cement characteristics with rheology of paste. *Cement and Concrete Research,* **37**, 1502–1511.

Vuk, T., V. Tinta, R. Gabrovšek, and V.Kaučič (2001) The effects of limestone addition, clinker type and fineness on properties of Portland cement. *Cement and Concrete Research,* **31**, 135-139.

Vydra, V., O. Kapickova, P. Demo, and P. Semerak (2007) Influence of temperature on induction period and on ultimate porosity of hardening cement paste. *Construction and Building Materials*, **21**, 1262–1266.

Winnefeld, F., S. Becker, J. Pakusch, T. Götz (2007) Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems. *Cement & Concrete Composites*, **29**, 251–262.

Yamada, K., T. Sugamata, and H. Nakanishi (2006) Fluidity performance evaluation of cement and superplasticizers. *Journal of Advanced Concrete Technology*, **4**, 241-249.

Yamada, K., S. Ogawa, and S. Hanehara (2001) Controlling of the adsorption and dispersing force of polycarboylate-type superplasticizer by sulfate ion concentration in aqueous phase. *Cement and Concrete Research,* **31**, 375-383.

Yamada, K., T. Takahashi, S. Hanehara, and M. Matsuhisa (2000) Effects of the chemical structure on the properties of polycarboxylate type superplasticizer. *Cement and Concrete Research,* **30**, 197-207.

Yamada, K. and S. Hanehara (2003) Working mechanism of polycarboxylate superplasticizer considering the chemical structure and cement characteristics. *Proceedings of 11th International Congress on the Chemistry of Cement,* G. Grieve and G. Owens (eds.) Durban, South Africa, 538-549.

Yoshioka, K., E. Tazawa, K. Kawai, and T. Enohata (2002) Adsorption characteristics of superplasticizers on cement component minerals. *Cement and Concrete Research*, **32**, 1507-1513.

Young, J.F. (2008) Looking ahead from the past: The heritage of cement chemistry. *Cement and Concrete Research*, **38**, 111-114.

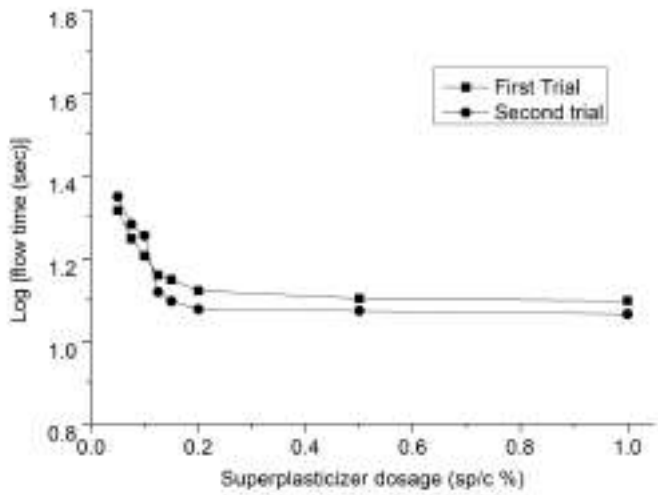
Zhang W., Y. Zhang, L. Liu, G. Zhang, Z. Liu (2012) Investigation of the influence of curing temperature and silica fume content on setting and hardening process of the blended cement paste by an improved ultrasonic apparatus. *Construction and Building Materials*, **33**, 32-40.

Zhang, M., K. Sisomphon, T.S. Ng, and D.J. Sun (2010) Effect of superplasticizers on workability retention and initial setting time of cement pastes. *Construction and Building Materials*, **24**, 1700–1707.

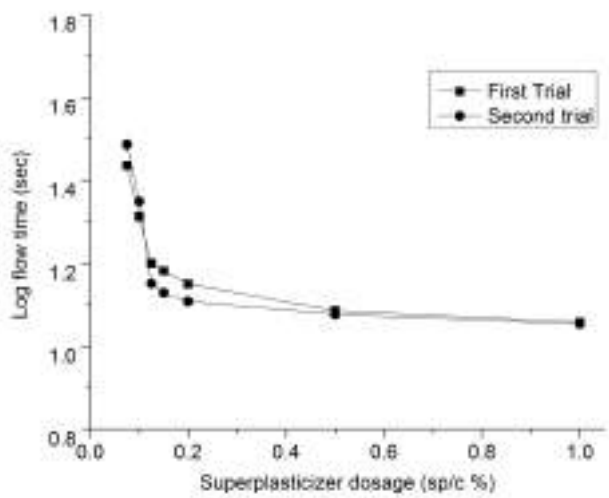
Zhao, H., and D. Darwin (1992) Quantitative backscattered electron analysis of cement paste. *Cement and Concrete Research*, **22**, 695-706.

APPENDIX A

MARSH CONE FLOW TIME CURVES OF THE TWO TRIALS AT DIFFERENT TEMPERATURES

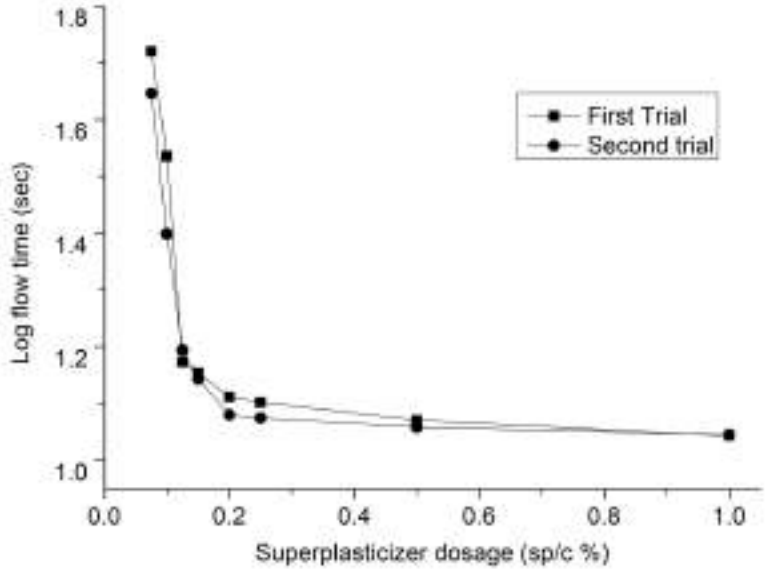


(a)

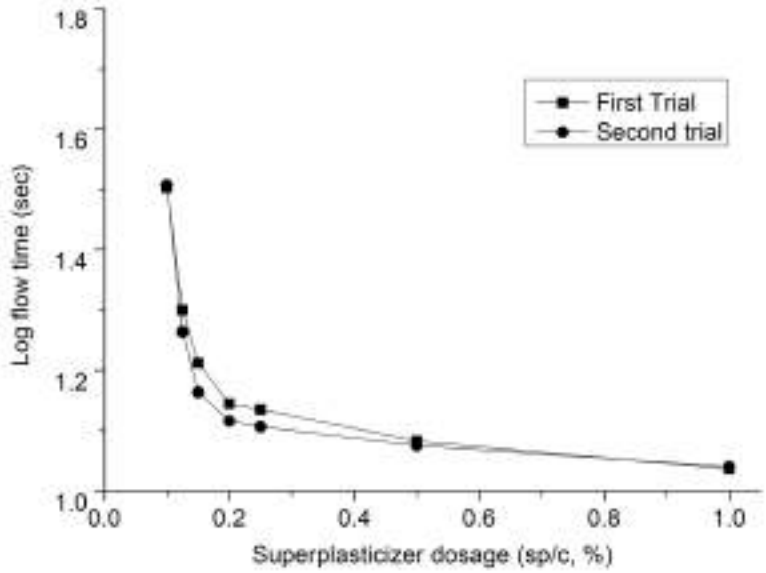


(b)

Figure A.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer at temperatures (a) 5°C and (b) 15°C

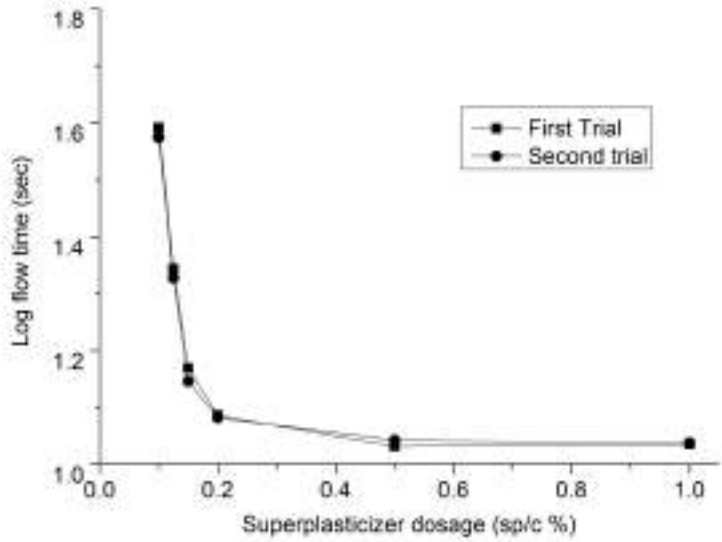


(c)



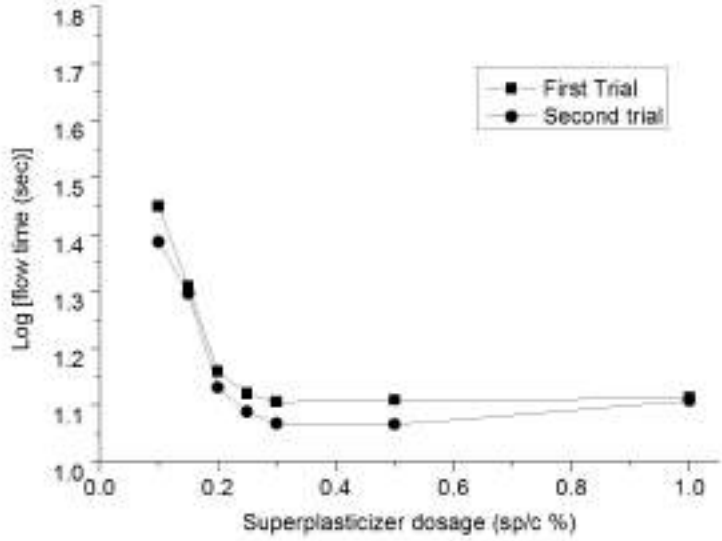
(d)

Figure A.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer at temperatures (c) 25°C and (d) 35°C



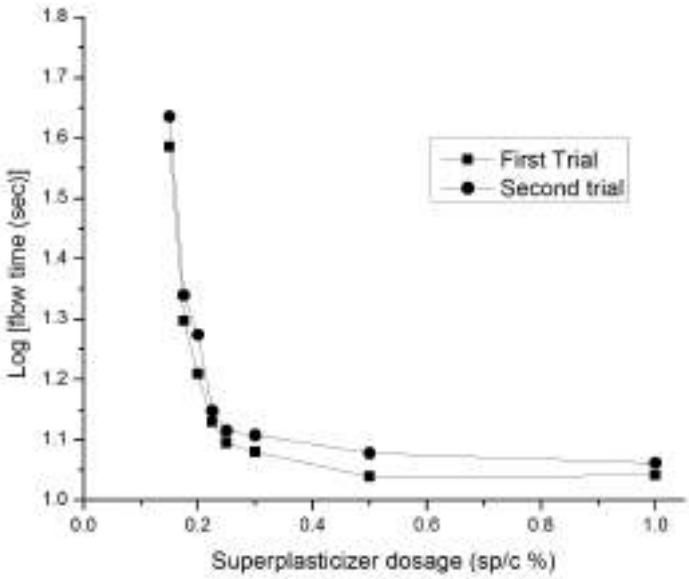
(e) 40

Figure A.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer at temperatures (e) 40°C

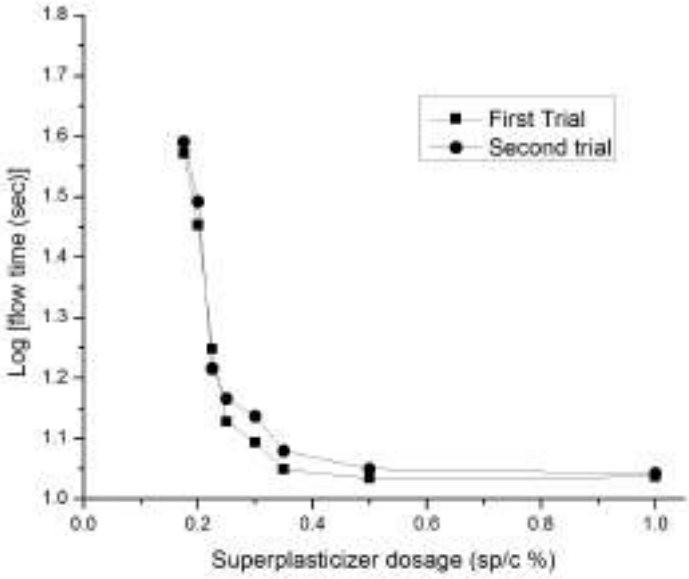


(a)

Figure A.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer at temperatures (a) 5°C

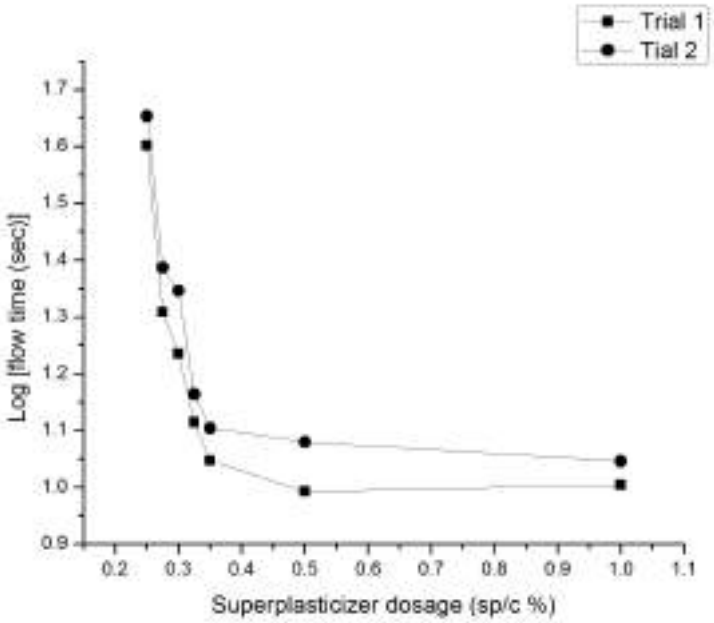


(b)

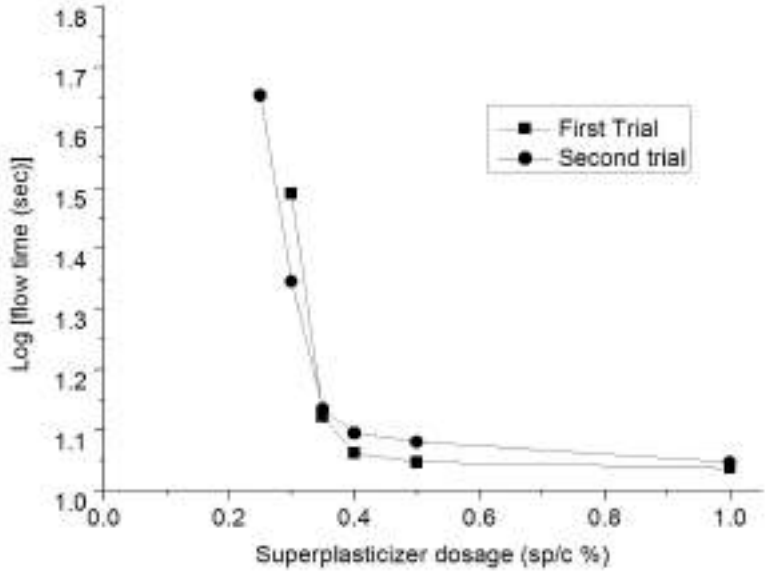


(c)

Figure A.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer at temperatures (b) 15°C and (c) 25°C

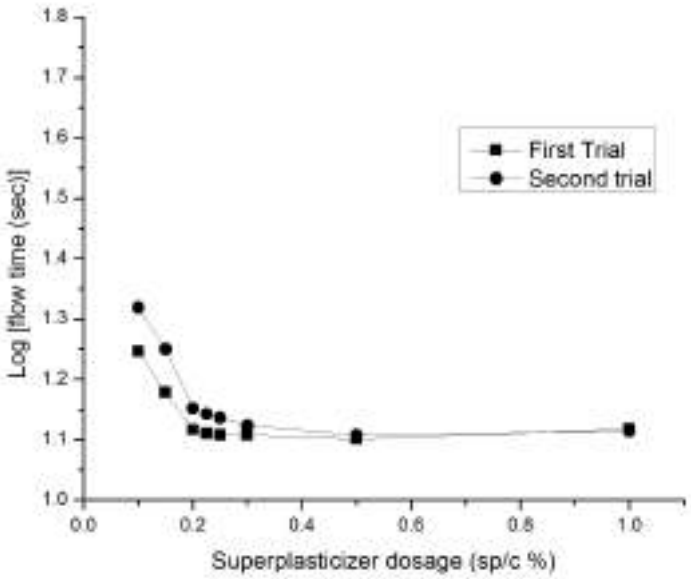


(d)

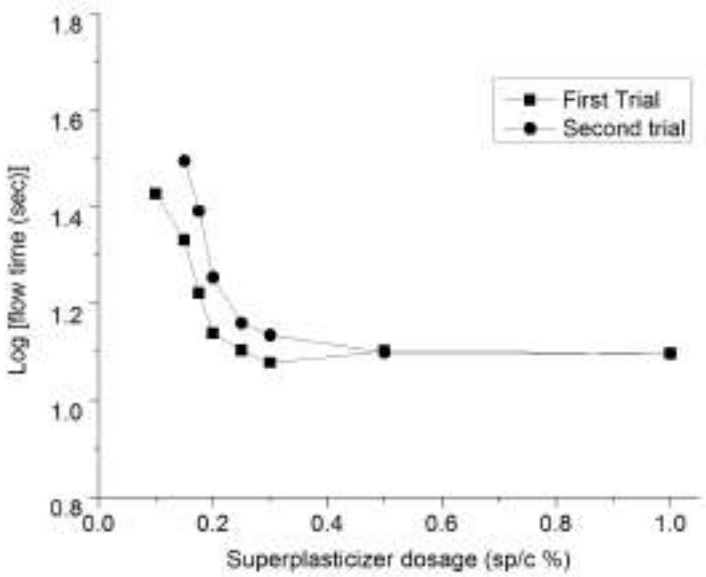


(e)

Figure A.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer at temperatures (d) 35°C and (e) 40°C

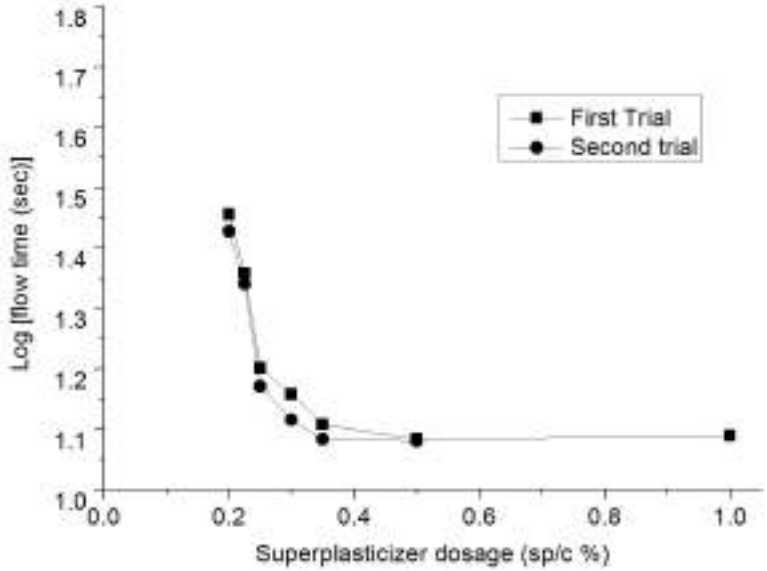


(a)

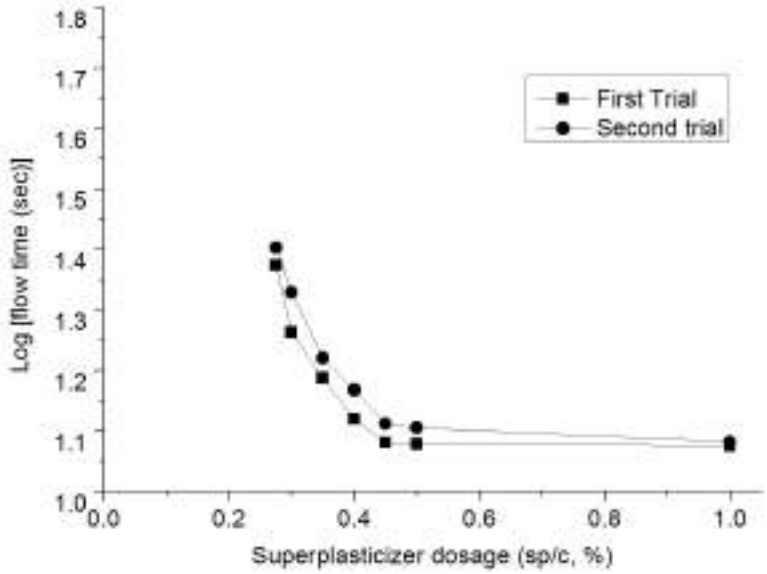


(b)

Figure A.3 Marsh cone flow time curves of the two trials with SMF based superplasticizer at temperatures (a) 5°C and (b) 15°C

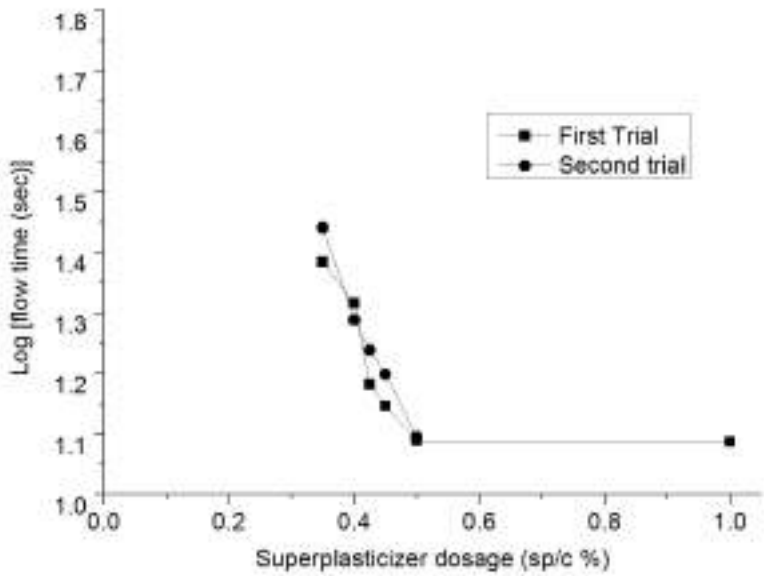


(c)



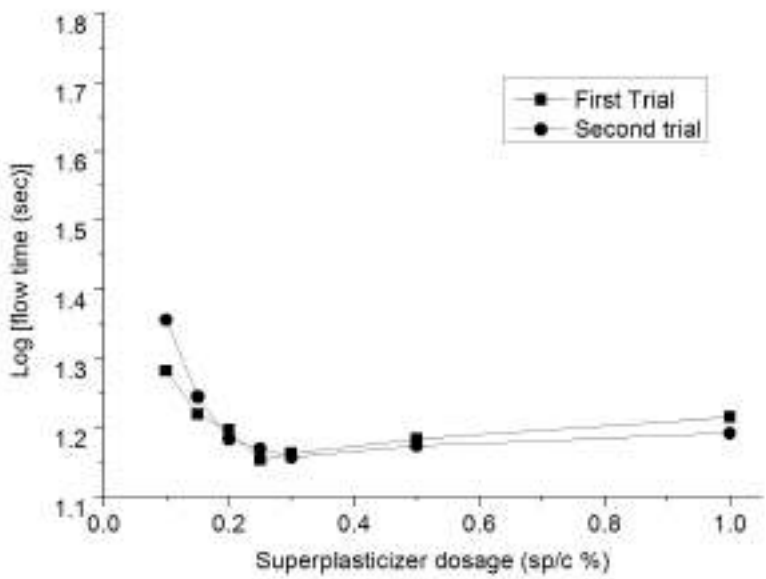
(d)

Figure A.3 Marsh cone flow time curves of the two trials with SMF based superplasticizer at temperatures (c) 25°C and (d) 35°C



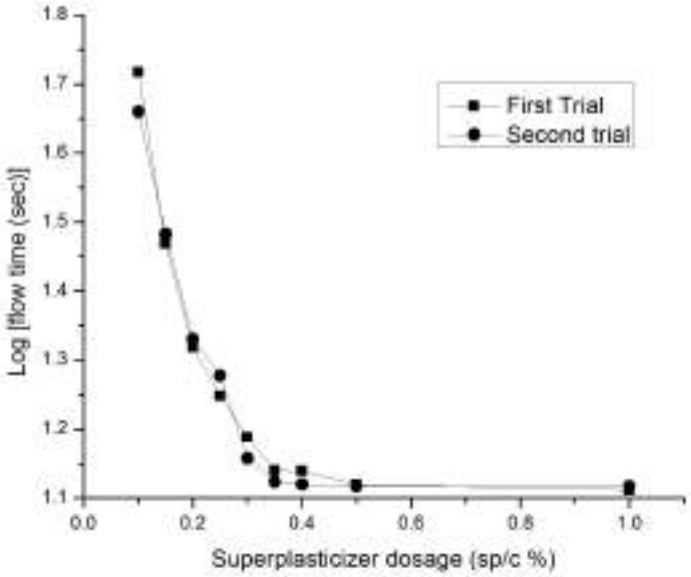
(e)

Figure A.3 Marsh cone flow time curves of the two trials with SMF based superplasticizer at temperatures (e) 40°C

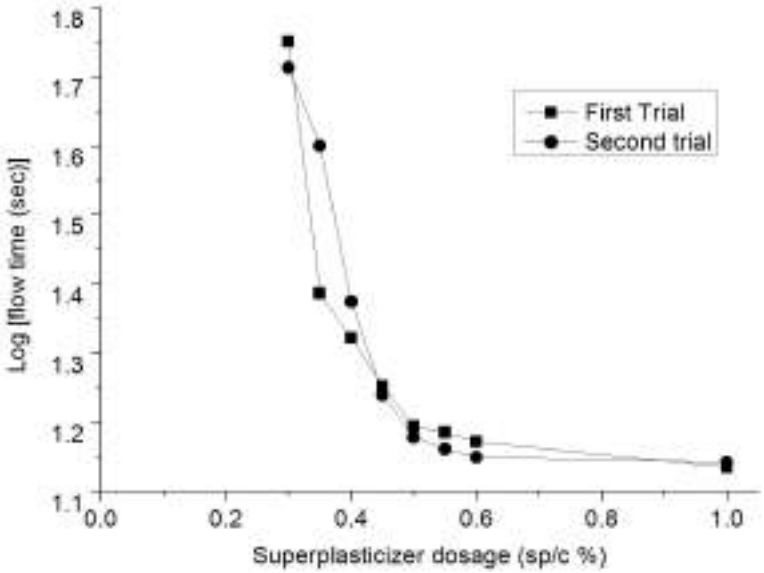


(a)

Figure A.4 Marsh cone flow time curves of the two trials with LS based superplasticizer at temperatures (a) 5°C

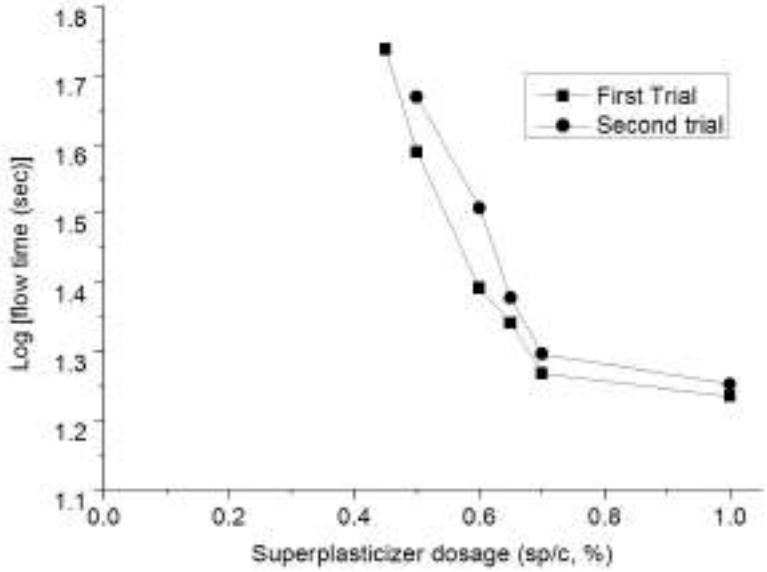


(b)

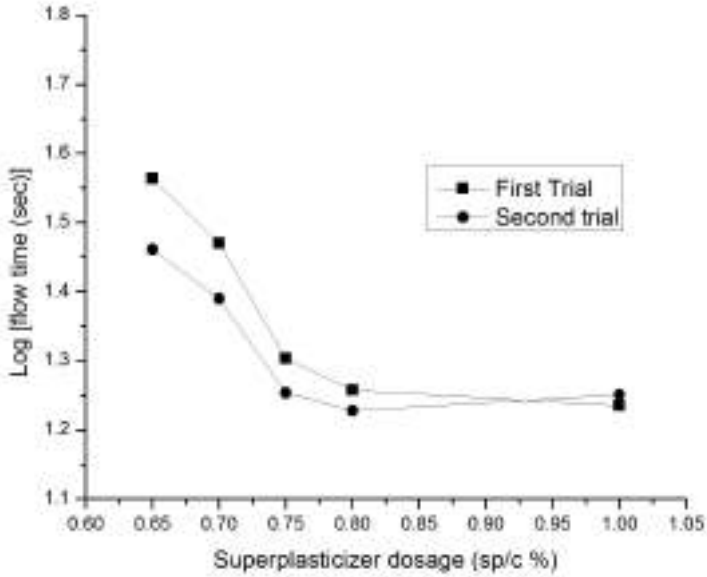


(c)

Figure A.4 Marsh cone flow time curves of the two trials with LS based superplasticizer at temperatures (b) 15°C and (c) 25°C



(d)

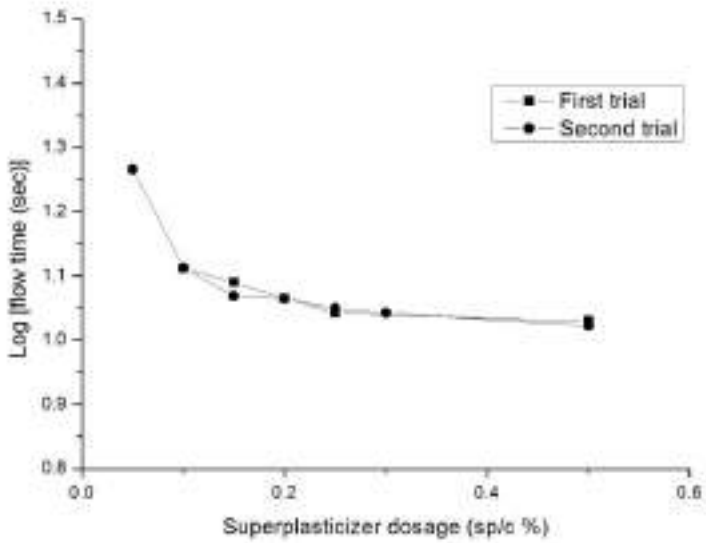


(e)

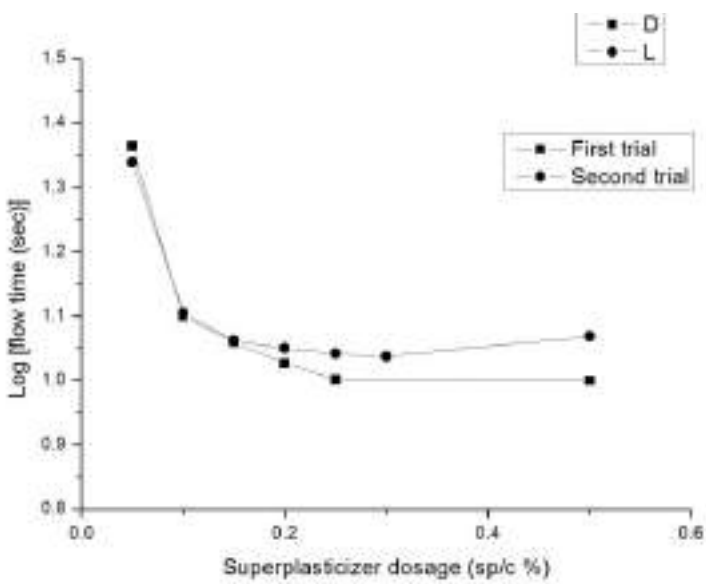
Figure A.4 Marsh cone flow time curves of the two trials with LS based superplasticizer at temperatures (d) 35°C and (e) 40°C

APPENDIX B

MARSH CONE FLOW TIME CURVES OF THE TWO TRIALS FOR THE CEMENTS HAVING DIFFERENT FINENESS

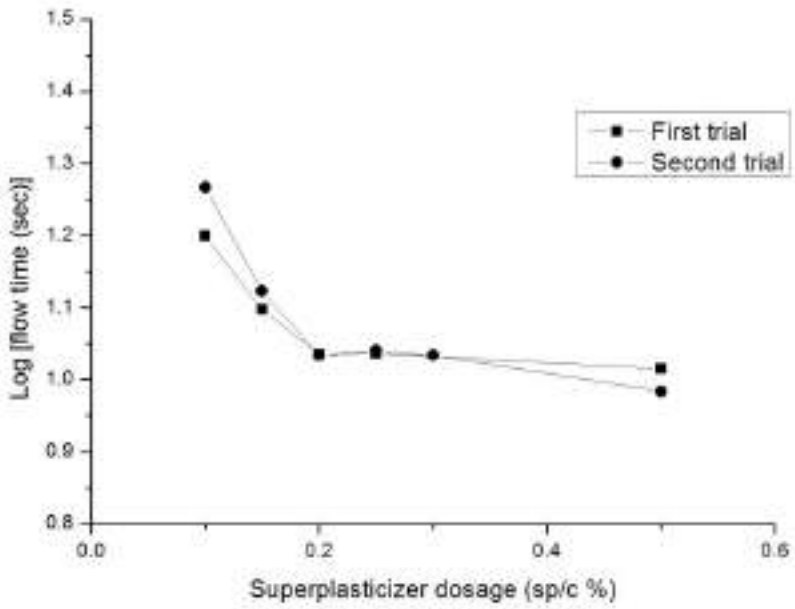


(a)

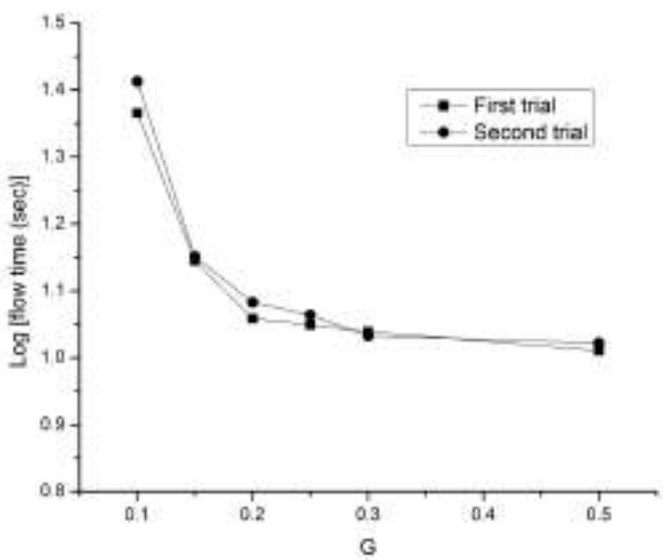


(b)

Figure B.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer for the cements having fineness of (a) F1-270 and (b) F2-290 kg/m^2

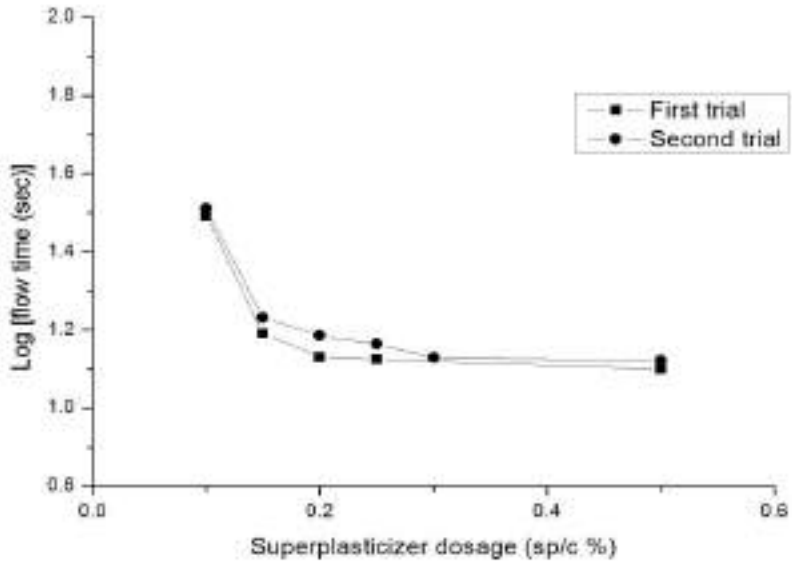


(c)

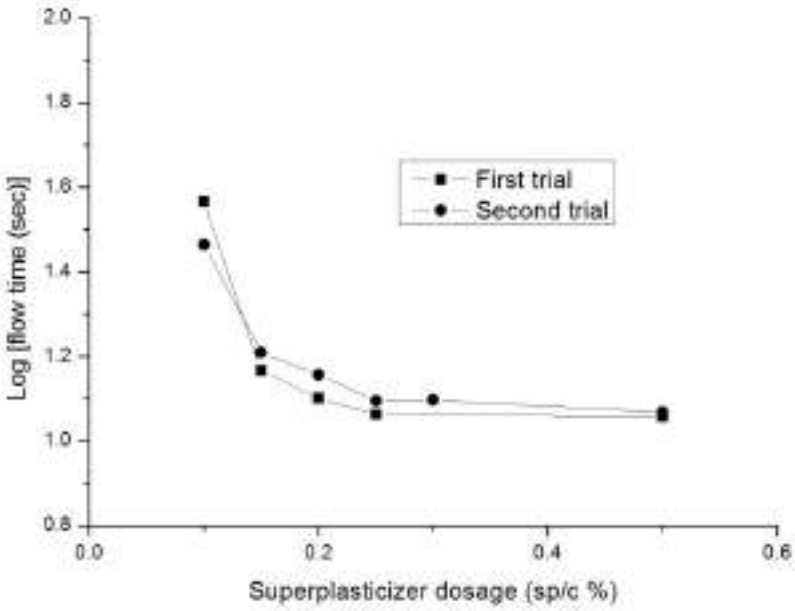


(d)

Figure B.1 Marsh cone flow time curves of the two trials with PCE based superplasticizer for the cements having fineness of (c) F3-340 and (d) F4-360 kg/m^2

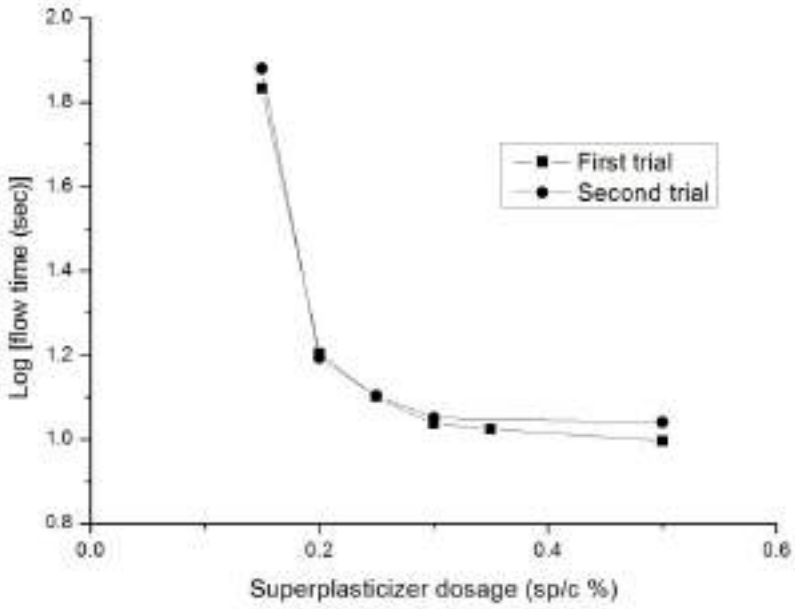


(e)

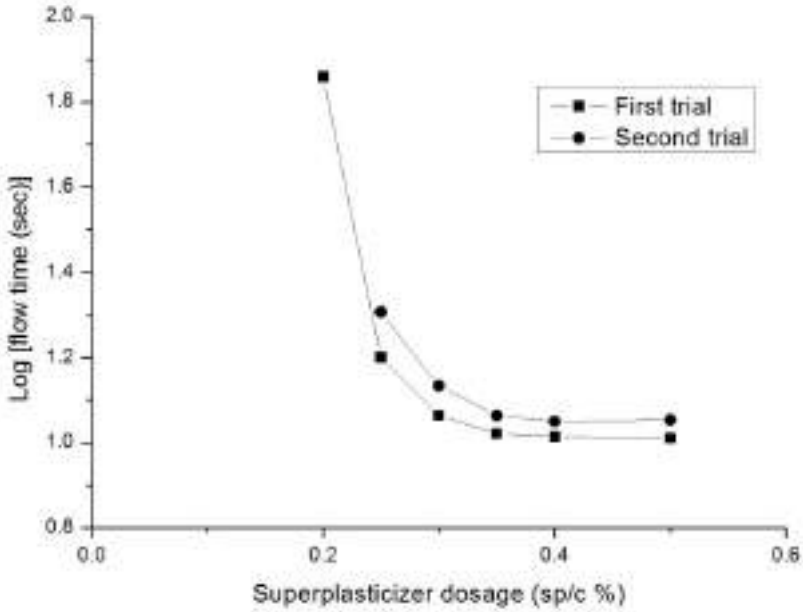


(f)

Figure B.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer for the cements having fineness of (a) F1-270 and (b) F2-290 kg/m^2



(g)

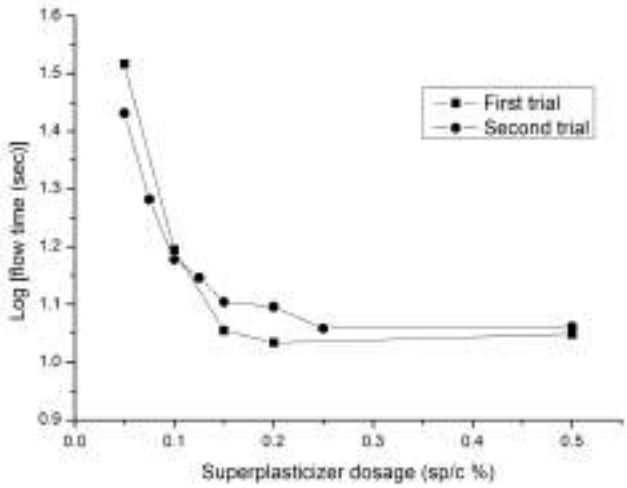


(h)

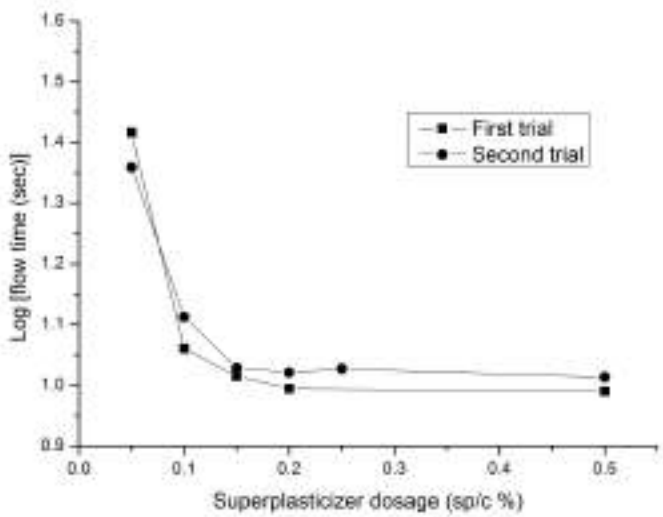
Figure B.2 Marsh cone flow time curves of the two trials with SNF based superplasticizer for the cements having fineness of (c) F3-340 and (d) F4-360 kg/m^2

APPENDIX C

MARSH CONE FLOW TIME CURVES OF TWO TRIALS FOR THE CEMENTS HAVING DIFFERENT SO_3 CONTENT

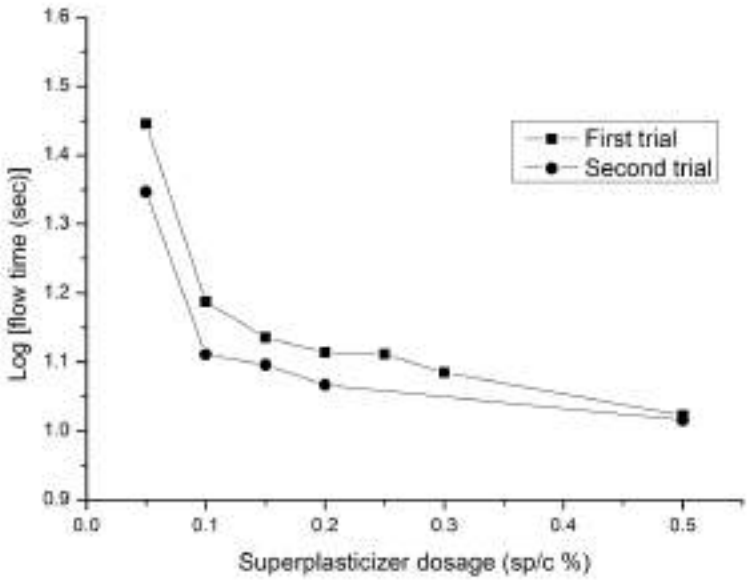


(a)

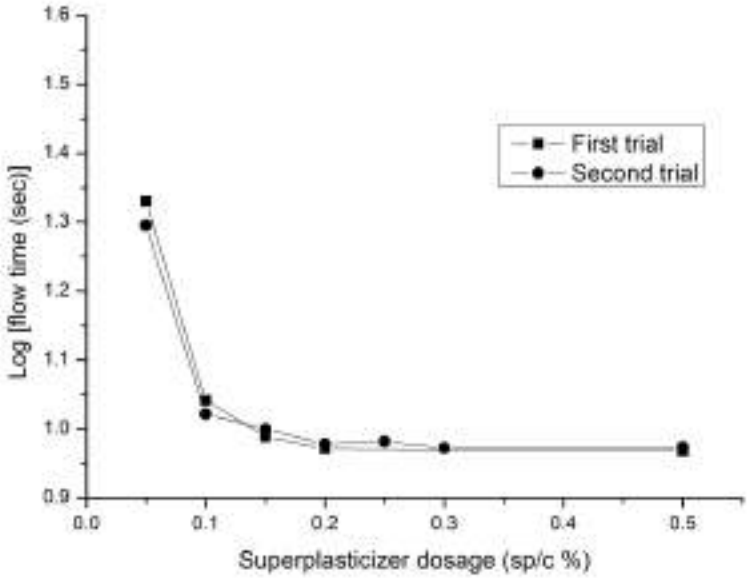


(b)

Figure C.1 Marsh cone flow time curves of two trials with PCE based superplasticizer for the cements having SO_3 content of (a) S1-1.7 and (b) S2-1.88 %

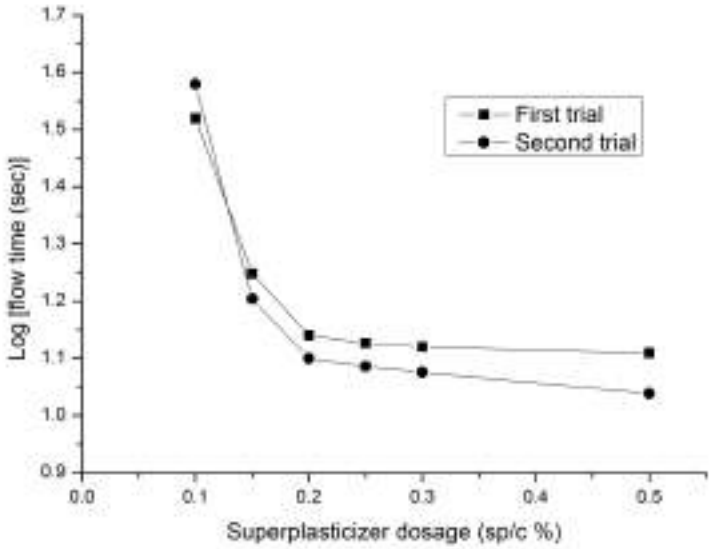


(c)

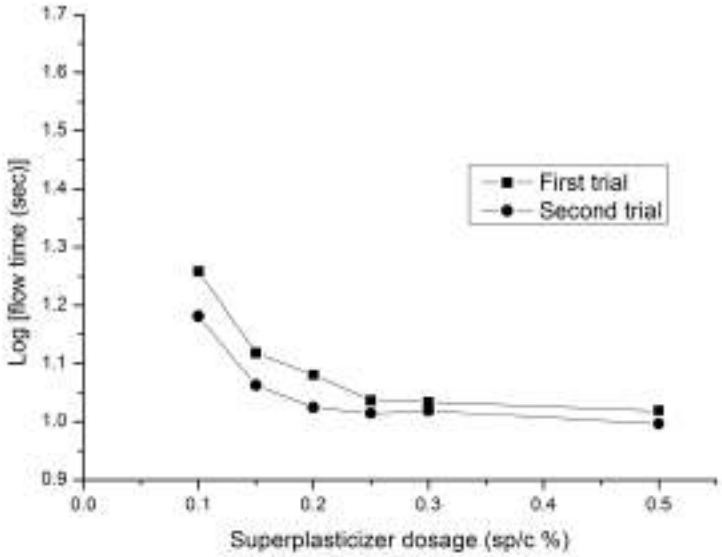


(d)

Figure C.1 Marsh cone flow time curves of two trials with PCE based superplasticizer for the cements having SO_3 content of (c) S3-2.19 and (d) S4-2.53%

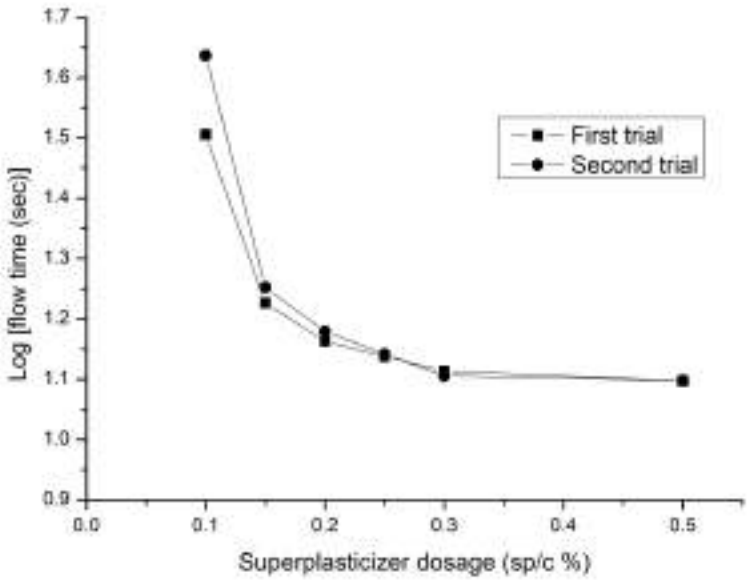


(a)

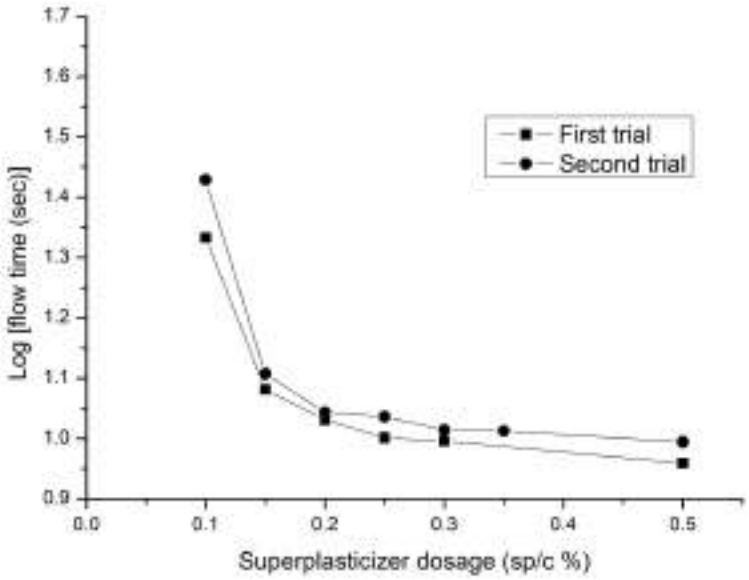


(b)

Figure C.2 Marsh cone flow time curves of two trials with SNF based superplasticizer for the cements having SO_3 content of (a) S1-1.7 and (b) S2-1.88 %



(c)

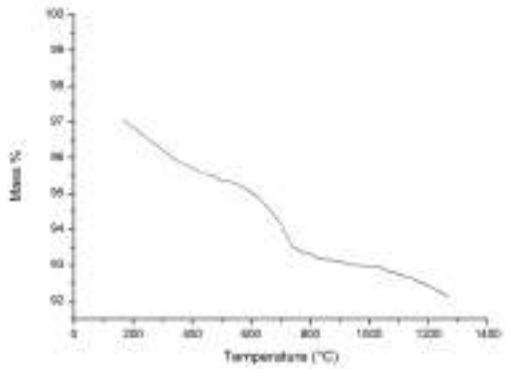


(d)

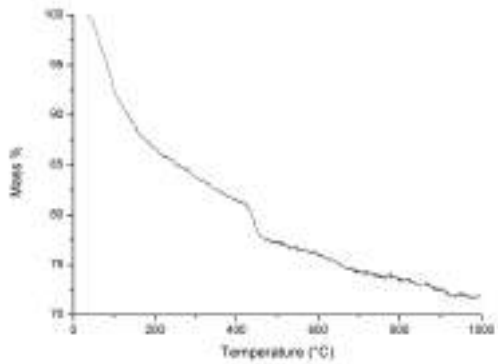
Figure C.2 Marsh cone flow time curves of two trials with SNF based superplasticizer for the cements having SO_3 content of (c) S3-2.19 and (d) S4-2.53 %

APPENDIX D

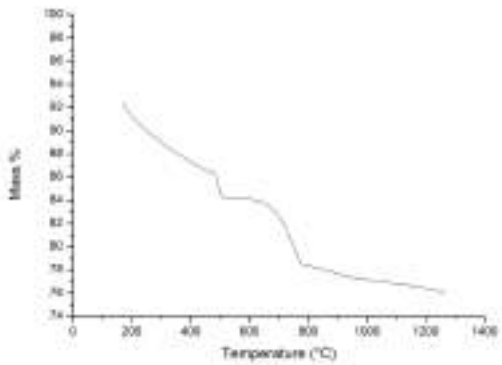
TG CURVES OF CEMENT PASTES



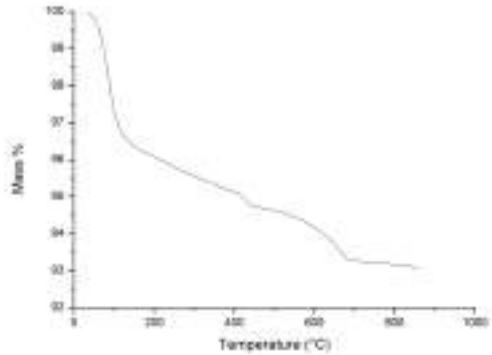
(a) 5°C - Control - half-setting



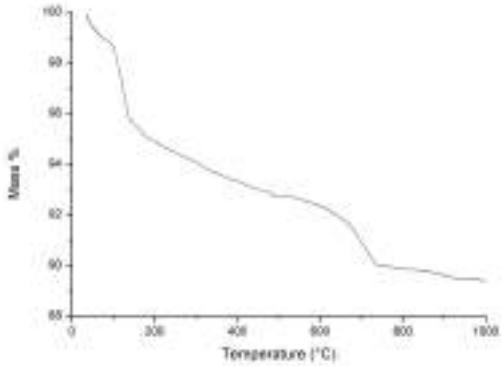
(b) 5°C - Control - 1day



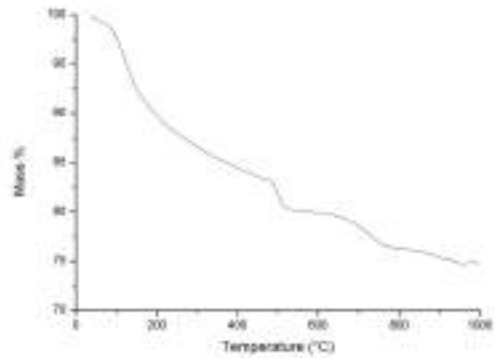
(c) 5°C - Control - 28 days



(d) 5°C - PCE - half-setting

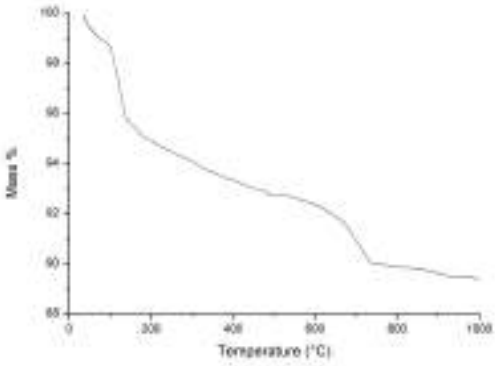


(e) 5°C - PCE - 1 day

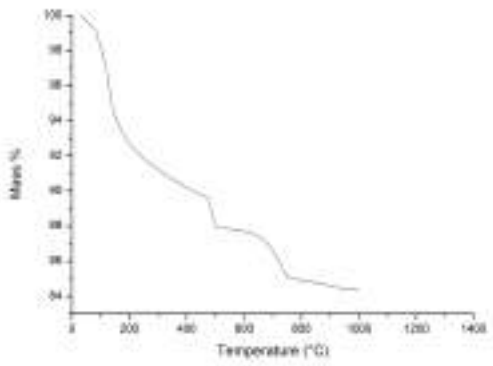


(f) 5°C - PCE - 28 days

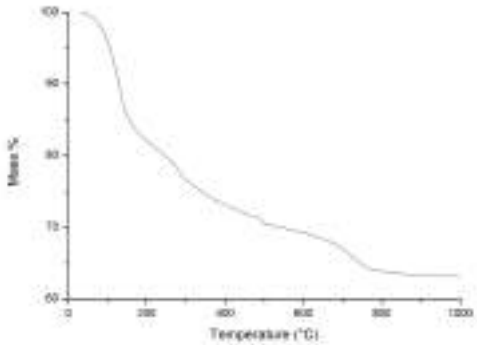
Figure D.1 TG curves of cement pastes with and without superplasticizer at half setting, 1 and 28 days of curing and casted at 5°C, 25°C and 40°C.



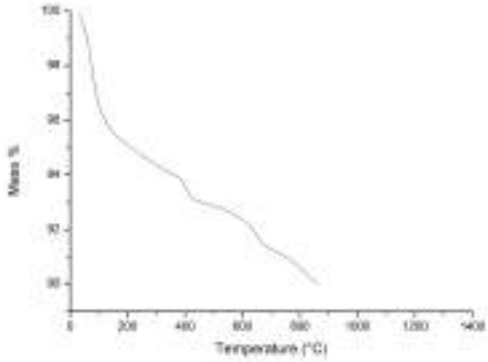
(g) 25°C - Control - half-setting



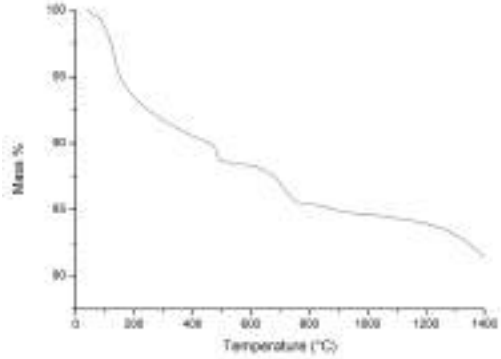
(h) 25°C - Control -1 day



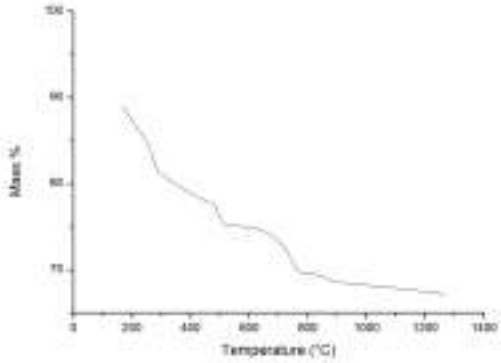
(i) 25°C - Control - 28 day



(j) 25°C - PCE - half-setting

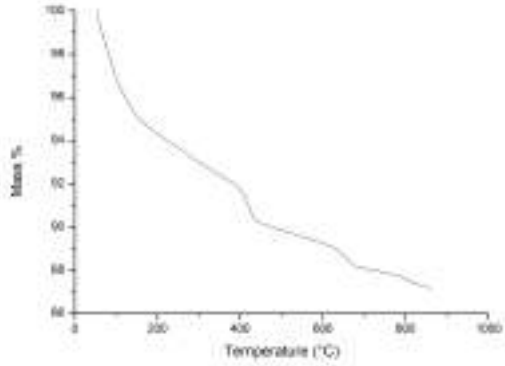


(k) 25°C - PCE - 1 day

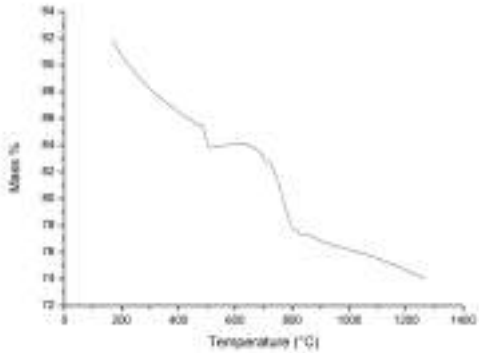


(l) 25°C - PCE - 28 days

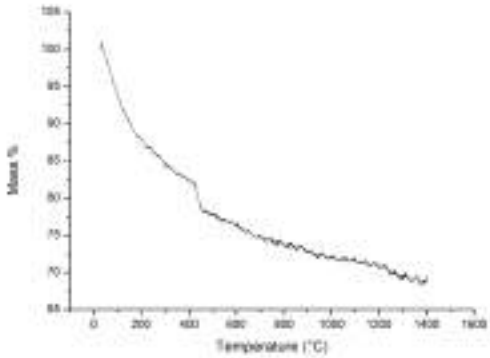
Figure D.1 TG curves of cement pastes with and without superplasticizer at half setting, 1 and 28 days of curing and casted at 5°C, 25°C and 40°C.



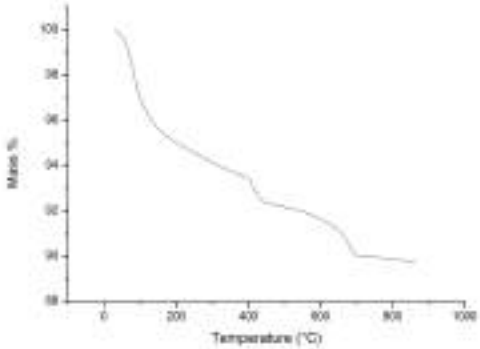
(m) 40°C - Control - half-setting



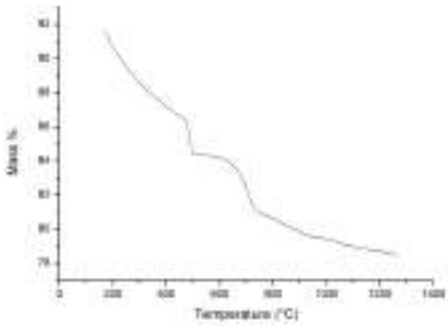
(n) 40°C - Control - 1 day



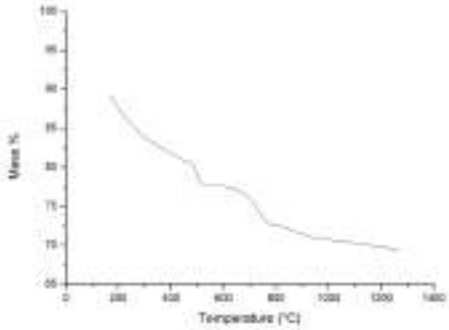
(o) 40°C - Control - 28days



(p) 40°C - PCE - half-setting



(q) 40°C - PCE - 1 day

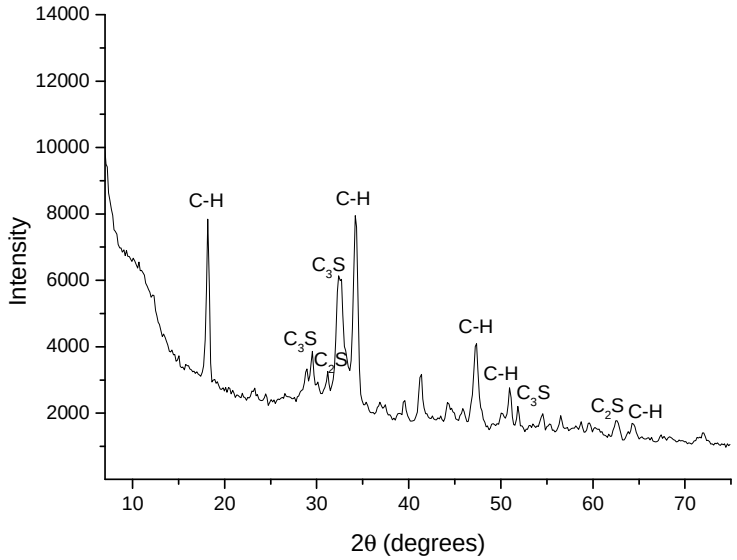


(r) 40°C - PCE - 28 days

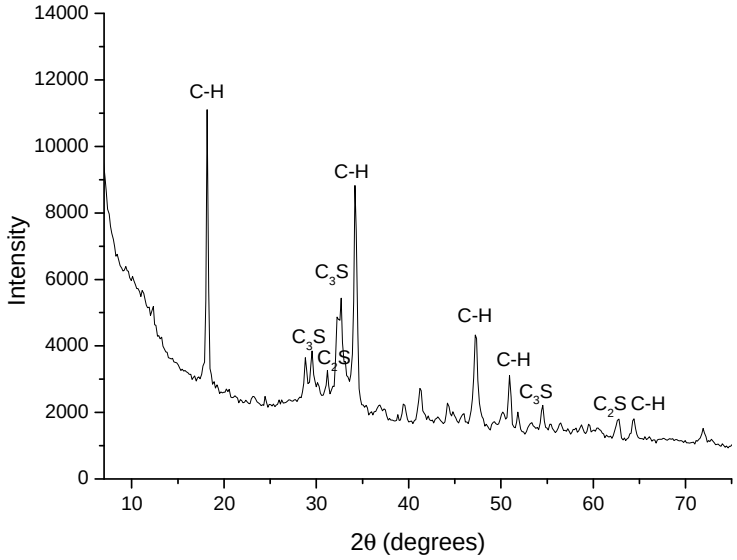
Figure D.1 TG curves of cement pastes with and without superplasticizer at half setting, 1 and 28 days of curing and casted at 5°C, 25°C and 40°C.

APPENDIX E

INDIVIDUAL CURVES OF X-RAY DIFFRACTOGRAM

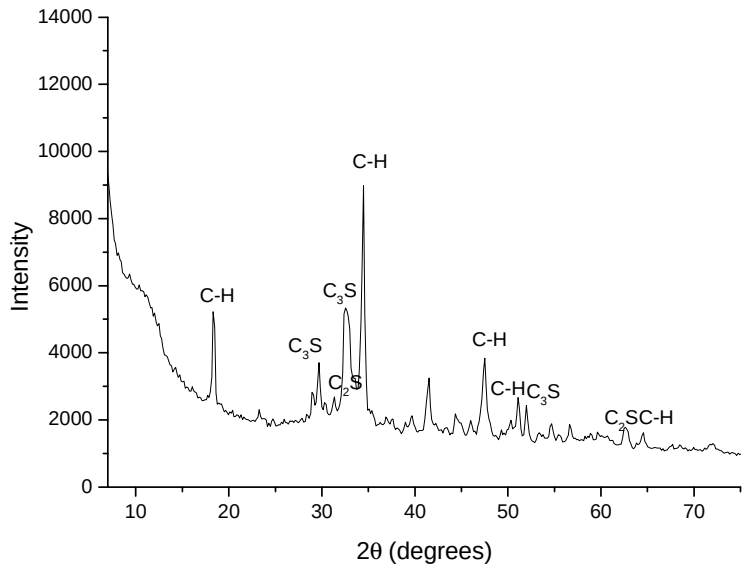


(a) 5°C-Control-1day

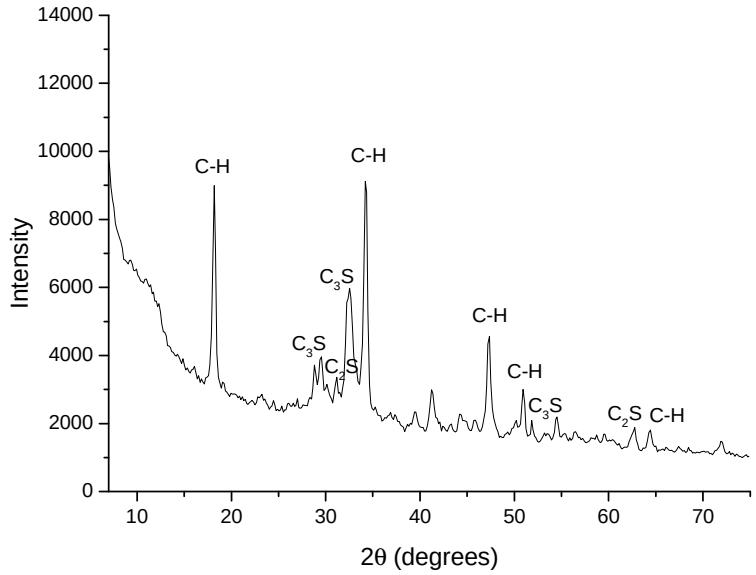


(b) 25°C-Control-1day

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

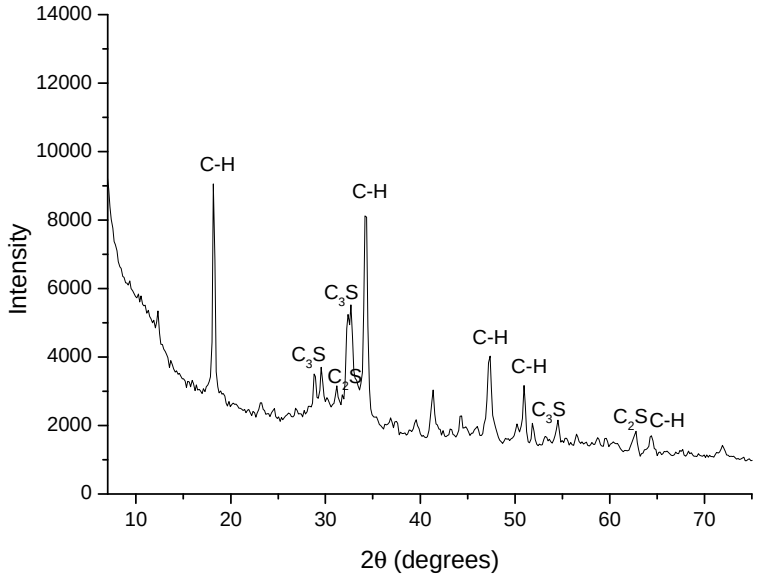


(c) 40°C-Control-1day

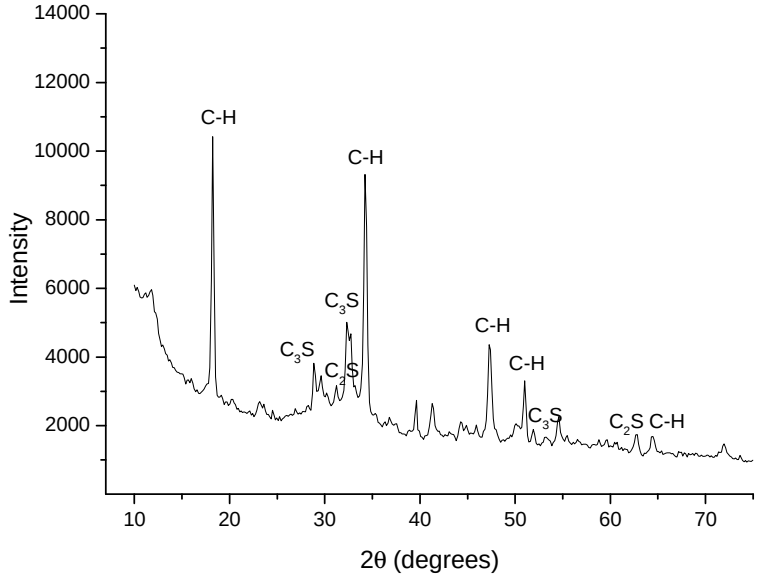


(d) 05°C-PCE-1day

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

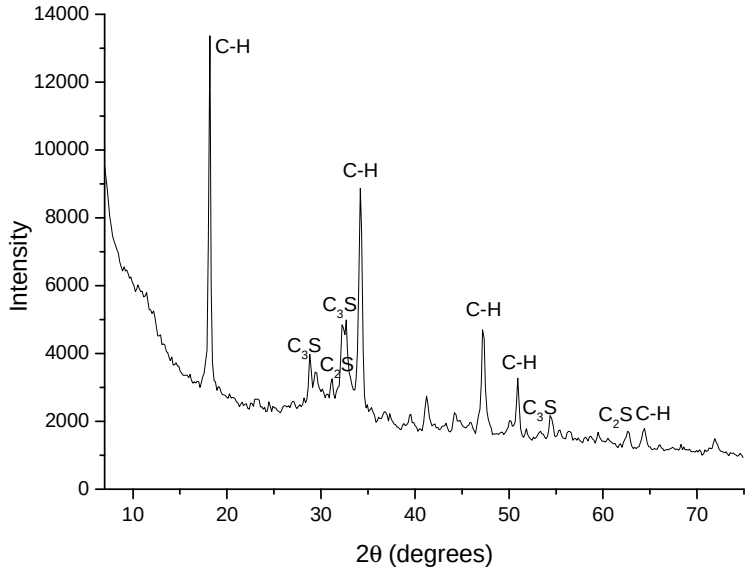


(e) 25°C-PCE-1day

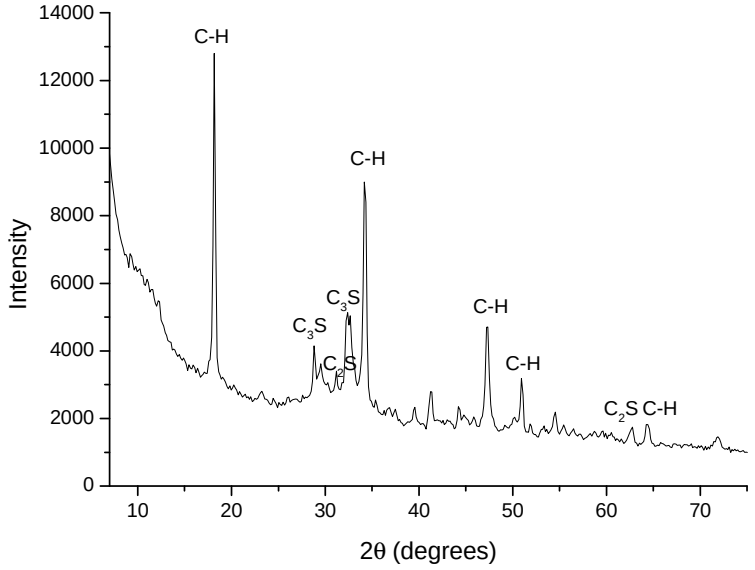


(f) 40°C-PCE-1day

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

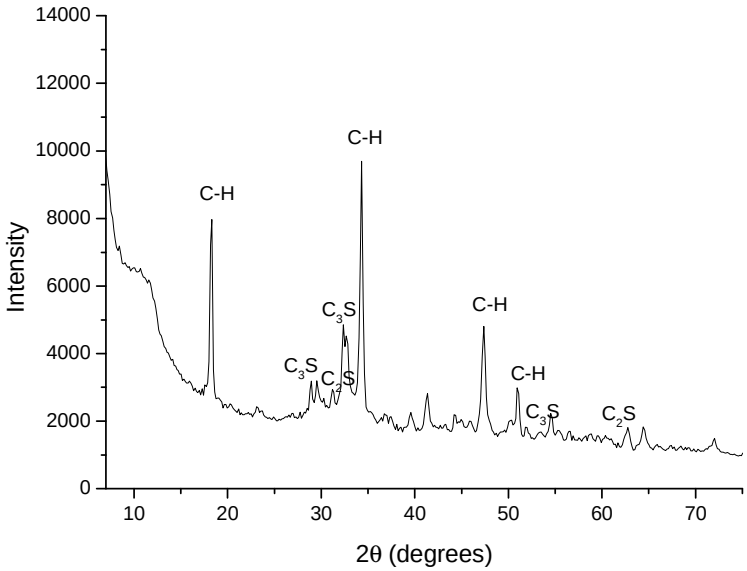


(g) 5°C-Control-3days

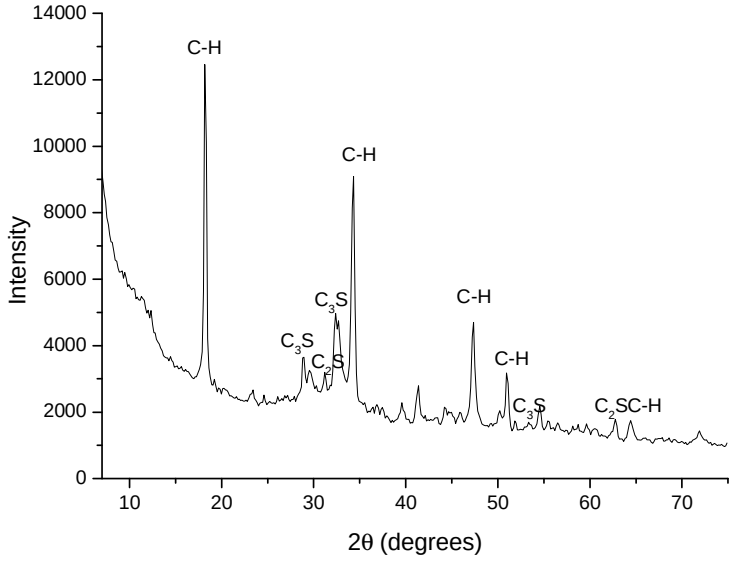


(h) 25°C-Control-3days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

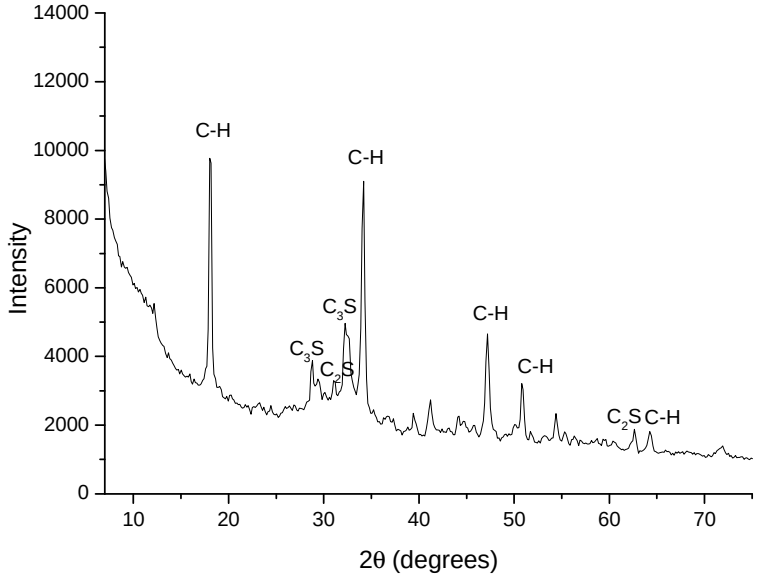


(i) 40°C-Control-3days



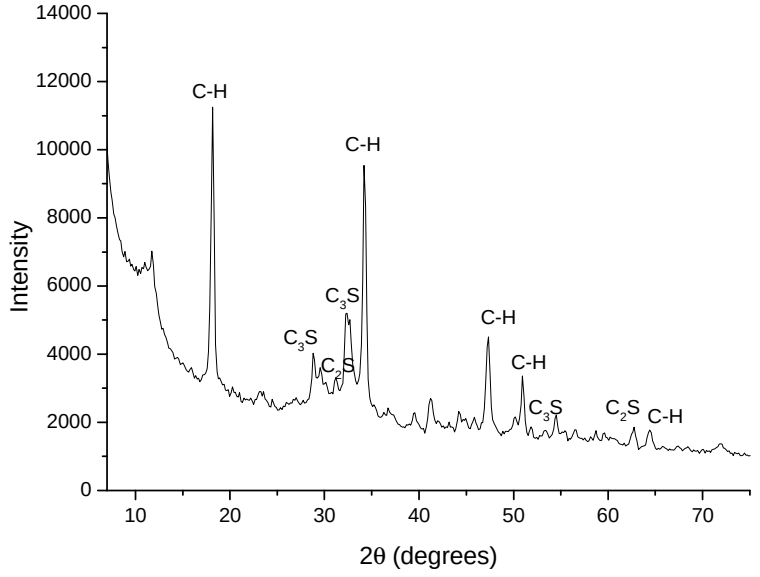
(j) 05°C-PCE-3days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.



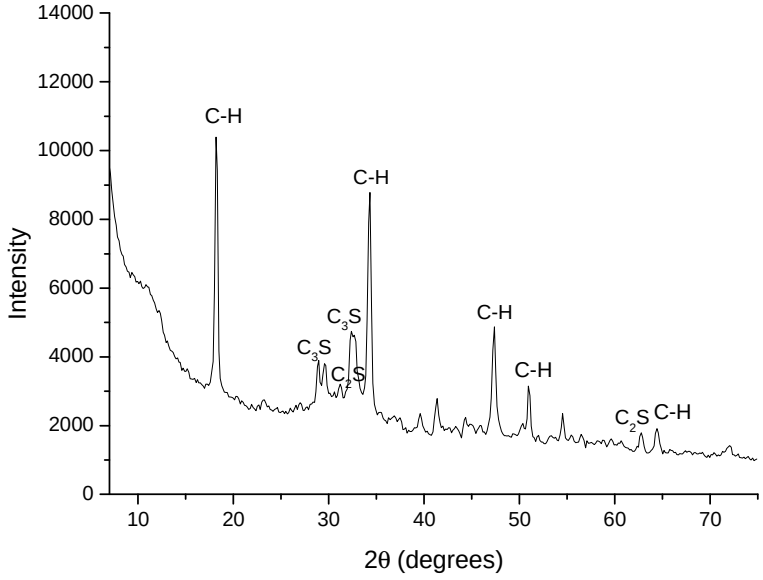
(k) 25°C-PCE-3days

C_3S

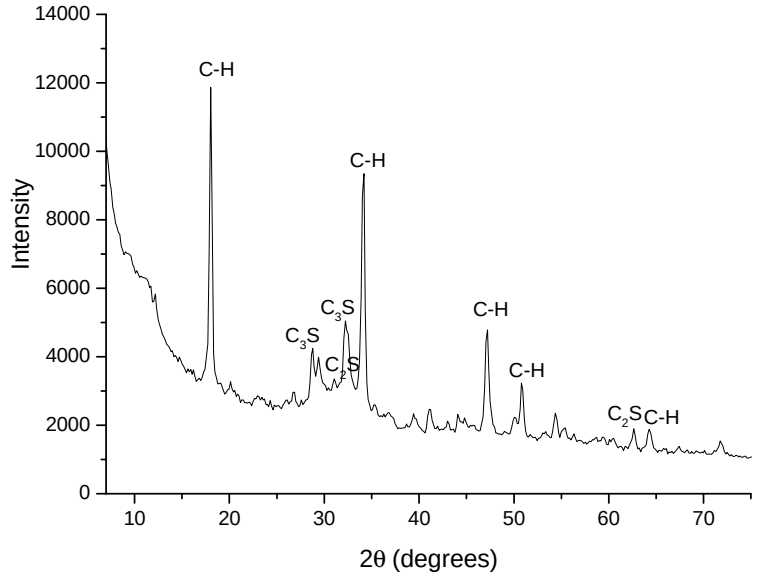


(l) 40°C-PCE-3days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

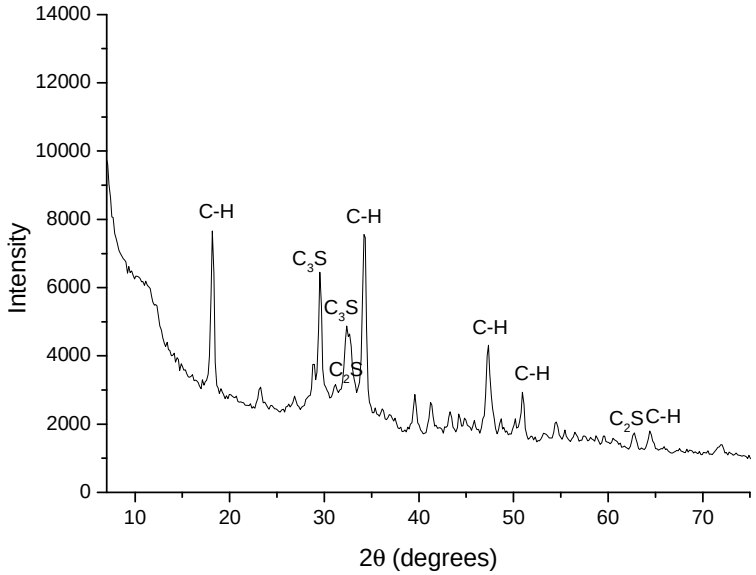


(m) 5°C-Control-7days

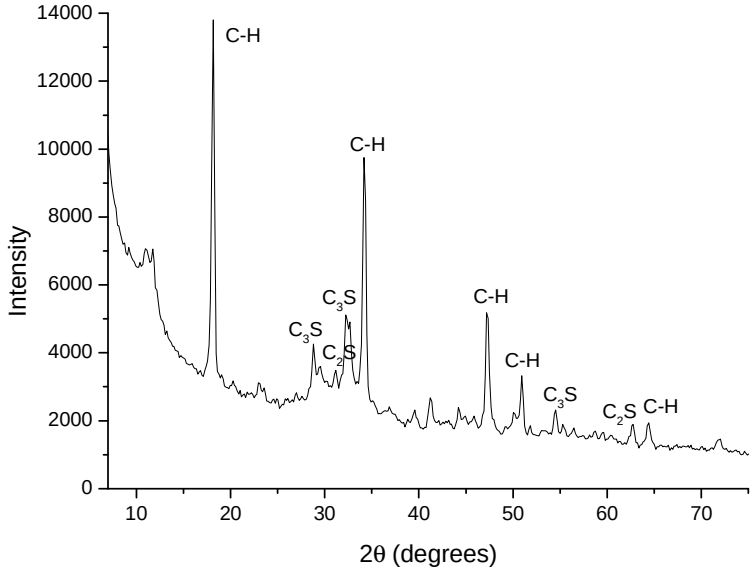


(n) 25°C-Control-7days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

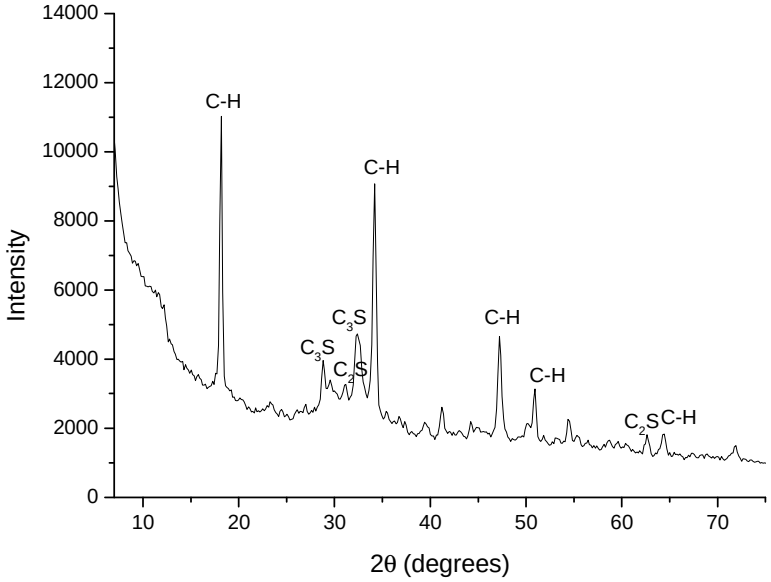


(o) 40°C-Control-7days

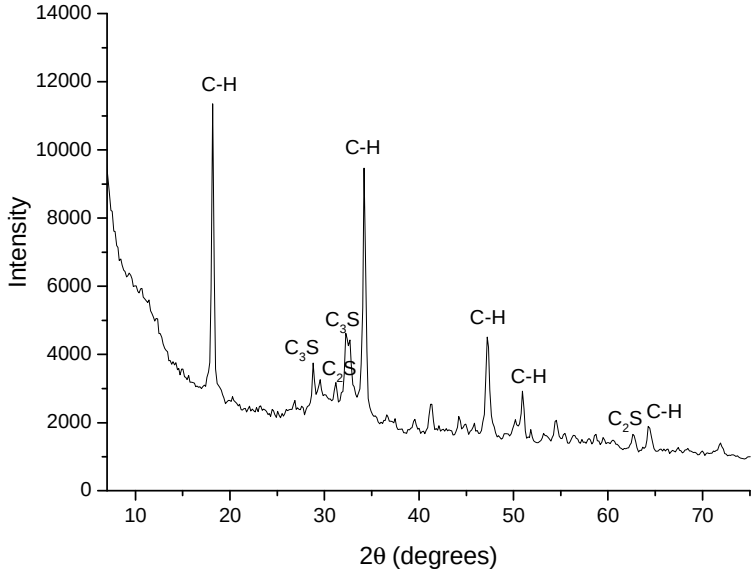


(p) 05°C-PCE-7days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

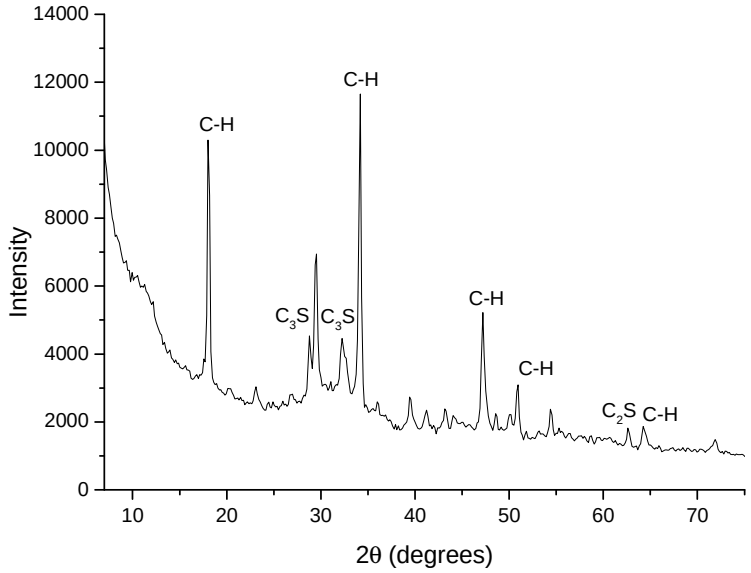


(q) 25°C-PCE-7days

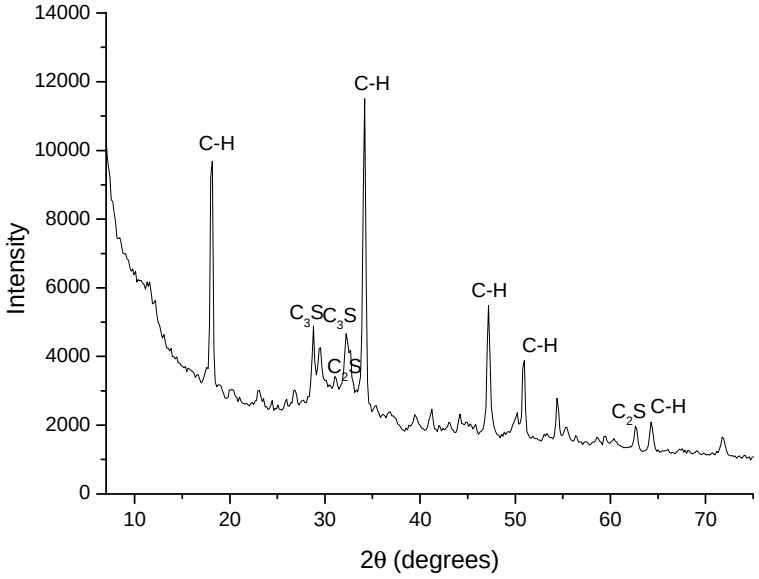


(r) 40°C-PCE-7days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

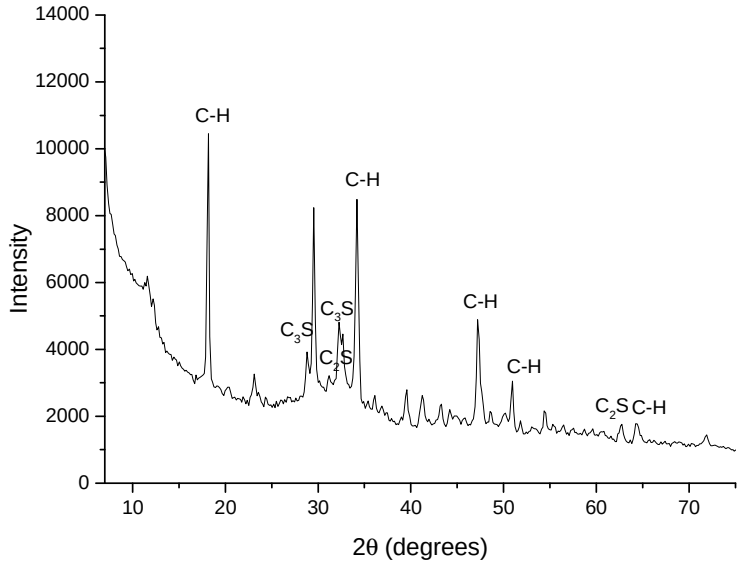


(s) 5°C-Control-28days

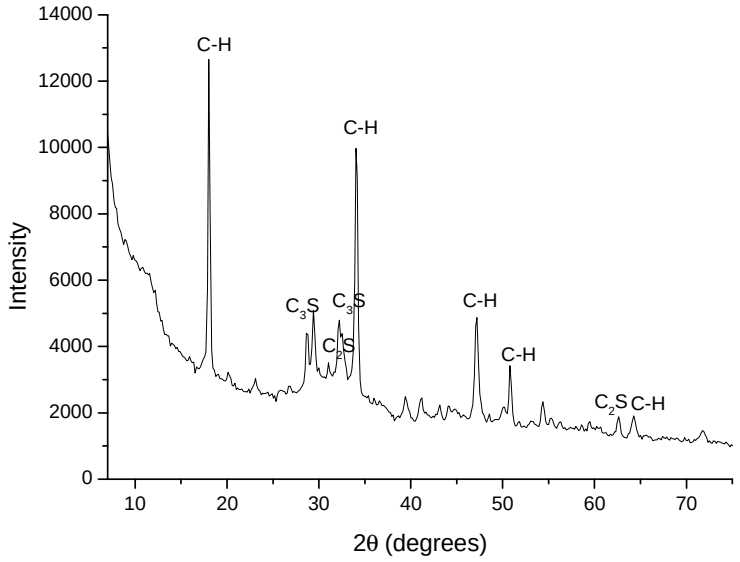


(t) 25°C-Control-28days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

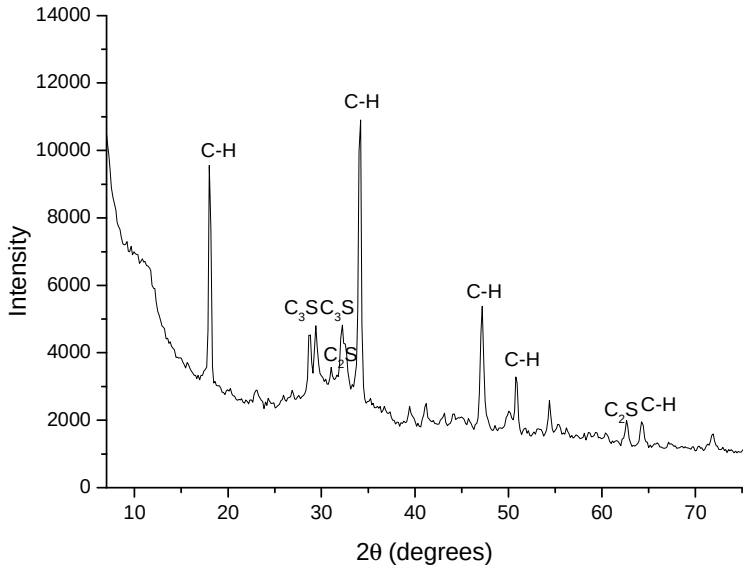


(u) 40°C-Control-28days

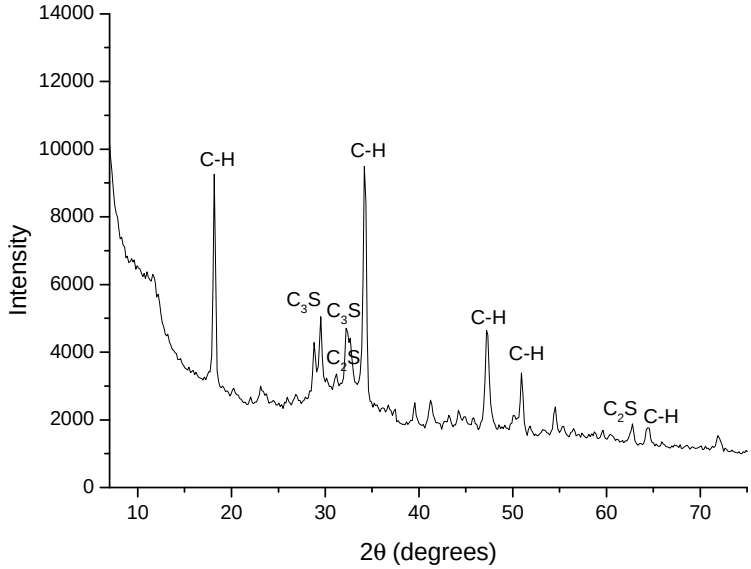


(v) 05°C-PCE-28days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.



(w) 25°C-PCE-28days



(x) 40°C-PCE-28days

Figure E.1 Individual curves of X-ray diffractogram of cement paste prepared at various temperatures with and without superplasticizer and cured for different ages.

LIST OF PAPERS
SUBMITTED ON THE BASIS OF THIS THESIS

I REFEREED JOURNALS

Elson John and Ravindra Gettu (2014) Effect of Temperature on Flow Properties of Superplasticized Cement Paste. *ACI Materials Journal*, **111**, 67-76.

II PRESENTATIONS IN CONFERENCES

Elson John and Ravindra Gettu Effect of temperature on fluidity and setting time of cement with a naphthalene based superplasticizer. *National Conference on Contemporary Challenges and Pioneering Technologies in Civil Engineering*, K.S.R College of Engineering, Erode, 2010.

Ravindra Gettu, Jayasree C., Elson John, Bhaskar S., Betiglu Eshete and Vinayak S. More sustainable concrete technology through the effective use of superplasticizers. *Third International Conference on Sustainable Construction Materials and Technologies*, Kyoto, Japan, Japan Concrete Institute, 2013.

DOCTORAL COMMITTEE

Chairman	:	Dr. A. Veeraraghavan Professor Department of Civil Engineering Indian Institute of Technology Madras
Guide	:	Dr. Ravindra Gettu Professor Department of Civil Engineering Indian Institute of Technology Madras
Members	:	Dr. M. Subramanyam Professor Department of Metallurgical and Materials Engineering Indian Institute of Technology Madras
		Dr. Ganesh Babu Professor Department of Ocean Engineering Indian Institute of Technology Madras
		Dr. G. Appa Rao Professor Department of Civil Engineering Indian Institute of Technology Madras
		Dr. Manu Santhanam Professor Department of Civil Engineering Indian Institute of Technology Madras

CURRICULUM VITAE

1. **NAME : ELSON JOHN**
2. **DATE OF BIRTH : 31.05.1978**
3. **EDUCATIONAL QUALIFICATIONS:**

1999 Bachelor of Technology (B. Tech)

Institution : M. A. College of Engineering, Kothamangalam

University : Mahatma Gandhi University

Specialization: Civil Engineering

2004 Master of Technology (M. Tech)

Institution : GIT Belgaum

University : Visweswaraya Technological University, Belgaum

Specialization: Structural Engineering

Doctor of Philosophy (Ph. D)

Institution : Indian Institute of Technology Madras

Specialization : Building Technology

Registration date : 17.08.2008