JOINT TRANSPORTATION RESEARCH PROGRAM

INDIANA DEPARTMENT OF TRANSPORTATION
AND PURDUE UNIVERSITY

COMPATIBILITY OF CEMENTITIOUS MATERIALS AND ADMIXTURES

Jan Olek
Professor of Civil Engineering
School of Civil Engineering
Purdue University
Corresponding Author

Chaitanya Paleti
Graduate Research Assistant
School of Civil Engineering
Purdue University

SPR-3212
Report Number: FHWA/IN/JTRP-2012/30
DOI: 10.5703/1288284315025

RECOMMENDED CITATION

Olek, J., and C. Paleti. *Compatibility of Cementitious Materials and Admixtures*. Publication FHWA/IN/JTRP-2012/30. Joint Transportation Research Program, Indiana Department of Transportation and Purdue University, West Lafayette, Indiana, 2012. doi: 10.5703/1288284315025.

CORRESPONDING AUTHOR

Professor Jan Olek
School of Civil Engineering
Purdue University
(765) 494-2165
olek@purdue.edu

JOINT TRANSPORTATION RESEARCH PROGRAM

The Joint Transportation Research Program serves as a vehicle for INDOT collaboration with higher education institutions and industry in Indiana to facilitate innovation that results in continuous improvement in the planning, design, construction, operation, management and economic efficiency of the Indiana transportation infrastructure.
https://engineering.purdue.edu/JTRP/index_html

Published reports of the Joint Transportation Research Program are available at: http://docs.lib.purdue.edu/jtrp/

NOTICE

TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
FHWA/IN/JTRP-2012/30		

4. Title and Subtitle	5. Report Date
Compatibility of Cementitious Materials and Admixtures	October 2012
	6. Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Jan Olek , Chaitanya Paleti	FHWA/IN/JTRP-2012/30
9. Performing Organization Name and Address Joint Transportation Research Program Purdue University 550 Stadium Mall Drive West Lafayette, IN 47907-2051	10. Work Unit No.
	11. Contract or Grant No. SPR-3212
12. Sponsoring Agency Name and Address Indiana Department of Transportation State Office Building 100 North Senate Avenue Indianapolis, IN 46204	13. Type of Report and Period Covered Final Report
	14. Sponsoring Agency Code

15. Supplementary Notes

Prepared in cooperation with the Indiana Department of Transportation and Federal Highway Administration.

16. Abstract

Growing demand for creating more sustainable and durable concretes lead to the increased usage of various cementitious materials and chemical admixtures in the mixtures. However, the increased usage of these components resulted in more complex mixtures that sometimes cause unexpected incompatibility problems. This report summarizes the results of the investigation of the parameters that may lead to workability problems, early age hydration irregularities and difficulties in achieving quality air void system in both plain and fly ash cementitious mixtures. The present research work was performed in three major phases and the statistical modeling was used to aid in interpretation.

Phase I involved evaluation of more than 100 different paste and mortar mixtures with respect to potential slump loss and hydration irregularities. The results showed that cements with high C3A and low SO3 content were more prone to incompatibility problems. It was also observed that mixes with lignin based water reducing agent (WRA) had higher tendency for rapid stiffening than mixes with polycarboxylate type superplasticizer (PCSP). Increased replacement of cement by class C ashes resulted in the development of abnormal secondary peaks in semi-adiabatic calorimetry curves and accelerated the setting behavior.

The focus of phase II was on identifying material combinations that can result in problems related to air void generation and stability. The experiments were conducted on 18 different systems and included determination of foam drainage and foam index parameters. The results show that the amount of air entrainers required to obtain target air percentage, increased with the increase in the fly ash content in the mixture. Lignin based WRA had, in general, a higher air entraining effect than the super-plasticizer when used in combination with air entrainers. Also, five out of the six mixtures with most unstable air void system, identified using the foam drainage experiments, contained the PCSP.

The third (and final) phase of the study involved production of 10 concrete mixtures to verify the incompatibility findings from the paste and mortar experiments performed in phases I and II. The observations from the concrete testing were in agreement with the findings from the paste and mortar testing.

Statistical modeling (performed using the material properties and results from phase I) identified the total C3A, SO3 and Na2Oequ contents of the binder system along with dosage of PCSP (if present in the mixture) as statistically significant in predicting the initial set time and area of spread (measured using the mini-slump test).

17. Key Words	18. Distribution Statement
materials incompatibility, early age stiffening, set time and hydration irregularities, admixtures, mini-slump, foam drainage, semi-adiabatic calorimetry, statistical modeling	No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161.

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	100	

Form DOT F 1700.7 (8-69)

EXECUTIVE SUMMARY

COMPATIBILITY OF CEMENTITIOUS MATERIALS AND ADMIXTURES

Introduction

The process of selection of both the constitutive materials and the proportions of modern concrete mixtures is becoming more complex due to the increasing pressure to meet various durability and performance requirements. As a result, modern concrete mixtures frequently contain numerous mineral and chemical ingredients, combinations of which may lead to so-called incompatibility problems. The term "incompatibility" has been applied to various types of abnormal performance of concrete in both plastic and hardened concrete, including:

- Setting and strength gain problems
- Excessive slump losses
- Increased water demand to achieve the desired slump
- Problems with the generation and stability of the air void system

These irregularities adversely influence workability, placing, consolidation and finishing characteristics, along with durability of concrete mixtures. Based on the extensive literature review conducted as a part of this study, the main incompatibility problems were found to be due to one or more of the following phenomena:

- Cement driven incompatibility problems
- Incompatibility due to the type and the amount of supplementary cementitious materials (SCMs) in the mixture
- Incompatibility problems related to the usage of chemical admixtures in the mixture
- Problems due to other reasons and substandard practices

An extensive summary of literature findings on the incompatibility problems is presented in Appendix A of this report.

Findings

- Even though all (except for one) cements were initially selected to result in potential incompatibility problems, only 45 out of the 70 mixtures (combinations) tested in the sub-phase I of Phase I did so, while the remaining 25 mixtures were identified as compatible. The observed signs of incompatibility included rapid stiffening of the mixtures, significant changes in set behavior and/or in the hydration process.
- In general, cements with high C_3A content and low sulfate content were more prone to incompatibility problems. It was also observed that mixes with Type A water reducer (WR), W1, had a higher tendency for rapid stiffening than mixes with PC type superplasticizer (SP). The addition of W1 to high C_3A content and low sulfate content fly ash cementitious systems resulted in significant changes to the hydration process. Increased replacement of cement by class C ashes often aggravated the rapid stiffening and abnormal setting behavior of the mixtures. Also, in most of the cases, other factors (amount of admixture or the timing of addition) further aggravated the problem of incompatibility.
- Fly ash content and the type of admixtures present in the mixture significantly influenced both the generation and the stability of the air void system. The air entraining agents (AEA) requirement increased with the increase in the class F ash content. Mixtures prepared with W2 and AEA were found to be more unstable than mixtures prepared with other admixture combinations.
- Various incompatibility problems observed during the concrete testing were consistent with the findings from the corresponding paste and mortar experiments. Concrete mixtures prepared with high (60%) volumes of class F ash exhibited poor strength development.

Implementation

Based on the findings from the present work, the last section of the report, titled "Recommendations to Avoid Incompatibility Problems," presents practical, implementable guidelines with respect to minimizing potential incompatibility problems in the field.

The recommendations to avoid potential early stiffening and abnormal setting problems were developed using findings from mini slump, Vicat's set time and semi-adiabatic calorimeter experiments. Foam drainage, foam index and air content in mortars tests were used to develop guidelines to prevent air void related incompatibility problems.

Figure 6.1 of the report presents the list of incompatible combinations of materials and can be used as a practical field aid for the quick check of potential problems, especially in cases when materials source change occurred during the construction.

Two other factors (increased addition levels of WRAs and delayed addition of admixtures) resulted in mixed results. Both of these practices accelerated the set time in some mixes but had no effect on other mixes. Hence, it is recommended not to use either of these practices during construction. If it is imperative to use either of these practices, then it is recommended to perform a preliminary study as outlined in Figure 6.2. Various test methods and the corresponding limiting criteria to identify potential incompatibility problems are listed in Table 6.1. This table can also serve as a practical field guide.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

The processes of selection of constitutive materials and proportioning of modern concrete mixtures are becoming more complex due to the increase in durability and performance requirements. As a result, modern concrete mixtures frequently contain numerous mineral and chemical ingredients, combinations of which may lead to so-called incompatibility problems. The term "incompatibility" has been applied to various types of abnormal performance of concrete in both plastic and hardened concrete, including:

- Setting and strength gain problems,
- Excessive slump losses,
- Increased water demand to achieve the desired slump
- Problems with the generation and stability of the air void system

These irregularities adversely influence workability, placing, consolidation and finishing characteristics along with durability of concrete mixtures. Based on the extensive literature review conducted as a part of this study, the main causes of the incompatibility problems were found to be due to one or more phenomena listed below:

- Cement driven incompatibility problems
- Incompatibility due to the type and the amount of supplementary cementitious materials (SCMs) in the mixture
- Incompatibility problems related to the usage of chemical admixtures in the mixture, and
- Problems due to other reasons and substandard practices.

An extensive summary of literature findings on the incompatibility problems is presented in Appendix A of this report.

2. PROBLEM STATEMENT

Although certainly not very common in commercial concrete production, the incompatible interactions between multiple mixture ingredients may occasionally result in set irregularities which will influence workability, placing, consolidation and finishing of the mixture. In addition, difficulties with creating an adequate air void system may be experienced, resulting in durability problems.

Verbal communication received from contractors and personnel working for the Indiana Department of Transportation (INDOT) indicated that combining class C fly ash with certain non-chloride accelerators resulted in severe set retardation of some concrete mixes placed in northern Indiana. In addition, high variability in the amount of entrained air and its sensitivity to temperature was reported in mixtures utilizing polycarboxylate superplasticizers. Finally, it was also reported that high dosage of a specific Type F HRWR created excessive retardation of the mix during cold weather concreting and that it took weeks for this specific mixture to gain enough strength for the construction operations to resume. It was also found that the point of introducing a specific Type A water reducer during batching sequence was critical with respect to achieving desired slump and desired reduction in the amount of the mixing water.

All of the above incidences indicate that in order to avoid such unexpected problems in the future a basic understanding of causes for various incompatibilities is necessary. More specifically, identification of all the contributing factors is required to offer practical and economical remedies to the problems of incompatibility (*1*).

3. RESEARCH OBJECTIVES AND SCOPE

The primary objective of this research work was to identify various combinations of concrete making materials (selected from the Indiana Department of Transportation (INDOT) list of approved materials) which may result in incompatibility problems in plain and fly ash cementitious systems. Incompatibility problems manifesting as abnormal early age stiffening, erratic setting behavior and problems related to air void system were selected for evaluation.

In order to identify causes of incompatibility problems, and to develop recommendation for their avoidance, the scope of the work included the following major tasks:

- Review of existing literature related to various incompatibility problems
- Identification and procurement of materials that have the potential to generate incompatibility problems
- Development of an experimental plan to evaluate numerous combinations of cements, fly ashes and chemical admixtures including selection of test methods and their corresponding limiting criteria, mixture proportions and water-binder (w/b) ratio.
- Testing of about 100 different combinations of plain and fly ash cementitious systems with and without chemical admixtures.
- Critical analysis of the results to identify trends and causes for incompatibility.
- Development of statistical models to predict the initial set time and mini slump test results.
- Development of the recommendations.

4. SUMMARY OF EXPERIMENTS AND RESULTS

The present research work was performed in three major phases. Phase I experiments were performed to study stiffening and setting related incompatibility problems while air void related incompatibility problems were investigated in Phase II. Altogether, more than 100 different paste and mortar mixtures were studied in the first two phases of the research work. Concrete mixtures were tested in Phase III to validate results from the previous two phases. (See Figure 4.1 for detailed plan of experiments.)

Four type I/II Portland cements, two class C fly ashes and four types of chemical admixtures (Tables 4.1

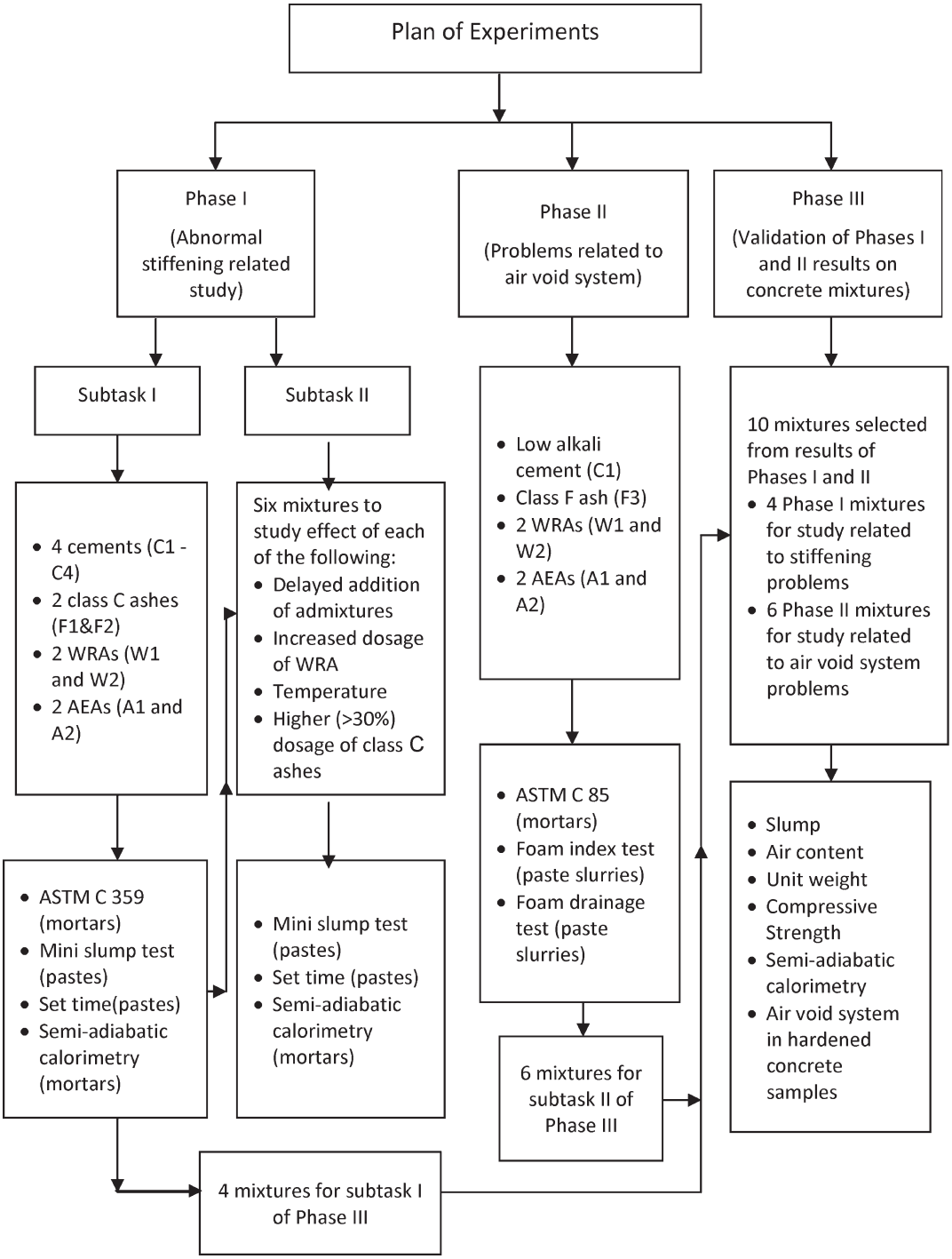

Figure 4.1 Plan of experiments.

through 4.3) were used to evaluate early age stiffening and abnormal setting related incompatibility problems in the subtask I of Phase I. In the subtask II of Phase I, the effect of high fly ash content and other factors (temperature, time of admixtures addition, and higher dosage of WRA admixtures) on compatibility was studied on selected mixtures. Early age stiffening test and mini slump experiments were performed to record the early stiffening behaviors of mixtures while Vicat's set time experiments were performed to identify abnormal setting characteristics of various mixtures. Semi-adiabatic calorimetry was performed on all mixture combinations to identify changes in the hydration process occurring due to interactions among various components.

The objective of Phase II experimentation was to identify air void related incompatibility problems. One low alkali cement, one class F ash and four chemical

TABLE 4.1
Chemical properties of the four cements used in the study

Chemical properties	Cements			
	C1 (Type I)	C2 (Type I)	C3 (Type I)	C4 (Type I/II)
C_3A content, %	9	10	10.1	7.7
SO_3 content, %	3.0	2.4	3.6	3.6
Na_2O_{equ}, %	0.29	0.3	1.04	0.97

TABLE 4.2
Chemical properties of fly ashes used in the study

Chemical properties	F1 (Class C ash)	F2 (Class C ash)	F3 (Class F ash)
SO_3 content,%	1.11	2.13	0.69
Soluble SO_3 content,* %	0.53	1.14	—
Na_2O_{equ}, %	2.18	1.94	2.21
L.O.I.	0.38 (M)	0.25	3.98

*Values obtained from Tanikella (*2*).

admixtures were used in this part of the study. Foam index testing, determination of air content in mortars and foam drainage experiments were performed on 18 different mixtures.

Phase III experiments were performed on 10 concrete mixtures to validate the findings from experiments performed on pastes and mortars in, respectively, phases I and II. Slump, air content and unit weight measurements, compressive strength testing, semi-adiabatic calorimetric temperature profiles and quality of air void system in hardened concrete were evaluated in Phase III. Further details regarding work plan, experimental methods and the corresponding limiting criteria used to identify various problematic combinations of materials are listed in the Appendix B.

The remaining sections of this chapter contain descriptions of various incompatibility problems studied during this research. These descriptions are organized by the originating source into the following three categories: cement driven, fly ash driver, and admixture driven incompatibilities. The summary of various component combinations resulting in incompatibility problems are given in Figure 4.2. Empty cells in the table indicate compatible results while cells filled with 'x' indicate potential incompatibility problems. Test methods and the corresponding limiting criteria used to identify various incompatibility problems are described in Appendix B (in Section B.5).

4.1 Cement Driven Incompatibility Problems

4.1.1 Abnormal Stiffening

Abnormal stiffening problems were identified using early age stiffening test performed according to the ASTM C 359 and mini slump cone experiments. Following is the general summary of the potential incompatibility problems identified using the early age stiffening test (ASTM C 359) performed on mortars from the perspective of the type of cement present in the test matrix (summarized in column 1 of Figure 4.2). This summary only serves to indicate the general trends observed and is not meant to be exhaustive list of incompatibilities. Discussions regarding fly ash cementitious systems, unless mentioned otherwise, pertain to mixtures prepared with 20% replacement of cement with fly ash.

- Plain cementitious mixtures prepared with cements C2 (high C_3A and low sulfate) and C4 (low C_3A and high sulfate) were found to exhibit false setting characteristics. Specifically, mixture C2 exhibited partial flash setting

TABLE 4.3
Chemical admixtures selected for the study

Chemical admixture	Type/chemical nature	INDOT recommended dosage (ml/100 kg)
WRDA 82 (W1)	Type A & Lignosulfonate based	195–390
Glenium 7500 (W2)	Type F & Poly-carboxylate type	130–260
Micro Air(A1)	Synthetic type	8–260
Pave Air (A2)	Vinsol resin (VR) based	16–260

NOTE: The upper limits of the INDOT's ranges were used for W1 and W2 admixtures except for 6 mixtures where the dosage was doubled (see section C.3.1 of Appendix C).

	1		2		3		4				
	Early age stiffening Test (mortars) (ASTM C 359)		Mini Slump Test (pastes)		Vicat's Set Time (pastes)		Semi-adiabatic Calorimetry Test (mortars)				
					Initial Set (mins)		Peak temp (F)		Time of peak (min)		
Mix #a	False set+	Flash set ++	False set*	Flash set**	Accb	Dlydc	Lwrdd	Incrsde	Accf	Dlydg	Secondary peaks
C1											No
C2	x	px									No
C3			x								No
C4	x			x							No
C1W1	x	px		x							No
C2W1	x		x	x	x					x	No
C3W1						x				x	No
C4W1	x			x		x				x	No
C1W2	x										No
C2W2	x			x		x					No
C3W2			x			x					No
C4W2	x					x					No
C1F1	x										No
C2F1	x		x				x			x	No
C3F1			x	x						x	No
C4F1	x									x	No
C1F2	x										No
C2F2	x	px			x		x				No
C3F2			x							x	No
C4F2			x							x	No
C1F1W1	x									x	No
C2F1W1	x				x				x		Yes
C3F1W1	x									x	No
C4F1W1	x			x		x				x	No

Figure 4.2 Summary of various incompatibility problems spotted in subtask-I of Phase I testing.

	1		2		3		4				
	Early age stiffening Test (mortars) (ASTM C 359)		Mini Slump Test (pastes)		Vicat's Set Time (pastes)		Semi-adiabatic Calorimetry Test (mortars)				
					Initial Set (mins)		Peak temp (F)		Time of peak (min)		
Mix #a	False set+	Flash set ++	False set*	Flash set**	Accb	Dlydc	Lwrdd	Incrsde	Accf	Dlydg	Secondary peaks
C1F2W1	x		x	x	x						No
C2F2W1	x		x	x	x		x				Yes
C3F2W1	x		x							x	No
C4F2W1	x					x				x	No
C1F1W2	x					x				x	No
C2F1W2	x		x	x	x				x		No
C3F1W2										x	No
C4F1W2						x				x	
C1F2W2	x		x		x					x	No
C2F2W2	x				x		x				No
C3F2W2			x							x	No
C4F2W2	x					x				x	No
C1F1W1A1	x			x						x	No
C2F1W1A1	x		x	x	x				x		Yes
C3F1W1A1										x	No
C4F1W1A1	x									x	No
C1F2W1A1	x			x						x	No
C2F2W1A1	x		x	x	x		x				Yes
C3F2W1A1	x		x		x					x	No
C4F2W1A1	x		x			-				x	No
C1F1W1A2	x			x							No
C2F1W1A2	x		x	x	x					x	No
C3F1W1A2											No
C4F1W1A2	x					x				x	No
C1F2W1A2				x					x		No
C2F2W1A2	x	px	x	x	x					x	No

Figure 4.2 Continued.

Mix #a	1		2		3		4				
	Early age stiffening Test (mortars) (ASTM C 359)		Mini Slump Test (pastes)		Vicat's Set Time (pastes)		Semi-adiabatic Calorimetry Test (mortars)				
	False set+	Flash set ++	False set*	Flash set**	Initial Set (mins)		Peak temp (F)		Time of peak (min)		Secondary peaks
C3F2W1A2			x	x							No
C4F2W1A2			x								No
C1F1W2A1	x										No
C2F1W2A1	x				x					x	No
C3F1W2A1						x					No
C4F1W2A1											No
C1F2W2A1	x										No
C2F2W2A1	x			x	x					x	No
C3F2W2A1											No
C4F2W2A1						x					No
C1F1W2A2	x					x					No
C2F1W2A2	x			x	x					x	No
C3F1W2A2			x			x					No
C4F1W2A2										x	No
C1F2W2A2	x			x					x		No
C2F2W2A2	x				x					x	No
C3F2W2A2			x		-						No
C4F2W2A2											No

(+) – A mixture was identified as false setting if the difference between 3 and 11 minute penetration of plunger measured following ASTM C 359 is greater than 40 mm and the fluidity is regained after remixing.
(++) – A mixture was identified as flash setting if the difference between 3 and 11 minute penetration of plunger measured following ASTM C 359 is greater than 40 mm and the remixing penetration is less than or equal to 10 mm.
px – Partial stiffening - a mixture was identified as partial stiffening if the difference between 3 and 11 minute penetration of plunger measured following ASTM C 359 is greater than 40 mm and does not completely regain fluidity
(*) – Mixture was identified as false set if false setting index (ratio of spread of pats at 5 and 2 minutes measured using the mini slump test) >1.3
(**) – Mixture was identified as flash set if stiffening index (ratio of spread of pats at 30 and 5 minutes measured using the mini slump test) < 0.8
a – Labels of mixtures in ***bold and italics*** font indicate base mixtures (i.e., C1, C1F1, etc.)
b – Indicates significant (>60 mins) acceleration of initial set time w.r.t. base mixture
c – Indicates significant (>60 mins) deceleration of initial set time w.r.t. base mixture
d – Indicates significant (>10 F) lowering of the maximum peak temperature
e – Indicates significant (>10 F) increase in the maximum peak temperature
f – Indicates significant (>60 mins) retardation of time of occurrence of the maximum peak temperature
g – Indicates significant (>60 mins) acceleration of time of occurrence of the maximum peak temperature

Figure 4.2 Continued.

behavior. Cements C1 and C4 by themselves did not show early stiffening behavior.

- It was observed that addition of lignin based Type A water reducing agent (W1) or poly-carboxylate (PC) type superplasticizer (W2) to plain cementitious mixtures containing high (>9%) C_3A and low (≤0.3) alkali cements (C1, C2) or low (7.7%) C_3A but over sulfated cement (C4) resulted in false setting behavior. In particular, C1W1 mixture exhibited partial false setting characteristics. However addition of W1 to C3 (high (10%) C_3A, high (3.6%) sulfate and high (>1%) alkali cement) did not result in abnormal stiffening behavior.
- Fly ash cementitious mixtures prepared with C1 or C2 (low (≤0.3) alkali cements) by 20% replacement of cement with class C ashes (F1 or F2) exhibited early stiffening behavior. However, no such behavior was observed when cement C3 (high (>1%) alkali cement) was replaced with the class C ashes.
- All the eight fly ash cementitious systems exhibited false setting characteristics when combined with W1.
- Fly ash cementitious prepared with cements C1 or C2 or C4 and W1 + A1 (synthetic type air entrainer) combination of chemical admixtures resulted in false setting characteristics.
- Addition of W2 to plain or fly ash cementitious mixtures (20% replacement by weight) containing low alkali cements (C1 or C2) resulted in early stiffening characteristics while no consistent trends were observed when W2 was added to the mixtures containing other cements.
- W2 when added along with A1 or Vinsol resin (VR) based air entraining agent (A2) to fly ash cementitious systems prepared with low alkali cements resulted in false setting characteristics. On the other hand, no such incompatibility problems were observed when W2 along with either of the air entraining agents (AEA) were added to high (>0.96%) alkali cements (C3 and C4).

Following is the summary of various incompatibility problems identified using the mini slump cone experiments performed on pastes (summarized in column 2 of Figure 4.2). Formulae for calculation of stiffening index (S.I.) and false setting index (F.S.I) are given in Appendix B.

- Addition of W1 to plain cementitious mixtures prepared with C1, C2 or C4 cements exhibited flash setting (S.I. <0.8) behavior.
- Only C2 plain cementitious mixture exhibited severe slump loss (S.I. < 0.8) characteristics when W2 was added while no stiffening related problems were observed when W2 was added to C1 or C4 plain cementitious mixtures.
- 20% replacement of cement C3 with either of the class C ashes resulted in false setting (F.S.I. >1.3) characteristics. In particular, C3F2 mixture was also found to exhibit early stiffening characteristics. However no stiffening related problems were identified by mini slump cone testing when C1 cement was replaced by fly ash.
- Although addition of W1 or W2 to some of the fly ash cementitious mixtures resulted in stiffening related problems, no distinguishable trends were observed. However, addition of W1 along with A1 or A2 to fly ash cementitious systems prepared with low alkali cements (C1 or C2) resulted in flash setting behavior.
- Similarly, W2 when added along with A2 to fly ash cementitious mixtures containing cement C3 resulted in false setting behavior while no such problems were observed when W2A2 combination of chemical admixtures were added to C4 fly ash cementitious mixtures.

4.1.2 Abnormal Setting

Following are the major conclusions drawn from Vicat's set time experiments performed on various paste mixtures (summarized in column 3 of Figure 4.2). The initial set time of all the combinations were compared with their corresponding base mixtures to identify significant changes in the setting time.

- Pronounced acceleration (≥60 mins) of the initial set time was observed when W1 was added to plain cementitious mixture prepared with low (0.3%) alkali and low (2.4%) sulfate cement (C2). However, significant (≥60 mins) retardation was observed when W1 was added to the high alkali and high sulfate cements (C3 and C4).
- Addition of W2 to high alkali and high sulfate cements (C3 or C4) or to low alkali and low sulfate cement (C2) resulted in significant delay of the initial set time w.r.t. to the base mixtures (plain cements without admixtures).
- Severe acceleration of set time was observed when W1 or W2 was added to fly ash cementitious mixtures prepared with cement C2 while fly ash cementitious mixtures prepared with cement C3 did not lead to incompatibility problems.
- W1 or W2 when added along with either of the AEAs (A1 or A2) to the fly ash cementitious mixtures prepared with cement C2 resulted in significant acceleration of the set time.

4.2 Fly Ash Driven Incompatibility Problems

4.2.1 Abnormal Stiffening

This section presents abnormal stiffening problems (columns 1 and 2 of Figure 4.2) which arose due to the presence of fly ash in the mixtures. Numerous cases were found from the ASTM C 359 testing where mixtures prepared with one type of class C fly ash resulted in abnormal stiffening problems while the other did not. 20% replacement of C4 by F1 (has lower sulfate content compared to that of F2) resulted in false setting characteristics while 20% replacement of C4 by F2 resulted in a normal stiffening combination. Also, W2 when combined with C4F1 system resulted in false set but exhibited normal stiffening characteristics when mixed with C4F2 system. Similarly C1F1 and C4F1 fly ash cementitious mixtures prepared by added W1A2 admixture combination resulted in false setting characteristics. However no such incompatible behavior was observed when F2 was used instead of F1.

Mini slump cone tests identified similar behavior where specific type of class C ash resulted in abnormal stiffening characteristics while the other did not. Following is the list of such cases. C2F1 and C4F2 fly ash cementitious mixtures were found to be false setting while C2F2 and C4F1 mixtures were found exhibit normal stiffening behavior. Addition of W1 to fly ash

cementitious system containing F2 and either of the low alkali cements (C1 or C2) resulted in rapid slump loss (S.I.<0.8) and false setting characteristics whereas fly ash cementitious mixtures prepared F1, low alkali cements and W1 exhibited normal stiffening behavior.

Addition of W1A1 or W1A2 admixtures combination to fly ash cementitious mixtures containing high alkali cements (C3 or C4) and F2 resulted in false setting characteristics. Using F1 instead of F2 eliminated the incompatibility problem. Also, C1F2 fly ash cementitious system when mixed along with W2A2 admixtures combinations resulted in flash setting behavior while no such behavior was observed when F1 was used in the place of F2.

4.2.2 Abnormal Setting

Following is the list of abnormal setting behavior can be attributed to fly ash in the mixtures (summarized in column 3 of Figure 4.2). The initial set times of various combinations were measured using the Vicat's set time experiment and were compared with their corresponding base mixtures to spot significant changes in the setting behavior.

In certain combinations, change in the fly ash source significantly altered the set time w.r.t. to base mixture. Addition of W1 to C1F2 system resulted in severe acceleration of the initial set whereas C1F1W1 mixture had set time very similar (change <60 mins) to the base mixture. Similarly, addition of W2A1 admixture combination to C3F1 retarded the initial set time while no such incompatibility was observed with C3F2 system.

In a few other cases, change in the fly ash source actually converted a slow setting mixture to rapid setting mixture. Addition of W2 to C1F1 system delayed the initial set time w.r.t. to base mixture. Whereas addition of W2 to C1F2 combination significantly accelerated the initial set time.

4.2.3 Effect of Fly Ash Content on Compatibility of a Mixture

Effect of higher volumes of class C ashes on early stiffening and abnormal setting related incompatibility problems was studied on a few selected mixtures (Section C.3.4). High (>30%) volumes of class C ash induced abnormal stiffening behavior in six out of sixteen HVFS mixtures which were found to be otherwise compatible at 20% replacement levels. Except for $C1F2_{(30)}W2A1$, all the higher volume fly ash cementitious mixtures significantly accelerated the initial set time w.r.t. to the corresponding 20% fly ash cementitious mixtures. Eleven out of the sixteen HVFS mixtures had initial set time less than or equal to 45 minutes. Higher (≥30%) replacement of cement by class C ashes also resulted in development of secondary peaks in nine out of the sixteen mixtures tested using the semi-adiabatic calorimetry. This suggested that the addition of class C ash in higher volumes affects the hydration process.

The amount of class F fly ash in a mixture also had a significant effect on the requirement of air entraining agent to produce stable air voids. ASTM C 185 and foam index testing indicated that the volume of class F ash had a significant effect on the amount of air entraining agent (AEA) required to produce a stable foam layer. The requirement for the dosage of AEA increased with the amount of class F ash in the system irrespective of the type of air entraining agent (see Figures 4.3 and 4.4).

4.3 Admixtures Driven Incompatibility Problems

This section summarizes various incompatibility problems which arise due to admixtures-binder interactions as well as admixture-admixture interactions. Admixture related problems are manifested them-

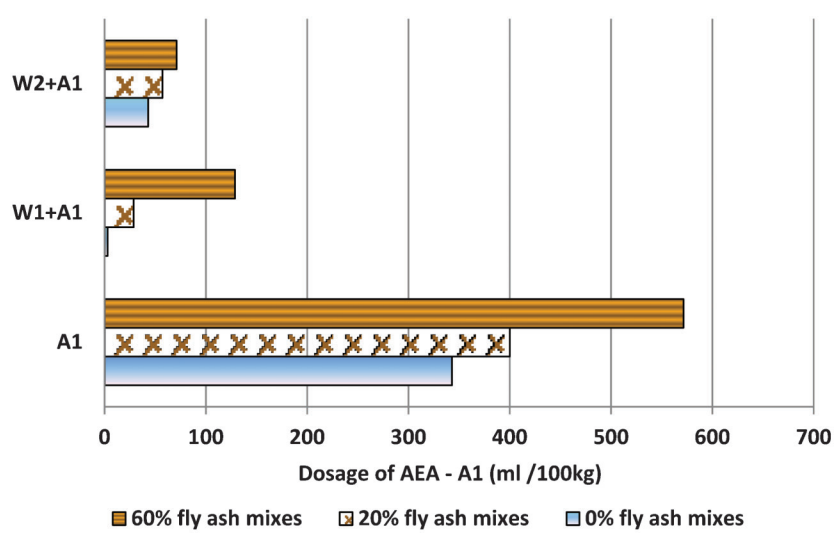

Figure 4.3 Effect of fly ash content on the requirement of AEA: ASTM C 185 test results of mixtures with A1.

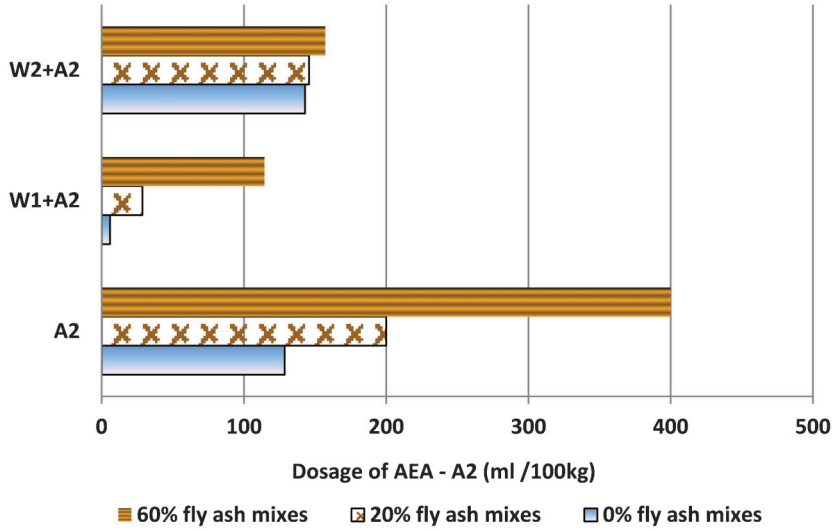

Figure 4.4 Effect of fly ash content on the requirement of AEA: ASTM C 185 test results of mixtures with A2.

selves as abnormal stiffening, abnormal setting and changes in characteristics of heat of hydration curves obtained from semi-adiabatic calorimetry (columns of Figure 4.2).

4.3.1 Abnormal Stiffening

Various early age stiffening problems caused by admixture interactions are reported in this section (columns 1 and 2 of Figure 4.2). Following is the list of stiffening related incompatibility problems identified using the early age stiffening test performed according to the ASTM C 359.

- W1 or W2 when added to plain cementitious mixtures prepared with cement C1, otherwise compatible, resulted in false setting characteristics.
- Addition of W1 to fly ash cementitious mixtures containing cement C3F1 resulted in false setting characteristics which were otherwise compatible when no admixtures were added. However, no such incompatible behavior was observed when W2 was used as the water reducer instead of W1.
- A similar phenomenon was observed when W1 and A1 admixtures were added to fly ash cementitious mixtures containing cement C4. W1A1 addition resulted in false setting characteristics while addition of W2A1 in the place of W1A1 to the fly ash cementitious mixtures containing cement C4.
- Addition of W1 along with A2 to C3 fly ash cementitious mixtures eliminated the false setting characteristics which were observed when W1 alone was added to C3F1 or C3F2 systems.

Also, mini slump test identified that addition of W1 to low alkali cements (C1 or C2) was associated with rapid slump loss (S.I. <0.8) characteristics. Similar findings were observed when W2 was added to plain mixtures prepared with C2. However, no incompatibility problems were observed when W2 was added to C1 plain mixtures for the water reducing action.

4.3.2 Abnormal Setting

Addition of W1 or W2 to plain cementitious mixtures prepared with high alkali and high sulfate cements (C3 or C4) resulted in significant retardation of the initial set time. Mixtures prepared with W1 and plain systems prepared with C2 exhibited very rapid setting behavior while severe retardation of set occurred when W2 added, in the place of W1, to the mixture (column 3 of Figure 4.2).

Severe accelerating effect was identified when W1 or W2 were added to fly ash cementitious mixtures containing cement C2. Fly ash cementitious mixtures prepared with C4 and either of the WRAs (W1 or W2) exhibited significant retardation of set time w.r.t. base mixtures. However, retarding effect due to addition of W1 alone to C4 systems was eliminated when W1A1 admixture combination was used instead. Similarly the abnormal setting characteristics observed when W2 was added to fly ash cementitious mixtures containing cement C1 were eliminated by using the W2A1 admixture combinations.

4.3.3 Changes in Characteristics of the Hydration Curves

Significant delay in the time of maximum peak temperature was observed in plain cementitious mixtures based on C2, C3 and C4 cements with W1 added (summarized in column 4 of Figure 4.2). Addition of W1 to fly ash cementitious mixtures prepared with cement C2 resulted in a significant decrease in maximum peak temperature and development of secondary peaks indicating changes in the hydration process. Addition of W1 or W2 to fly ash cementitious mixtures containing cements (C3 or C4) delayed the occurrence of maximum peak.

4.3.4 Changes in the Demand for AEA

With respect to the ability to obtain the desirable and stable air void system, the incompatibility problems manifested themselves in the form of an increased demand for the air entrainer quantity (see Figures 4.3 and 4.4). Foam index test identified, in general, that the demand (dosage requirement) of A2 AEA was greater than that of the A1. ASTM C 185 indicated that addition of either of the water reducing agents (W1 or W2) significantly reduced the amount of AEA (A1 or A2) dosage required to produce a stable air void system. Additionally, mixtures prepared with W1 required lower AEA dosages compared to that of mixes with W2.

4.3.5 Early Age Stiffening Test on Mortars (ASTM C 359) vs. Mini Slump Test Method

Both early age stiffening tests on mortars (ASTM C 359) and mini slump tests on pastes were performed to identify potential false and flash setting behavior of mixtures. 45 out of 68 mixtures tested using ASTM C 359 test were identified as false setting mixtures while only four mixtures were identified as mixtures exhibiting partial flash setting characteristics. On the other hand, mini slump test identified 22 flash setting mixtures and 13 mixtures that exhibited false setting characteristics. Thus ASTM C 359 was found to be ineffective in identifying flash setting behavior and overestimated false setting characteristics. Similar conclusions were also reported by Tang and Bhattacharja (*3*). The ineffectiveness of ASTM C 359 test method was attributed to less intense mixing action and short (11 minutes) duration of the experiment. Therefore only the findings from mini slump test method were used to formulate recommendations to mitigate stiffening related incompatibility problems.

4.4 Effect of Miscellaneous Factors on Compatibility of Mixtures

Effect of the following miscellaneous factors was investigated on few mixtures selected on the basis of findings from subtask I of Phase I.

1. Double dosage of water reducing admixture (WRA) with respect to the INDOT's recommended maximum value
2. Temperature
3. Delayed addition of admixtures

The use of the double dosage of the WRA was motivated by the desire to address the issue of the accidental overdose of the admixture during the production of the mixture or the introduction of additional amount of admixture as the result of an attempt to "save" the mixture experiencing premature stiffening. Section 6.1 reports the findings from the study related to double dosage of WRAs. Section 6.2 reports the major conclusions that highlight the significance of temperature followed by summary of observations from the delayed addition study in Section 6.3.

4.4.1 Double Dosage of Water Reducing Agents

The influence of increased dosage of plasticizers was studied on three, each, normal and early stiffening mixtures. Dosages of W1 and W2 were chosen to be double the INDOT's maximum recommended values (see Table 4.3) recommendations. Mini slump tests, semi-adiabatic calorimetry and Vicat's set time experiments were performed on each of the six mixtures (Section C.3.1 of Appendix C).

Mini slump experiments indicated that the three early stiffening mixtures prepared with double dosage of WRAs still exhibited abnormal stiffening characteristics. However, double dosage of WRA had no effect on the compatibility of normal stiffening mixtures.

Semi-adiabatic calorimetry results recorded significant changes in time of occurrence of the max peak temperature in five of the six mixtures. Initial set times of five out of the six mixtures tested were significantly altered by addition of double dosage of WRA. In general, double dosage of W1 severely accelerated the set time.

4.4.2 Temperature

The effect of low (10°C) temperature on compatibility was evaluated on three-normal and slow stiffening mixtures while normal and early stiffening mixtures were used to study the effect of high (37°C) temperature. The basis for selection of specific temperature was explained before in Section B.2.1. Mini slump tests, semi-adiabatic calorimetry and Vicat's set time experiments were used to draw study the effect of temperature (Section C.3.2 of Appendix C).

Mini slump tests at low temperature identified that two of the six mixtures tested resulted in false setting behavior. Semi-adiabatic calorimeter testing indicated longer dormant periods and serious retardation in the time of occurrence of maximum peak temperature. Low temperature treatment of the slow stiffening mixtures retarded the initial set though this effect was significant only in one of the mixtures.

Five of the six mixtures tested using the mini slump tests at high temperature were found to exhibit abnormal stiffening characteristics. Semi-adiabatic calorimeter experiments performed at high temperature indicated significant acceleration of the occurrence of the maximum peak temperature in four out of six mixtures tested. Abnormal secondary peaks were observed in the remaining two mixtures which indicated significant changes that occurred in hydration process. Figure 4.5 presents the effect of high temperature (HT) on semi-adiabatic temperature profile of early stiffening mixes. Also, severe acceleration of the initial set time was recorded in all the mixtures tested at high temperature using the Vicat's initial set time experiments.

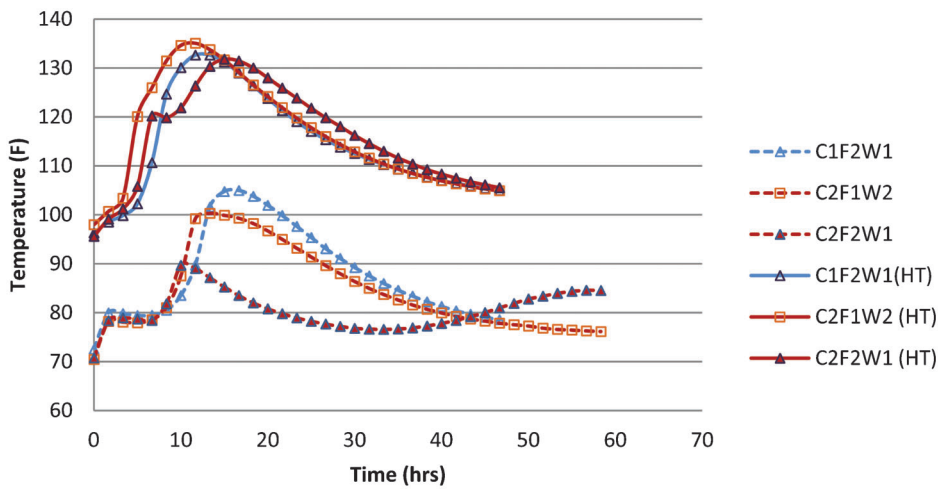

Figure 4.5 Effect of high temperature (HT) on semi-adiabatic temperature profile of early stiffening mixes.

4.4.3 Delayed Addition of Chemical Admixtures

Effect of delayed addition of admixtures on the compatibility was studied on three-normal and slow stiffening mixtures. The following conclusions were drawn from the semi-adiabatic calorimetry and Vicat's set time experiments performed on each of the combinations (Section C.3.3 of Appendix C).

No significant changes in the semi-adiabatic temperature profile curves were observed except in two mixtures. Time of maximum peak in two of the three normal (compatible) mixtures was significantly altered w.r.t. that of mixtures prepared with simultaneous addition of admixtures.

Delaying the addition of admixtures by 60 s significantly altered the initial set time, w.r.t. mixtures prepared with simultaneous addition of admixtures, in five of the six mixtures tested. Pronounced acceleration of initial set time was observed in four of the six mixtures prepared by delayed addition of admixtures while, retardation of set time occurred in the remaining two mixtures. It is therefore inferred that the effect of delayed addition depends on the chemical nature of components in the mixture.

4.5 Results of Concrete Testing

A total of 10 concrete mixtures were studied in Phase III of the research work to validate the results from Phase I and Phase II testing. Four concrete mixtures were used to study abnormal stiffening problems while the remaining six mixtures were used for air void related study. A brief summary of results is presented below. (Details are presented in the Appendix D)

The two early stiffening mixtures selected for the concrete testing exhibited significant (>50 mm) slump loss within 60 minute from the start of mixtures. On the other hand, the two slow stiffening mixtures did not show significant slump loss; thus validating the findings from the early stiffening study performed in Phase I on various paste and mortar mixtures. Semi-adiabatic calorimetric testing of concrete samples identified development of secondary peaks in C2F2W1 mixture similar to that observed in experiments performed in Phase I on the mortar samples. 7-day average compressive strength of all the four samples was greater than the critical value of 3000 psi. 56-day compressive strengths of early stiffening mixtures were higher (at least 8%) than that of the slow stiffening mixtures.

Five incompatible mixtures were selected based on the Phase II testing for concrete testing. An additional concrete mixture was also studied to evaluate the effect of temperature on air voids stability. Total air content of the fresh concrete was found to decrease significantly (>30%) in all the six concrete mixtures tested within 60 minutes from the start of mixing. Thus the less stable air void characteristics of the mixtures selected from Phase II were also confirmed through concrete testing. 7-day compressive strengths of the two high (60%) volume fly ash cementitious mixtures and high temperature mixture were less than the critical value of 3000 psi. Also, the 56-day strengths of these three mixtures were significantly (at least >30%) less than that of the remaining three mixtures (see Figure 4.6).

4.6 Statistical Modeling

Statistical modeling was performed using the results of mixtures tested in subtask I of Phase I. The prediction models were constructed using the SPSS statistical package. Stepwise linear regression modeling was adopted wherein chemical characteristics of binder and dosages of chemical admixtures were used to model initial set time and mini slump parameters (details are presented in the Appendix E). The C_3A, SO_3 and Na_2O_{equ} contents of the binder, along with the type of plasticizer, were found to be statistically significant in predicting the initial set time as well as the areas of spread measured at 2, 5 and 30 minutes.

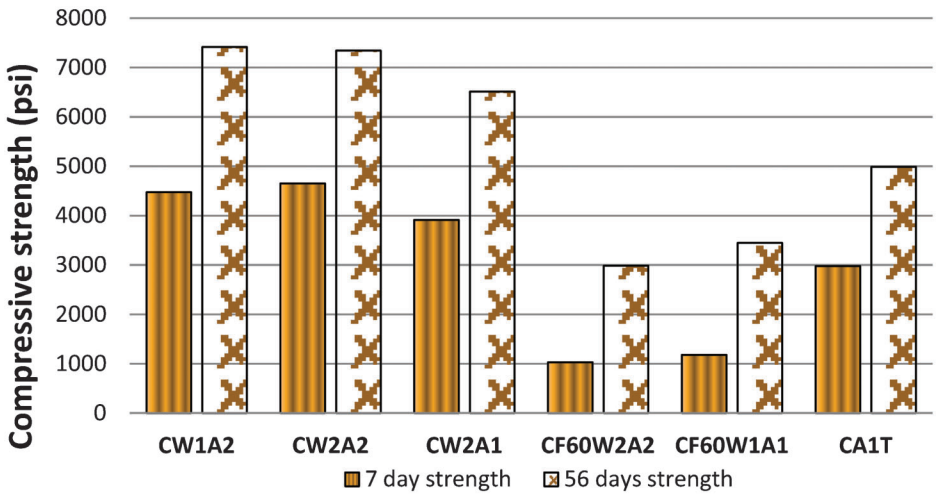

Figure 4.6 Summary compressive strength results of concrete samples cured at 23°C.

5. CONCLUSIONS

Even though all (except for one cement) were initially selected to result in potential problems only 45 out of the 70 mixtures (combinations) tested in the sub-phase I of Phase I did so while the remaining 25 mixtures were identified as compatible. The observed signs of incompatibilities included rapid stiffening of the mixtures, significant changes in set behavior and/or the hydration process.

In general, cements with high C_3A content and low sulfate content were more prone to incompatibility problems. It was also observed that mixes with Type A WR (W1) had higher tendency for rapid stiffening than mixes with PC type superplasticizer (SP). The addition of W1 to high C_3A content and low sulfate content fly ash cementitious systems resulted in significant changes to the hydration process. Increased replacement of cement by class C ashes often aggravated the rapid stiffening and abnormal setting behavior of the mixtures. Also, in most of the cases, other factors (amount of admixture or the timing of addition) further aggravated the problem of incompatibility.

Fly ash content and the type of admixtures present in the mixture significantly influenced both the generation and the stability of air void system. AEA requirement increased with the increase in the class F ash content. Mixtures prepared with W2 and AEA were found to be more unstable compared to the mixtures prepared with other admixture combinations.

Various incompatibility problems observed during the concrete testing were consistent with the findings from the corresponding paste and mortar experiments. Concrete mixtures prepared with high (60%) volumes of class F ash exhibited poor strength development.

6. RECOMMENDATIONS TO AVOID INCOMPATIBILITY PROBLEMS

This section presents the recommendations to avoid incompatibility problems based on the findings from the present work. The recommendations to avoid potential early stiffening and abnormal setting problems were developed using findings from mini slump, Vicat's set time and semi-adiabatic calorimeter experiments. Foam drainage, foam index and air content in mortars tests were used to develop guidelines to prevent air void related incompatibility problems. Figure 6.1 presents the list of incompatible combinations of materials and can be used as a practical field aid for quick check of potentials problems, especially in cases when materials source change occurred during the construction.

Two other factors (increased addition levels of WRAs and delayed addition of admixtures) resulted in mixed results. Both these practices accelerated the set time in some mixes but had no effect on other mixes. Hence, it is recommended not to use either of these practices during construction. If it is imperative to use either of these practices, then it is recommended to do a preliminary study as outlined in Figure 6.2. Various test methods and the corresponding limiting criteria to identify potential incompatibility problems are listed in Table 6.1. This table can also serve as a practical field guide.

Potential Incompatibility Problems	Cements*				Class F Ash		Class C Ash		Plast.**		AEA		Temp.	
	C1	C2	C3	C4	20%	60%	20%	> 20%	lignin based	PCSP	Synthetic	VR	Low	High
Early stiffening behavior observed as rapid slump loss	x								x					
		x							x					
				x					x					
		x								x				
	x								x		x			
	x								x		x			
		x							x			x		
		x							x			x		
False set characteristics			x				x							
			x				x			x		x		
Severe acceleration of initial set		x							x					
		x					x			x				
Severe acceleration of initial set and changes in the hydration process		x					x		x					
														x
Retardation of initial set			x	x					x					
			x	x						x				
Results in significant changes to the hydration process and rapid setting								x	x					
								x		x				
Extended dormant region and false set characteristics													x	
Increases the dosage requirement of AEAs					x	x								
Significant increase in total air content									x		x			
Less stable air void system	x					x				x	x			
	x				x					x		x		
	x					x				x		x		
Low compressive strength	x					x								
	x										x			x

*Following are the chemical properties of the cements listed:
C1 – High (>=9%) C_3A; moderately high (3.2%) sulfates; low (<=0.3%) total alkalis.
C2 – High (>9%) C_3A; low (2.4%) sulfates; low (<=0.3%) total alkalis.
C3 – High (>9%) C_3A; moderately high (3.6%) sulfates; low (1.04%) total alkalis.
C4 – Low (<=7.7%) C_3A; high (3.6%) sulfates; high (0.97%) total alkalis.
**Indicates type of plasticizer in the mixtures.

Figure 6.1 List of material combinations and associated incompatibility problems.

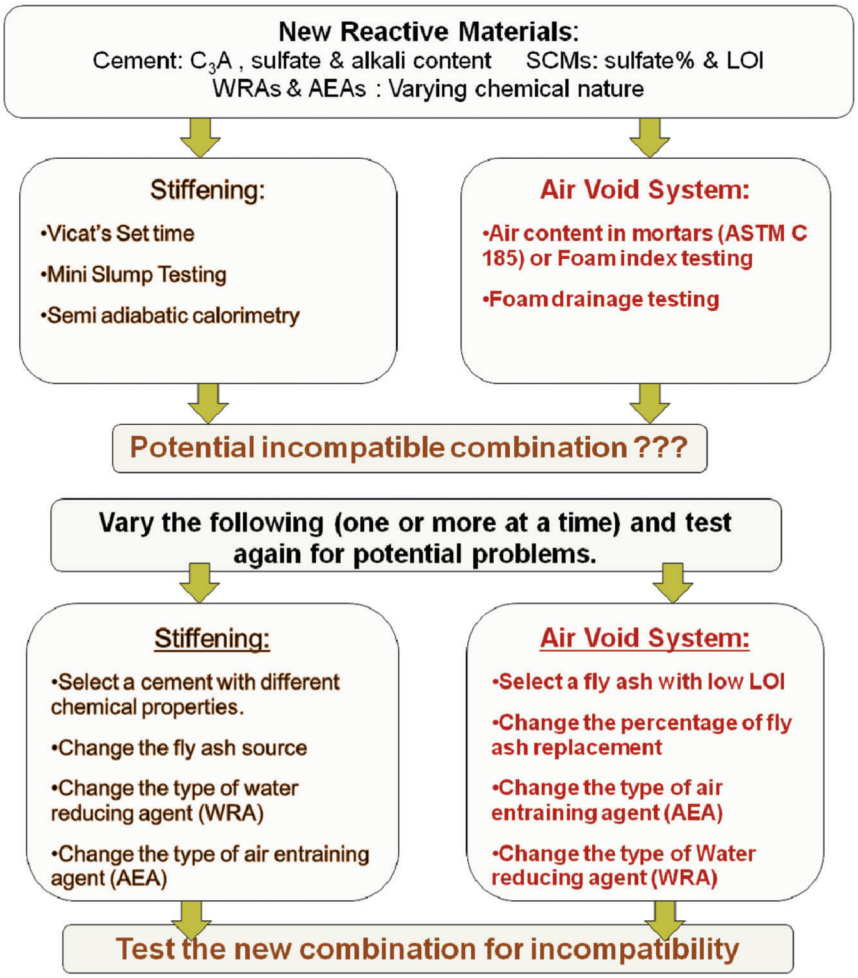

Figure 6.2 Guidelines for preliminary incompatibility study.

TABLE 6.1
Test methods and limiting criteria to identify incompatibility problems

Test method	Limiting criteria
Vicat's set time (pastes) (ASTM C 191)	• Change in initial set time by 60 min or more w.r.t. base mixture is significant and can be an indication of potential incompatibility.
Mini slump cone test (pastes)	• False setting index (F.S.I. = $Area_{5\ min}/Area_{2\ min}$) greater than 1.3 indicates potential problem with placement, especially when the concrete is mixed only for a short time. • Stiffening index (S.I. = $Area_{30\ min}/Area_{5\ min}$) when calculated to be less than 0.8 implies the problem of rapid stiffening.
Semi-adiabatic calorimetry (mortars)	• Changes in the time of occurrence of the maximum peak temperature being greater than 60 minutes w.r.t. the base mix indicates a potential incompatibility. • Change in the maximum peak temperature by 6°C (10°F) or more was considered significant. • Development of secondary peaks indicates that something significant has changed in concrete composition.
Foam index test (slurries)	• A change in the amount of air-entraining admixture required to achieve a stable and complete coverage of foam of more than 30% w.r.t. base mix was considered significant.
Air content in mortars (ASTM C 185)	• A change in the amount of air-entraining admixture required to achieve 18 +/− 2% air (in the mortars) of more than 20% compared to base mixture was considered to be an indication of potential incompatibility.
Foam drainage test (slurries)	• Mixtures were ranked based on the values of % foam drainage and 1/K where a low value of 1/k in combination with high value of % foam drainage represents a mix with potentially unstable air void system.

APPENDIX A. LITERATURE REVIEW

A.1 INTRODUCTION

The focus of the literature review was to collect and critically review information on incompatibility problems in concrete related to cementitious materials and chemical admixtures. The major objectives of the present literature review were to:

- Establish the role of various construction materials in determining the compatibility of a mixture. This included an up-to-date list and nature of unexpected problems occurring in the field as well as in laboratory studies.
- Study the effect of miscellaneous factors like temperature, delayed addition and increased dosage of admixtures on compatibility.
- List various test methods and the corresponding limiting criteria used to evaluate incompatible combinations.

This chapter is divided into six sections. The Section A.1 provided a brief introduction to the Appendix A followed by Section A.2 which summarizes the chemistry of cement hydration and the contribution of various components of cement clinker towards incompatibility problems. Section A.3 focuses on the effect of fly ash usage on the compatibility of a mixture followed by a listing of various admixture driven incompatibility problems in Section A.4. Section A.5 discusses other incompatibility problems occurring due to miscellaneous reasons. Section A.6 of this chapter briefly describes different test methods used in previous studies to identify various incompatibility problems.

A.2 CHEMISTRY OF CEMENT HYDRATION

Basic knowledge of cement composition and the corresponding hydration reactions is necessary to understand causes of incompatibility problems. This section summarizes the various phases of cement clinker and the chemistry of the hydration reactions involved.

Tri-calcium aluminates (C_3A), Tetra-calcium alumino-ferrites (C_4AF), Tri-calcium silicates (C_3S or alite) and di-calcium silicates (C_2S or belite) are the major components of cement clinker that can undergo hydration reaction. Alite and belite are commonly referred as calcium silicates, while C_3A and C_4AF are termed as interstitial phases. Various phases of cement clinker are shown in Figure A.1.

The two calcium silicates are the major cementitious components of the cement. Calcium hydroxide and CSH gel, major component responsible for strength gain and hardening of concrete, are the two products resulting from the hydration of calcium silicates hydration reaction. In general, C_3S hydration characterizes the behavior of cements as it is the major (around 60%) component of regular cement clinkers and its hydration reaction is faster than that of the C_2S. Hydration reactions of C_3S and C_2S are given by Equations A.1 and A.2.

Hydration reaction of the C_3A phase is very violent and it is constrained by addition of sulfate (usually in the form of gypsum) to the cement clinker. Uncontrolled C_3A hydration due to improper aluminate-sulfate balance is responsible for early stiffening behavior of mixtures. C_3A hydration in presence of adequate sulfates forms Ettringite ($C_6A\hat{s}_3H_{32}$) which forms a layer on the C_3A particle preventing it from further hydration. Eventually ettringite decomposes to form mono sulfate ($C_4A\hat{s}H_{12}$) when the sulfate in the system depletes (*5*). Equations A.3, A.4 and A.5 present the hydration reactions of C_3A and equation A.6 shows hydration of C_4AF. In all the equations listed below, commonly adopted abbreviations are used to represent various chemical components, where C = CaO; H = H_2O; A= Al_2O_3; F = Fe_2O_3; S = SiO_2; $\hat{s}$ = SO_3; CH = $Ca(OH)_2$

$$\underset{\text{(CSH gel)}}{2C_3S + 11H \rightarrow C_3S_2H_8} + \underset{\text{(calcium hydroxide)}}{3CH} \tag{A.1}$$

$$\underset{\text{(CSH gel)}}{2C_2S + 9H \rightarrow C_3S_2H_8} + CH \tag{A.2}$$

$$C_3A + 26H \rightarrow 3C\hat{s}H_2 + \underset{\text{(Ettringite)}}{C_6A\hat{s}_3H_{32}} \tag{A.3}$$

$$\underset{\text{(Ettringite)}}{2C_3A + 4H \rightarrow C_6A\hat{s}_3H_{32}} + \underset{\text{(mono-sulfate)}}{3C_4A\hat{s}H_{12}} \tag{A.4}$$

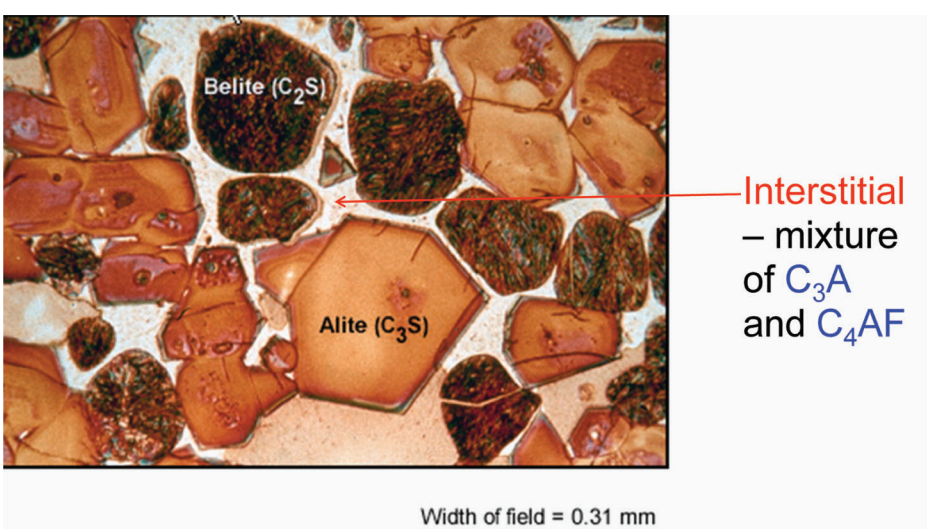

Figure A.1 Clinker as viewed under petro-graphic microscope (*4*).

$$3C_3A + 12H \rightarrow CH + C_4A\hat{s}H_{13} \quad \text{(mono sulfate)} \tag{A.5}$$

$$C_4AF + 10H \rightarrow 2CH + C_6AFH_{12} \tag{A.6}$$

Hydration reaction is exothermic in nature and rate of heat release curves can be used to identify various phases of hydration reaction. Figure A.2 summarizes the heat release signature of a typical ASTM type I/II cement obtained through isothermal calorimetric testing. Zones A to D represent significant phases of hydrations reaction. Cement hydration is divided in to five major phases:

1. **Dissolution phase:** Dissolution phase, indicated by 'A' in Figure A.2 is associated with rapid dissolution of ions (soluble alkalis and sulfates) in to the solution and rapid evolution of heat. Rapid hydration of very fine C_3S along with tri-calcium aluminates (C_3A) phases is responsible for the heat generation.
2. **Dormant phase:** Dormant phase, indicated by 'B' in Figure A.2 is also known as induction period. It is the phase that allows for the transportation of concrete to job site.
3. **Acceleration phase:** Cement particles undergo rapid hydration and setting of the mix begins in the acceleration phase, represented by 'C' in Figure A.2. This phase consists of both the initial onset of the acceleration phase and final setting.
4. **Deceleration phase:** Hydration reaction shifts from dissolution type to diffusion controlled reaction during this phase. This phase is sometimes associated with a hump (secondary peak, represented by 'D' in Figure A.2), which indicates sulfate depletion in the system. When the soluble sulfate in the system decreases, Ettringite formed during the initial reaction between C_3A and sulfates, transforms to mono sulfate releasing sulfate into the system.
5. **Steady state phase:** And the final stage of hydration is slow and is a completely diffusion controlled reaction. And this ultimately leads to the hardening of the mix.

A.3 CEMENT DRIVEN INCOMPATIBILITY PROBLEMS

This section discusses in brief about the major components of cement which govern the compatibility of a mixture along with a list of incompatibility problems associated with each of the components. Section A.3.1 summarizes the role of C_3A content in governing the compatibility of mixture. Section A.3.2 describes the importance of sulfate content. A brief discussion on the significance of alkali content is presented in Section A.3.3. This is followed by few comments on role of fineness and cement content in Section A.3.4.

A.3.1 Significance of Tri-Calcium Aluminate Content (% C_3A)

Aluminates are the most reactive phase in the cements and consume a lot of water during their hydration process. In the absence of adequate sulfates, aluminates undergo rapid early hydration resulting in flash setting and workability problems. Also, a porous calcium aluminates hydrate is formed if C_3A is allowed to completely hydrate first. As a result, hydration products of the remaining components would form in the porous frame work adversely affecting the strength characteristics of the mixture (*5*).

Certain superplasticizers, poly naphthalene sulfonate (PNS) type in particular, get preferentially adsorbed on the aluminate phase (*7*). This was reported to be the reason for reduced plasticizing effect of certain water reducing admixtures. Similar findings were reported by Zingg et al. (*8*) in relation to the adsorption of poly-carboxylate (PC) type superplasticizers. Competitive adsorption between sulfate ions and carboxylic groups of PC superplasticizer was thought to be the reason for shift of the sulfate depletion peak.

A.3.2 Significance of Sulfate Content (%SO_3)

Sulfate content is a significant factor which governs the nature and occurrence of incompatibility problems. Major incompatibility issues like early age stiffening, delayed setting times, rapid slump loss, and, poor early strength development can all be related to inadequate or excess sulfate contents. It is well established that reactions between sulfate and aluminates are the basis of majority of stiffening related incompatibility problems. Appropriate sulfate-aluminate balance in a cementitious system is critical to attain appropriate workability and strength as well as for performance of admixtures (*9*).

In sulfate deficient systems, the rapid hydration of C_3A yields calcium aluminate hydrates and leads to flash setting characteristics. In the presence of excessive sulfate (anhydrite and hemi hydrate forms of sulfate), nucleation and growth of gypsum crystals, in association with short concrete mixing time

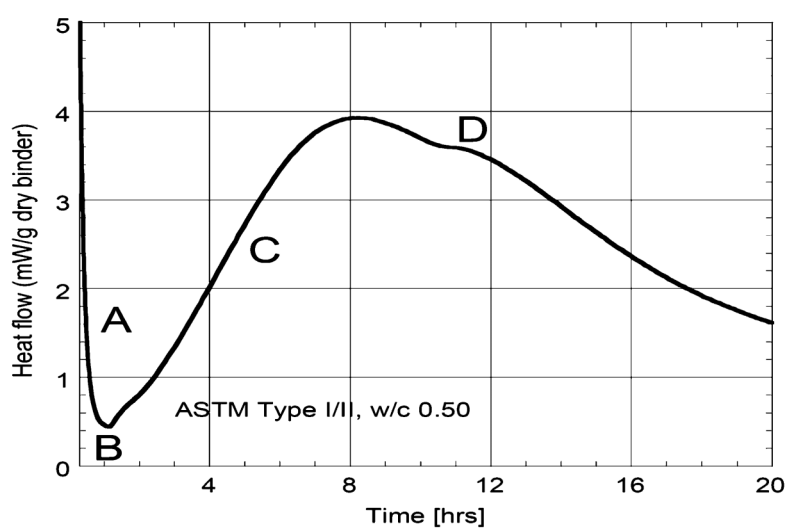

Figure A.2 Rate of hydration of cement w.r.t. time obtained from isothermal calorimetry (*6*).

can lead to false setting behavior (*6*). Also a system with high sulfate content is more prone to serious durability problems like deterioration due to sulfate attack. Standards like ASTM C 150 have set upper limit on the sulfate content of cements confirming to ASTM C 150. The specification set a maximum of 3% on the sulfate content in system with C_3A content less than 8% and 3.5% in a system which has C_3A content more than 8%. It was also reported by Taylor et al. (*10*) that one state in particular limited the maximum sulfate content to 3%. However, there are no specifications regarding the minimum of sulfate content in the system which is necessary to control the violent aluminate hydration reaction.

Sulfates also play a key role in preventing retardation of calcium silicate hydration due to presence of ferrite (Fe_2O_3). It was reported (*6*) that in under-sulfated cements with high ferrite content, a layer of iron hydrates of low solubility is formed around the silicates delaying the normal hydration process. Therefore, presence of adequate sulfates is also necessary to prevent coating of ferrite products on calcium silicates.

The nature of sulfates in the pore solution strongly influences the performance of chemical admixtures (*5*). Andersen et al. (*11*) reported that amount of superplasticizer adsorption, measured using an UV-spectrophotometer, varied inversely with the concentration of calcium sulfate. Ohno and Yamamoto (*12*) studied viscosities of cement pastes with poly-carboxylate type superplasticizer prepared by adding alkali sulfates. It was found that fluidity was decreased as the alkali sulfate content increased. This was attributed to the shrinking of EO chains (responsible for fluidity through steric repulsions) in presence of high soluble sulfates.

Thus it is crucial to have an optimum amount of soluble sulfates in the mix to assure compatible mixes. Solubility of sulfates is also dependent on the form in which they are present in the cement clinker. Thus knowledge of form of sulfate present in the system would help identify potential problems and appropriate measures can be taken to avoid such phenomena. The order of solubility of various forms of sulfates is listed below (*6*):

Alkali sulfate (calcium langbeinite) > plaster of Paris (calcium sulfate hemi hydrate) > chemical anhydrite (soluble calcium sulfate anhydrite) > gypsum (calcium sulfate di-hydrate) > syngenite > natural anhydrite.

A.3.3 Significance of Alkali Content (% Na_2O_{equ})

The amount of soluble alkalis present in the system during the first few minutes of hydration was found to be a key parameter in controlling fluidity of cement paste made with superplasticizer (*13*). Increase in alkalis in the system accelerate the hydration of cementitious materials and therefore result in rapid setting and difficulties with placement and curing of concrete. Prince et al. (*14*) found that cementitious system containing high soluble alkali sulfates content experienced problems related to rapid stiffening. This was believed to be due to the lack of crystalline ettringite formation in the presence of high alkalis. Also, premature deterioration of concrete pavements was correlated to the alkali content in cementitious materials by Jennings et al. (*15*).

The amount of soluble alkali content was found to strongly influence the adsorption of various chemical admixtures. Kim et al. (*16*) found that adsorption of PNS type plasticizer is low in a system with high soluble alkali content when compared to that with low alkali content. It was also reported that adsorption of SNFC (sulfonated naphthalene formaldehyde) type superplasticizer was found to be higher in low alkali system than in the high alkali ones (*17*). Jiang et al. (*13*) established (in a system with sulfonated superplasticizer) optimum soluble alkali content required to increase initial workability and avoid loss of fluidity to be on the order of 0.4–0.5%. It was found that addition of Na_2SO_4 to mixtures with suboptimal alkali content increased the initial fluidity while addition of Na_2SO_4 to mixtures with super-optimal alkali content decreased the initial fluidity.

Alkali content of the cement was also thought to be significant parameter affecting the air void system (AVS) in concrete. Concretes with low alkali content were prone to problems related to AVS stability. Also alkali content of the cement was found to influence the amount of air entraining agent (AEA) required to attain required air content. The amount of AEA required to produce concrete mixtures with moderate and high cement alkali level (0.60% or greater) 6 $\pm$ 1% air was about 50% lower than in concrete mixtures containing low-alkali cement. It was reported by Dubovoy et al. (*18*) that concretes with low alkali cement and VR AEA exhibited very high spacing factor valued at 90 mins (0.53 mm) when compared to that at 10 mins (0.15 mm). Also concretes prepared with an air-entraining admixture based on salts of wood resins (NVR) showed a tendency for less severe scaling at the highest cement-alkali content.

Pigeon et al. (*19*) observed similar results in their study on the influence of soluble alkalis on air void system stability. Test matrix included VR based & synthetic AEAs and two superplasticizers: naphthalene based and melamine based. Air void system characteristics (air content and spacing factor) were studied at 10 min, 30 min and 60 mins from the start of the mixing. Significant increase in the spacing factor was observed in mixes with low alkali cements in certain cases after addition of superplasticizers.

In a separate study by Plante et al. (*20*), it was suspected that high alkali content of cement helped produce a stable air void system. A comprehensive study on the loss of strength in concrete pavements was conducted by the SDOT (*21*). It was concluded that low alkali cement and synthetic air entrainer combination resulted in severe loss of strength and higher temperatures often aggravated this problem.

A.3.4 Fineness and Content of Cement

Requirement of admixture dosages for performance increases with increase in the fineness of cementitious materials, as well as, with increase in cement content. This is due to the increase in the surface area available for adsorption with increase in either of the two parameters. Also, increased fineness of the cement can change the dissolution rate of various ions. In general, water requirement increases with increase in fineness of components. This is especially significant in systems with silica fume and ultrafine mineral admixtures like micronized diatomite (*10*). However this cannot be considered as an incompatibility issue as it is known fact that increase in the water demand is due to increased surface rather than unexpected interactions induced due to increased fineness or cement content.

A.4 INCOMPATIBILITY PROBLEMS DRIVEN BY FLY ASH

Feedback from contractors working for INDOT indicated that class C fly ash and non-chloride accelerators combination when used in mixes placed in northern Indiana results in severe set retardation. Wang et al. (*22*) reported that class C fly ash prolonged the onset of acceleration phase and hence caused retardation with ASTM type I and II cements. This behavior was found to be much more pronounced when the fly ash cementitious system was prepared with water reducing agent and retarding admixtures. Ravina and Mehta (*23*) studied setting characteristics of fresh concrete mixtures containing large amounts of fly ash (35 to 50% replacement). It was observed that the initial set time was severely delayed by more than 4 hours (in comparison with control mixture that has no fly ash) in certain fly ash cementitious mixtures. It was also found the delay in setting time was also higher for mixtures containing class C ash than that of mixtures with class F ash.

However, addition of fly ashes may introduce reactive aluminate phases like C_3A and Klein's compound (calcium sulfo-aluminate) which disturb the delicate sulfate-aluminate balance resulting in serious stiffening related problems. Also, sulfates and alkalis that come along with fly ash may disturb the sulfate balance of the system (*24*). In a response to request of information by Taylor et al. (*10*) regarding incompatibility problems in the field, it was reported that excessive stiffening and poor strength occurred in field concrete prepared with cement

and fly ash along with water reducing agent. Another case of material incompatibility was also reported in same survey where, presence of class C ash was thought to be one of the significant parameter responsible for the problem. Jennings et al. (*15*) cited the use of Class C fly ash as one of the factors strongly associated with pavement deterioration.

Thus fly ash replacement was associated both with retardation of hydration process and as well as with early stiffening characteristics. The exact reasons for the problems related to fly ash addition are not clearly known. It is believed that the free lime, sulfates, alkalis and aluminates in the fly ash are the key parameters that influence the compatibility (*24*).

Unburned carbon particles in fly ash were found to be major reason for variable AEA dosage requirement. Gebler and Klieger (*25*) observed as much as 59% reduction in air content after 90 minutes (from completion of mixing) in concretes made with class F ash. It was also observed that concrete with class C ashes had less loss in air when compared to that concrete with class F ashes.

Zhang (*26*) studied the effect of pozzolanic fly ashes on air entrainment. It was has found that the inclusion of fly ash in concrete increases the AEA dosages from one to five times that required in plain Portland cement concrete. Data from this study showed that concrete mixes with VR based AEAs gave the lowest retention of air content and highest variability with source of fly ash.

The carbon content of fly ash is usually thought to have higher adsorptive surface areas than Portland cement grains. The higher dosage requirement of AEAs was attributed to the following properties of unburned carbon particles in fly ash: (1) the amount; (2) the specific surface area; (3) the accessibility of the surface area; (4) the chemical nature of the surface (*27,28*). In general, class C fly ashes were found to have carbon with much higher specific surface areas than Class F ash does. However, worst case scenario is offset in class C ashes due to lower LOI value than class F ashes (*27*).

A.5 ADMIXTURE DRIVEN INCOMPATIBILITY PROBLEMS

Lignin based WRAs are one of the commonly used water reducing agents in concrete production. Dodson and Hayden (*29*) reported that addition of lignin based water reducing agents reduced the solubility of sulfates, sulfates in the form of anhydrite in particular. This leads to a sulfate-starved system in the concrete which results in rapid set and increased rate of concrete slump loss. Sandberg and Robert (*6*) stated that similar observations were reported by Khalil and Ward (*30*). In response to the request for information by Taylor et al. (*10*) regarding incompatibility problems in the field, it was reported that lignosulfonate based WRA when used with low alkali cement resulted in severe retardation in concrete. Aitcin et al. (*31*) also stated that excessive dosage of lignosulfonate based water reducing agents resulted in strong retardation and excessive entrainment of large air bubbles.

Superplasticizers (SPs) are commonly used in low w/c ratio mixes to obtain high slump for longer durations. Hanehara and Yamada (*32*) reported that both PNS (poly naphthalene sulfonate) and PMS (poly melamine sulfonate) type SP were not suitable for ready mix concrete which require a long slump retention and hence are restricted to factory production in Japan. In the feedback collected from contractors working for INDOT, it was reported that very high dosage of a specific Type F (high range water reducing) admixtures created excessive retardation of the mix during use in cool weather (i.e., it took weeks to gain strength for construction operations to continue). Hanehara and Yamada (*33*) reported that high alkali sulfates (which were added externally in the form of Na_2SO_4) in the mixture were found to increase the amount of poly-carboxylate type of superplasticizers required to obtain optimum fluidity.

Traditionally VR based AEAs were used for air entrainment. Later, various other types of AEAs were used due to limited supply of VR based AEA and relatively higher costs. Nagi et al. (*34*) in their study, found that type of AEA admixture had a statistically significant effect on the spacing factor and hence the durability of the concrete. Various incompatibility problems related to air void system parameters and stability were reported when VR based and synthetic AEAs were used for air entrainment.

Cross et al. (*21*) observed that use of synthetic AEAs with low alkali cements resulted in low compressive strength of concrete. Similar conclusions were drawn in a field study conducted for New Jersey DOT where use of synthetic AEA was found to be the predominant factor resulting in low compressive strengths. Similar findings also were observed in a study by SDOT (*21*) which investigated low compression strengths in concrete. It was concluded that use of synthetic AEAs results in air void clustering around the aggregates which in turn resulted in de-bonding of aggregates and low compressive strengths.

Similarly, results from research by Ansari et al. (*35*) indicated that concretes produced by the synthetic air entraining admixtures exhibited lower compressive strengths than those produced by Vinsol resin agents. The primary reason for the strength loss associated with the Synthetic air-entraining admixtures was creation of larger air bubbles (voids) by these admixtures

Admixture- admixture interactions were also reported to be cause of various incompatibility problems. Contractors working for INDOT, reported that high variability in the amount of entrained air and its sensitivity to temperature was observed in the presence of poly-carboxylate superplasticizers (HRWR).

Wang et al. (*36*) studied the effect of admixture interactions on the hydration process using an isothermal calorimeter. It was reported that type D (water reducing and retarding) admixture when used with type F (high range water reducer) admixture resulted in severe delay of onset of acceleration. Bedard and Mailvaganam (*37*) reported that addition of lignin based water reducer (WRA) to concrete along with AEAs substantially increased the total air content. Despite the two fold increase in air content, the specific surface of the bubbles was substantially reduced. When the addition is delayed, the stability of the AVS is further reduced. These adverse effects were attributed to sugars and other contaminants present in commercial lignosulfonates and superplasticizers. Lignosulfonate based plasticizers were reported (*38*) to reduce the surface tension of water and thus can have adverse effect on the air entrainment.

A.6 EFFECT OF MISCELLANEOUS FACTORS ON COMPATIBILITY OF A MIXTURE

This section discusses various kinds of incompatibility problems associated with miscellaneous reasons like retempering, addition of increased dosage of admixtures, delayed addition of chemical admixtures and temperature.

Retempering (late addition of water to restore fluidity) and addition of increased dosage of plasticizer are some of the practices seen in hot weather concrete mixing. Kozikowski et al. (*39*) reported that retempering aggravated the problem air void clustering in concrete system made with non-Vinsol based admixtures. Air void clustering is associated with de-bonding of aggregates and low strength in concrete samples. Addition of increased dosage of water reducing admixtures may affect the strength development. Also, severe slump loss has been encountered in certain cement and superplasticizer combinations (*31*). Plante et al. (*20*) reported that increased dosage of water reducing admixtures had negative influence on the production and stability air void system.

Delayed addition of plasticizers is sometimes practiced to enhance the performance of the admixtures in the system. Masood and Agarwal (*40*) observed that the delayed (split) addition of superplasticizers increased the flow up to 15%. Similar observations were made by Uchikawa et al. (*41*) that delayed addition of PNS based; PC type and lignin sufonic type admixtures improved the flow of cement pastes. Significant retardation of set time also occurred in all the cases of delayed addition. Chiocchio and Paolini (*42*) studied the effect of delayed addition of sulfonated naphthalene and melamine formaldehyde based admixtures on the workability of paste systems. It was recommended that addition of admixture should be delayed until the beginning of dormant phase

of cement hydration (without admixture) to obtain maximum workability.

Construction temperature is thought to be significant factor which makes it difficult to control air content. Hot weather concrete mixing and placing require higher dosage of WRAs and is often associated with rapid slump loss. The increased water demand is due to acceleration of hydration reaction under high temperature conditions. Also, higher dosages of AEAs were required at high temperatures to attain the required air content. An increase of concrete temperature from 21 to 38 C may reduce air contents by 25% (*43*). Higher temperatures also aggravated the incompatible combinations of synthetic AEA and low alkali cement (*21*). From the information provided by INDOT contractors regarding incompatibilities in the field, it was concluded that a very high dosage of a specific Type F HRWR admixtures created excessive retardation of the mix during use in cool weather.

A.7 TEST METHODS TO IDENTIFY INCOMPATIBILITY PROBLEMS

This section presents various test methods used to study the common incompatibility problems. A detailed explanation of the procedure and the limiting criteria adopted for various experiments used in this study is provided in Appendix B.

A.7.1 Tests on Pastes and Mortars

This section lists the various experiments that were performed on pastes and mortars to identify problems related to early stiffening, irregular set time, slump loss characteristics and inappropriate air void system.

A.7.1.1 Experiments to Identify Early Stiffening Behavior

ASTM C 451 and ASTM C 359 are the two standard test methods to evaluate early age stiffening behaviors of pastes and mortars respectively. ASTM C 359 test method, more common among the two, was used to examine if a mixture under study stiffened quickly and whether the fluidity is recovered after remixing. Early stiffening rate and early stiffening amount were calculated based on the penetration of 10 mm plunger measurements made at 3, 5, 8, 11 minutes and after remixing the mixture. However, it was reported by Wang et al. (*44*) reported that in some cases, ASTM C 359 test alone could not be used to explain the origin of false and flash setting behaviors. Tang and Bhattacharja (*3*) also observed that these methods are not very effective due to the usage of low intensity mixers.

Mini slump test was first used by Kantro (*45*) for evaluating the effect of water reducing agents on the workability of plain cement pastes. A provisional standard, AASHTO TP54, for the mini slump cone method was first published in 1997 which was reconfirmed in January, 2000. A high intensity paste mixing was used to simulate the shearing action involved in concrete mixing. The diameter of spread of mini slump cones was measured at regular intervals of time until 60 minutes from the beginning of mixing. Modified forms of this test were used to evaluate the performance of WRAs and stiffening characteristics of mixtures by various researchers (*3,46,47*).

A.7.1.2 Rheological Measurements

Helmuth et al. (*48*) studied abnormal concrete performance in the presence of admixtures using rheological measurements. Results of shear stress at yield and plastic viscosity, measured using the viscometer were correlated with results from the mini slump testing. Park et al. (*49*) studied the rheological properties (yield stress and plastic viscosity) of cementitious systems containing finely ground blast furnace slag, fly ash and silica fume. Similar measurements were also by Hanehara and Yamada (*32*) to study rheology and early age properties of cement systems.

A.7.1.3 Experiments to Identify Set Irregularities

Vicat's set time experiment performed according to the ASTM C 191 is most common method of estimating initial and final setting time of paste samples. Initial set time is when the 1 mm diameter needle penetrates to a depth of 25 mm while final set time is when the needle fails to make a circular impression on the surface of the paste sample.

Set times, measured using penetrometer, are recorded according to the ASTM C 403 on mortars, obtained by sieving fresh concrete on a #4 sieve. Initial set is when a pressure of 3.5 MPa (500 psi) is required to penetrate a one inch diameter plunger in to the sieved mortar sample. Mixture is considered to final set when a pressure of 27.6 MPa (4000 psi) is required to penetrate one inch.

A.7.1.4 Heat of Hydration Measurements

Calorimetric measurements were commonly used to measure heat of hydration. Isothermal conduction calorimeter experiments were performed on small paste samples while adiabatic and semi-adiabatic calorimeter methods were used to monitor temperature profile of mortar and concrete samples.

Adiabatic calorimetry was used to simulate conditions similar to that present in the center section of a very large cross-section concrete structures. It was reported by Poole (*50*) that adiabatic temperature rise in the center of mass concrete is important. This is because cracking in mass concrete is caused due to temperature differentials between interior section and exterior skin of concrete. Fick (*51*) recommended guidelines for using adiabatic calorimeter in the field conditions to identify various early age stiffening related incompatibility problems.

Semi-adiabatic calorimeter (SAC) is same as the adiabatic calorimeter except that some loss of heat is allowed in SAC. Taylor et al. (*52*) reported that change in the time and magnitude of the temperature peak and an observation of any secondary peaks can help in identification of incompatibility problems. Semi-adiabatic calorimetry was also used by various researchers (*10,53,54*) to study the effect of fly ash addition, influence of admixtures and significance of w/c ratio on cement hydration.

A.7.1.5 Experiments to Identify Problems with Air Void System

Foam index test, foam drainage test and ASTM C 185 are the three test methods that were used to identify air void related incompatibility problems in paste and mortar samples.

Taylor et al. (*10*) attributed the first foam index testing to Dodson in 1980 to determine the stability of air void system in concrete. In this test method, the amount of AEA dosage required to form a stable uniform layer of foam on the liquid surface is estimated. Abnormal changes in the required dosage of AEA w.r.t. base mix indicate potential incompatibility problem. Gebler and Klieger (*25*) used this test method to estimate the amount of AEA required to produce adequate air void system in fly ash mixtures and also to evaluate the stability of air void system.

Air content in mortars is determined according to the ASTM C 185.% Air content in mortars is estimated by measuring the weight of 400 ml of mortar samples. Lashley (*47*) estimated the amount of AEA to attain 18 $\pm$ 2% air content in mortars. Correlation between the results of foam index testing and that of the ASTM C 185 was studied.

Foam drainage testing was first used by Guttman (*55*) to study the stability of air voids. This tested was later modified by Cross et al. (*56*). Drainage of water from the foam produced using high intensity mixer is monitored for 60 minutes. Taylor et al. (*10*) also used this method to evaluate the stability of air voids produced by different air entraining agents.

A.7.2 Tests on Concrete Samples

This section summarizes various test methods used to study early age stiffening and air void related problems in concrete samples.

A.7.2.1 Concrete Slump Test

In literature, workability of concrete is commonly represented by the slump measured following the ASTM C 143. Slump retention characteristics of fresh concrete in presence of various mineral and chemical admixtures were studied by measuring the slump at regular intervals until the end of 60 to 90 minutes (*3,10,47*).

A.7.2.2 Total Air Content Measurement in Fresh Concrete

All the incompatibility studies reviewed, which involve testing of concrete mixtures, measured total air content in fresh concrete is measured following the ASTM C 231 standard. This is the most common test method for quality control in ensuring durable concrete. In general, the total air content in a concrete mixture measured according to ASTM C 231 is targeted to be around 6.5 $\pm$ 1%. However, it is widely known that total air content alone cannot ensure freeze thaw and scaling durability as frost resistance is dependent on the size and spacing factor of the entrapped air.

A.7.2.3 Experiments to Evaluate Air Void Parameters

The evaluation of air void parameters in the hardened concrete is typically performed using ASTM C 457 method. This method has been employed by numerous researchers (*10,39,57,58*) to measure air void parameters like Spacing ratio, surface area of void per unit volume, size of air voids and identify signs of air void clustering. In this experiment, air voids of concrete samples are microscopically examined on a cut and polished section.

Air void analyzer (AVA) is a novel technology developed in mid 1980s in the Europe. Air void analyzer, unlike the microscopic analysis, is used to measure the air void parameters of fresh concrete. Working of AVAs based on the Stoke's law and is performed on mortars collected from fresh concrete. In simple terms, it is based on the fact that larger air bubbles travel faster through a column of liquid compared to that of smaller bubbles. It was reported (*10*) that Maine State DOT evaluated the use of AVA during 1998 construction season. Many research works (*10,59,60*) tried to correlate the results from air void analyzer to the findings from ASTM C 457.

A.7.2.4 Compressive Strength of Concrete Samples

Virtually every published work on the incompatibility involved evaluation of compressive strength of concrete performed according the ASTM C 39. This test was usually performed on 4 in. $\times$ 8 in. cylindrical concrete samples at 1, 3, 7, 28 and 56 days from the time of casting. This test method was used to evaluate strength gain characteristics of concrete samples.

Apart from the experiments discussed above, ultrasonic measurements and impedance measurements were also made to predict the setting of concrete samples. Adiabatic and semi-adiabatic monitoring of temperature in concrete samples was commonly used to evaluate incompatible combinations. Figure A.3, test methods proposed to study incompatible problems (*61*), summarizes the various test methods recommended by Taylor et al. (*61*) to identify various incompatibility problems.

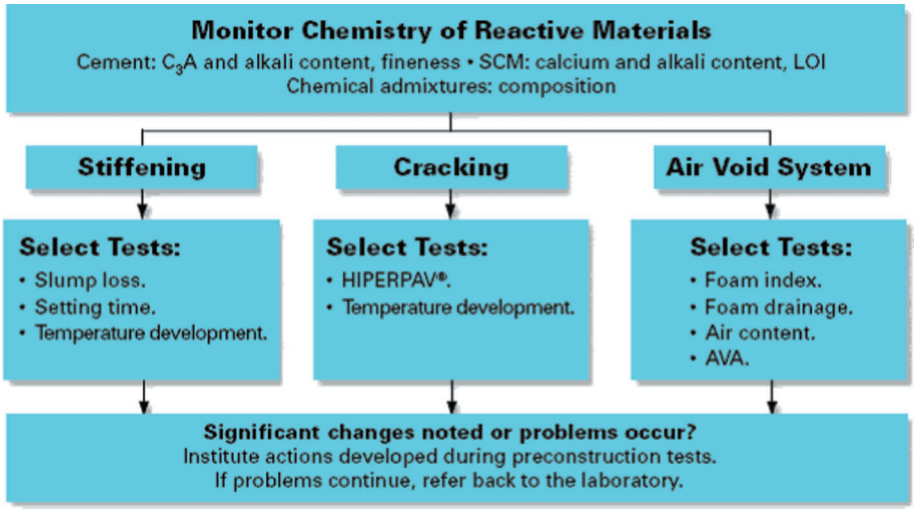

Figure A.3 Test methods proposed to study incompatible problems (*61*).

APPENDIX B. EXPERIMENTAL PROGRAM

This appendix is divided in to five major sections summarizing the details of the research program. Section B.1 discusses about the types of cements, fly ashes and chemical admixtures used in the study. Next in Section B.2, the various phases of the experimental program are explained. In Section B.3, the concrete mix proportions that have been tested are presented. In Section B.4, the nomenclature followed in naming the mixes is detailed. Finally in Section B.5, the test methods used to identify incompatibility problems are presented.

B.1 MATERIALS

Four cements, two class C ashes and one class F ash with different chemical compositions were used in this study. Along with the cementitious materials, two types of water reducing agents (WRA) and two types of air entraining agents (AEA) were also included in the test matrix. All the raw materials were selected from the Indiana department of transportation (INDOT) approved list of materials except for one class F fly ash. This fly ash with high loss on ignition value (LOI) was chosen to study the incompatibility problems related to production and stability of the air void system. All the materials used in the study were selected to result in incompatibility problems, except for one cement (C4).

B.1.1 Cements

Based on the literature review, the content of tri-calcium aluminates (C_3A), the content of sulfate (SO_3) and the total content of alkali (Na_2O_{equ}) were identified to be significant parameters which govern compatibility of a mixture. A list of about 40 cements along with their chemical properties was compiled from the various research studies performed to understand the incompatibility problems. Among them the cements, and their respective chemical compositions, associated with various incompatibility problems were identified. Out of the 26 cements, thus chosen, 21 cements exhibiting the incompatibility problems had the following composition (see Figure B.1):

- Sulfate content was found to be in the range of 2.5% to 3.5%;
- Low alkali content (<0.5%) as well as high alkali content (>1%) was present.

High C_3A content (≥10%) in cement was targeted to increase the potential for stiffening behavior.

The chemical properties of all the four cements, along with their labels, used in the study are summarized in Table B.1. Cements C1, C2, and C3, were classified as ASTM C 150 type I cements while C4 was ASTM C 150 Type I/II Portland cement. Mill certificates comprising the chemical and physical properties of all the cements are presented in Figures B.2 through B.5.

B.1.2 Fly Ash

Two class C ashes (F1 and F2) were used in this research work to study abnormal setting and stiffening related incompatibility problems. Mixtures with either of these two ashes were found to cause incompatibility problems. Tanikella (*2*) reported that fly ash cementitious mixtures with F1 ash resulted in delay of initial setting time where as those with F2 were found to accelerate the initial set. One class F ash (F3) with high L.O.I., which represents the amount of carbon content, was selected to study air content related problems. Properties of the three ashes are presented in Table B.2 and a complete list of chemical and physical properties are listed in Figure B.6 and Figure B.7.

B.1.3 Chemical Admixtures

Two water reducing agents (WRA) and two air entraining agents (AEA) were used to study the effect of interactions between binder and admixtures on compatibility. Both the WRAs and the AEAs confirmed to the ASTM C 494 and have different Chemical properties. Table B.3 lists the admixtures used along with their chemical nature and INDOT recommended dosages.

B.2 EXPERIMENTAL PLAN

The present research work is divided in to three major Phases. This section summarizes the objectives and important details of each phase. The objectives of Phase I was to identify incompatible problems related to early age stiffening and abnormal setting time in paste and mortar samples. Problems related to air voids production and stability was studied in the Phase II followed by concrete testing in Phase III.

B.2.1 Phase I

In the Phase I, various tests were performed to identify incompatibility problems related to early age stiffening, erratic set time and abnormal slump loss behaviors. Both plain and fly ash cementitious (20% replacement of cement by fly ash by weight) systems were studied. Phase I testing is further divided into two subtasks (see Figure B.8).

Objective of subtask I is to identify the combinations of materials which result in stiffening related incompatibility problems. In total, 68 different combinations comprising of four cements, two class C ashes and four chemical admixtures were studied. Mini slump and Vicat's set time experiments were performed on the pastes while early age stiffening test and semi-adiabatic calorimetry were performed on the mortars for all the 68 combinations.

In the subtask II of Phase I, the effects of the following miscellaneous factors on compatibility were studied on a few selected mixtures.

- Effect of increased dosage of plasticizer.
- Effect of temperature.
- Effect of delayed additions of chemical admixtures.

Based on the results obtained from Phase I testing, three mixtures, each, which exhibited highest early stiffening and slow stiffening characteristics were identified along with three mixtures which were found to be normal compatible behavior. These few selected mixtures were used to study the effect of various miscellaneous factors.

To study the effect of increased dosage of admixtures the amount of water reducing agents double that of INDOT

TABLE B.1
Chemical properties of the four cements

	Cements			
Chemical properties	**C1 (Type I)**	**C2 (Type I)**	**C3 (Type I)**	**C4 (Type I/II)**
C_3A content %	9	10	10.1	7.7
SO_3 content%	3.0	2.4	3.6	3.6
Na_2O_{equ}%	0.29	0.3	1.04	0.97

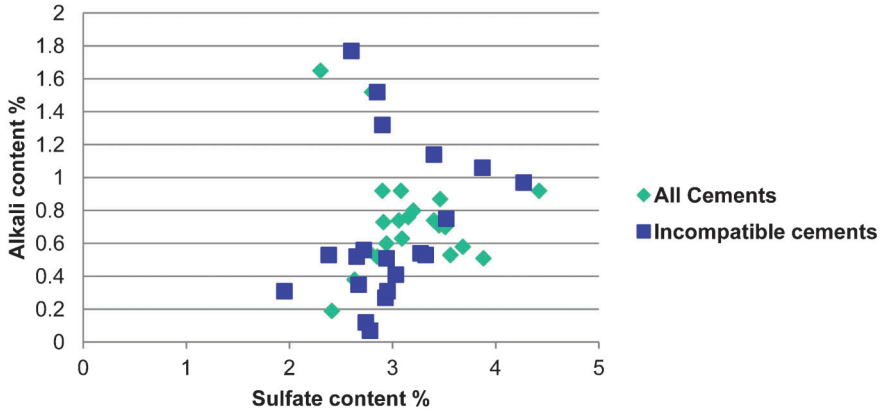

Figure B.1 Alkali and sulfate content of cements used in various incompatibility studies.

Cement Analyte	Min limit	Max limit	0143
SiO2			20.59
Al2O3			4.76
Fe2O3			1.96
CaO			63.77
MgO			2.68
SO3			3
Na2O			0.13
K2O			0.25
TiO2			0.35
P2O5			0.11
Mn2O3			0.13
SrO			0.03
Compounds (C150):			
C3S			60
C2S			14
C3A			9
C4AF			6
Total Alkali Na2O eq			0.29
Free CaO			1.02
L.O.I(950deg)			2.61
Water Soluble:			
Na2O			0.01
K2O			0.09
Na2O eq			0.08
SO3			
Cement Fineness			
BSA (m2/kg)			379
Density (g/cc)			3.15
-325 Sieve (%)			
D[v,0.5]			12.79
<6.6%			32.6
C-359 with 180 g water			181 g H2O
2 min (Temp)			78.6
3 min			43
5 min			23
8 min			12
11 min			8
Remix			25

Figure B.2 Mill certificate of cement C1.

LAFARGE NORTH AMERICA

CEMENT MILL TEST REPORT

CONSIGNEE:

YEAR:	**2009**
MONTH:	**June**
PLANT:	**Paulding**
CEMENT TYPE:	**I**

PHYSICAL DATA		
Fineness by Air Permeability *(m^2 /kg; ASTM C204)*		401
Fineness by 45 um (No. 325) Sieve		
(% passing; ASTM C430)		96
(% retained; ASTM C430)		4
Compressive Strength *(ASTM C109 / C109M)*	**Mpa**	**psi**
1-day	15.5	2245
3-day	26.8	3892
7-day	35.9	5210
28-day (previous month)	44.7	6486
Time of Set, Vicat (Truck Samples) *(initial minutes; ASTM C191)*		112
Air Content of Mortar *(%; ASTM C185)*		8
Autoclave Expansion *(%; ASTM C151)*		0.19

CHEMICAL ANALYSIS	**Percent**
Silica Dioxide *(SiO_2; ASTM C114)*	20.0
Aluminum Oxide *(Al_2O_3; ASTM C114)*	5.3
Ferric Oxide *(Fe_2O_3; ASTM C114)*	2.3
Calcium Oxide *(CaO; ASTM C114)*	63.6
Magnesium Oxide *(MgO; ASTM C114)*	3.2
Sulphur Trioxide *(SO_3; ASTM C114)*	2.6
Loss on Ignition *(L.O.I.; ASTM C114)*	1.8
Insoluble Residue *(ASTM C114)*	0.27
Free Lime *(f-CaO)*	1.0
Tricalcium Silicate *(C_3S; ASTM C150)*	61
Tricalcium Aluminate *(C_3A; ASTM C150)*	10
Equivalent alkalies *(NaEq, %)*	0.41

Certified by:

John R. Judd II, Optimization Manager
July 9, 2009

The cement represented by this analysis is certified to comply with the current ASTM C-150 and AASHTO M-85 specifications. The cement was produced at the Lafarge North America Paulding Plant in June 2009.

CEMENTITIOUS GROUP / PAULDING PLANT
11435 Road 176, P.O. Box 160
Paulding, Ohio 45879

Figure B.3 Mill certificate of cement C2.

Buzzi Unicem USA

Stockertown Plant
501 Hercules Drive

Stockertown, PA 18083
Phone:
Fax:

Mill Test Report

Cement Type: Type I Light
Manufacture Date: N/A
Silo Number:

From: July 1, 2009
To: July 31, 2009

Chemical		Physical		
SiO2 (%)	20.1	Time of Set (Vicat)		
Al2O3 (%)	5.2	Initial Set (min.)	106	
Fe2O3 (%)	2.1	Final Set (min.)	219	
CaO (%)	61.8	Compressive Strength	PSI	MPa
MgO (%)	3.7	1 Day	2949	20.3
SO3 (%)	3.6	3 Day	4051	27.9
Total Alkali (Na2O + 0.658K2O)	1.04	7 Day	4900	33.8
		28 Day	5767	39.8
Ignition Loss	1.2			
Insoluble Residue (%)	0.25	Cube Flow		
C3S (%)	50.7	Fineness, Blaine (cm2/g)	3998	
C2S (%)	19.5	325 Mesh (%)	92.9	
C3A (%)	10.1	Air Content (%)	7.0	
C4AF (%)	6.4	Normal Consistency (%)	27.8	
C3S + 4.75C3A	98.7	False Set (%)	73	
CO2 (%)	-	Autoclave Expansion (%)	0.23	
Limestone (%)	-	ASTM C563 (%)	4.6	
CaCO3 in Limestone (%)	-	ASTM C1038 (%)	0.007	

We certify that the above described cement, at the time of shipment, meets the chemical and physical requirements of ASTM C-150, AASHTO M-85, or ASTM C-91.

Charles Ogle, Manager of Quality Control

Date: 8/10/2009 12:47:02PM

Figure B.4 Mill certificate of cement C3.

Buzzi Unicem USA

Stockertown Plant
501 Hercules Drive

Stockertown, PA 18083
Phone:
Fax:

Mill Test Report

Cement Type: Type I/II
Manufacture Date: N/A
Silo Number:

From: July 1, 2009
To: July 31, 2009

Chemical		Physical		
SiO2 (%)	20.7	Time of Set (Vicat)		
Al2O3 (%)	4.4	Initial Set (min.)	130	
Fe2O3 (%)	2.4	Final Set (min.)	249	
CaO (%)	61.6	Compressive Strength	PSI	MPa
MgO (%)	4.1	1 Day	2963	20.4
SO3 (%)	3.6	3 Day	4156	28.7
Total Alkali (Na2O + 0.658K2O)	0.97	7 Day	5058	34.9
		28 Day	6163	42.5
Ignition Loss	0.9			
Insoluble Residue (%)	0.25	Cube Flow		
C3S (%)	49.9	Fineness, Blaine (cm2/g)	4006	
C2S (%)	21.8	325 Mesh (%)	92.7	
C3A (%)	7.7	Air Content (%)	6.6	
C4AF (%)	7.3	Normal Consistency (%)	26.8	
C3S + 4.75C3A	86.6	False Set (%)	69	
CO2 (%)	-	Autoclave Expansion (%)	0.24	
Limestone (%)	-	ASTM C563 (%)	4.2	
CaCO3 in Limestone (%)	-	ASTM C1038 (%)	0.006	

We certify that the above described cement, at the time of shipment, meets the chemical and physical requirements of ASTM C-150, AASHTO M-85, or ASTM C-91.

Charles Ogle, Manager of Quality Control

Date: 8/10/2009 12:48:36PM

Figure B.5 Mill certificate of cement C4.

TABLE B.2
Properties of fly ashes

Properties	F1 (Class C ash)	F2 (Class C ash)	F3 (Class F ash)
SO_3 content%	1.11	2.13	0.69
Soluble SO_3 content* %	0.53	1.14	—
Na_2O_{equ}%	2.18	1.94	2.21
L.O.I.	0.38 (M)	0.25	3.98

recommend dosage was used to prepare six (three each for normal and early stiffening ones) test mixtures. Mini slump experiments along with set time and semi-adiabatic calorimetry were used to determine the effect of addition of higher dosage of WRAs on compatibility of a mixture.

Similarly, a total of six mixtures, three each for normal and slow stiffening mixtures, were used to study the effect of low temperature. The 10°C was selected for the low temperature regime based on the recommendations given in ACI 306R-88 to simulate concreting conditions in the winter time. Table 3.1 of the document listed 10°C as the minimum temperature for cold weather construction of concrete structures with section size in between 12 in. and 36 in. 10°C was also used by Taylor et al. (*7*) in their work to study the effect of low temperature on incompatibility.

High temperature study was performed on a total of six mixtures, three each for normal and early stiffening mixtures. A chamber maintained at 37°C was selected for the high temperature regime testing to simulate hot weather conditions during the summer time. The research findings listed in ACI 305R formed the basis for selection of 37°C as the high temperature regime for this study. Although, no upper limit on the maximum concrete temperature was mentioned in the ACI 305R, it was, however, mentioned that concrete samples cured (in air or water) at 38°C (100°F) exhibited significant (10–15%) reduction in the 28 day concrete strengths. Some DOTs like Florida DOT allow maximum fresh concrete temperature as high as 38°C. Mini slump cone tests along with Vicat's set time experiments and semi-adiabatic calorimetry were performed at 10°C and 37°C to study effect the low and high temperatures, respectively, on the compatibility of a mixture.

Based on the literature review, it was identified that delayed addition can lead to retardation effects. Therefore the effect of delayed addition of admixtures was evaluated on a total of six mixtures, three each for normal and slow stiffening mixtures. Addition of chemical admixtures was delayed by 60 seconds. 60 s delay was adopted based on the preliminary semi-adiabatic calorimetry performed on normal stiffening mixtures. It was observed that highest retardation of the maximum peak occurred in mixtures prepared by 60 s delay of WRA addition when compared to those of the mixtures prepared by 15 s and 45 s delayed addition of WRAs. Vicat's set time measurements and semi-adiabatic calorimetry were performed to study the effect of delayed addition of WRA on compatibility.

In the end, early age stiffening and abnormal setting related incompatibility study was extended to high volume (30%, 50% and 70% replacement by weight) fly ash systems (HVFS). Paste and mortar mixtures prepared with 30%, 50% and 70% replacement (by weight) of cement with class C ashes (both F1 and F2) were studied. Mixtures containing C4 were not considered for the high volume fly ash study (HVFS) due to shortage of supplies. Therefore the test matrix comprised of mixtures containing three cements (C1, C2 and C3) along with the two class C ashes (F1 and F2) and four chemical admixtures (W1, W2, A1, and A2). In total, 16 mixtures were selected using the orthogonal experiment design approach as explained below.

REPORT OF FLY ASH ANALYSIS

Project Name: Indiana Fly Ash Analysis
Contact Person: Zhaozhou
Project Number: 1254

Source Plant	Kenosha
Sample Number	6559-08
Silicon Dioxide (SiO_2), %	37.78
Aluminum Oxide (Al_2O_3), %	20.11
Iron Oxide (Fe_2O_3), %	5.87
Sum of SiO_2, Al_2O_3, Fe_2O_3, %	63.76
Calcium Oxide (CaO), %	23.35
Magnesium Oxide (MgO), %	5.52
Sulfur Trioxide (SO_3), %	1.11
Sodium Oxide (Na_2O), %	1.80
Potassium Oxide (K_2O), %	0.58
Total Alkalies (as Na_2O), %	2.18

Figure B.6 Mill certificate of fly ash F1.

MINERAL RESOURCE TECHNOLOGIES, INC.

A CEMEX COMPANY

Fly Ash
Physical & Chemical Analysis Report

Database ID Number: 1056
Fly Ash Source: MRT Labadie
Class of Fly Ash: C
Sample Date: 7/25/05 to 7/29/05
Date of Report: 10/6/2005

Cemex USA, Tampa Technical Center
6725 78th Street, Riverview, FL 33569
Phone: (813) 671-2266
Fax: (813) 677-7597

	AASHTO-M295-93 Requirements for Class C	ASTM C-618 Requirements for Class C	Actual
Fineness Retained (+325 Mesh)	34% Max	34% Max	17.3 %
Moisture Content	3% Max	3% Max	0.23 %
Specific Gravity	*****	*****	2.75
Loss on Ignition	5% Max	6% Max	0.39 %
Soundness	0.8% Max	0.8% Max	0.04 %
S.A.I., 7 Days*	75% Min	75% Min	93.0 %
S.A.I., 28 Days*	75% Min	75% Min	102.9 %
Water Req. % Control	105% Max	105% Max	95.9 %
Silica SiO2	*****	*****	30.94 %
Aluminum Oxide Al2O3	*****	*****	19.12 %
Ferric Oxide Fe2O3	*****	*****	4.71 %
Total	50% Min	50% Min	54.77 %
Sulfur Trioxide SO3	5% Max	5% Max	2.64 %
Calcium Oxide CaO	*****	*****	26.93 %
Magnesium Oxide MgO	*****	*****	5.30 %

We certify that all above test were done in accordance with ASTM C-618
* Meeting the 7 or 28 day Strength Activity Index will indicate specification compliance.

CEMEX USA, Tampa Technical Center
Hugh H. Wang, Ph.D
Hugh H. Wang, Ph.D
Corporate Technical Director

Figure B.7 Mill certificate of fly ash F2.

TABLE B.3
Chemical admixtures selected for the study

Chemical admixture	Type/chemical nature	INDOT recommended dosage (ml/100 kg)
WRDA 82 (W1)	Type A and lignosulfonate based	195–390
Glenium 7500 (W2)	Type F and poly-carboxylate type	130–260
Micro Air (A1)	Synthetic type	8–260
Pave Air (A2)	Vinsol resin (VR) based	16–260

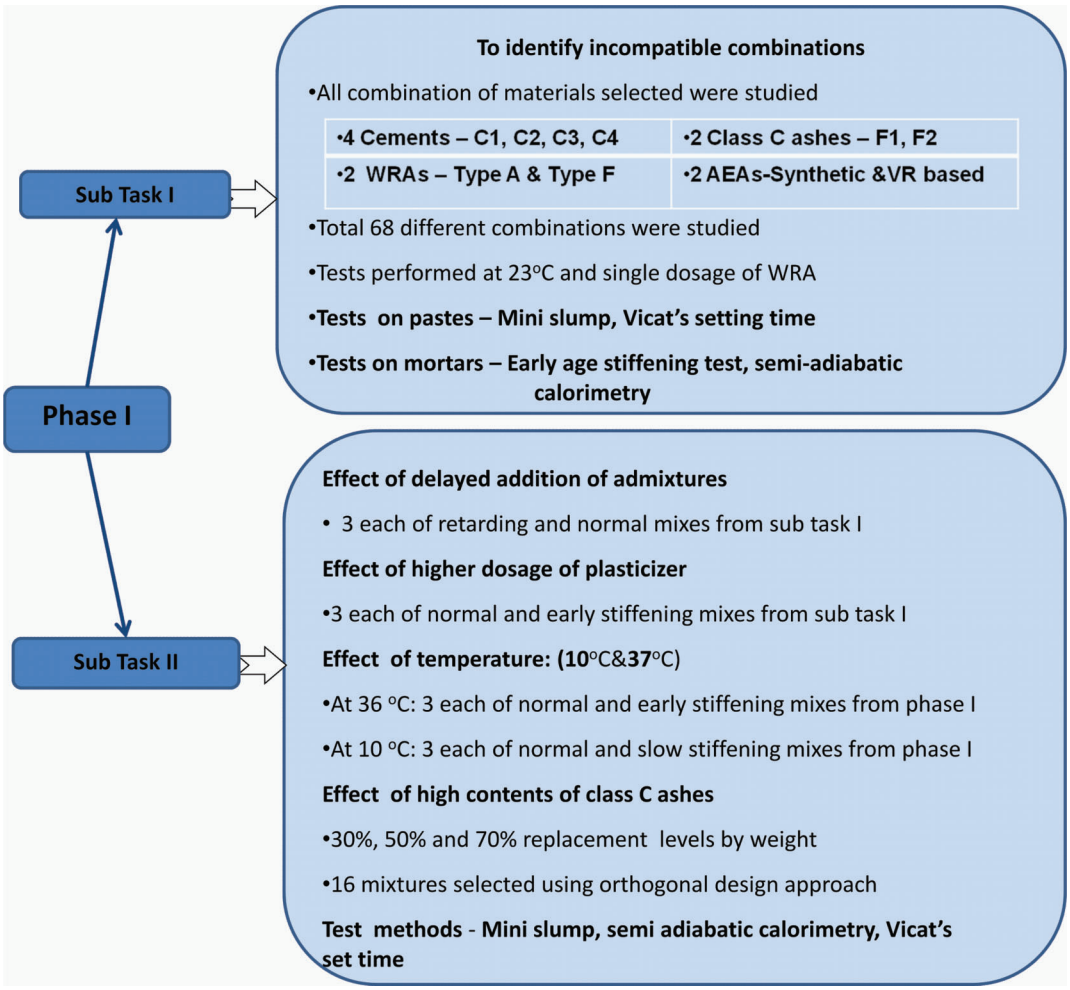

Figure B.8 Summary of the subtasks of Phase I.

TABLE B.4
List of factors and levels used for high volume fly ash (HVFS) study

Factors/independent variables	# of levels	Level 1	Level2	Level 3
Cement	4	C1	C2	C3
% replacement of cement by fly ash	3	30	50	70
Class C fly ash	2	F1	F2	—
WRA	2	W1	W2	—
AEA	2	A1	A2	—

Factorial orthogonal approach was used by various research works to minimize the number of mixtures to be tested given a large number of test variables. Guidelines from one such research work performed by Lawler et al. (*62*) were used to identify various factors and levels and also to build up the test matrix. Factors and levels in the orthogonal design approach represent the independent variables and values or variations of the independent variables to be tested respectively. In this study, cements, class C ashes, % replacement of cement by fly ash, water reducing agents (WRA) and air entraining agents (AEA) are the independent variables while the three cements (C1, C2 and C3) used for the HVFS form the three levels associated with the independent variable of cement. Similar interpretation of levels can be extended to that of the fly ashes and chemical admixtures. Thus in the present study, there are three 2-level factors (two class C ashes, two WRAs, two AEAs) and two 3-level factor (three cements and three % replacement levels). List of all the factors and their corresponding levels are listed in Table B.4.

Design charts from NCHRP report were used for the selection of mixtures for the study of high volume fly ash systems (HVFS). The number of mixtures to be tested depends upon the number of factors and the corresponding number of levels associated with each factor. From Figure B.9, it was determined that a minimum of 16 mixtures were required for the HVFS study. Exact combination of materials for each mixture was determined using Figure B.10 and the same is summarized in Table B.5. Early stiffening and abnormal setting characteristics of these 16 mixtures were evaluated using Vicat's initial set time experiment, mini slump testing and semi-adiabatic calorimetry.

B.2.2 Phase II

In the Phase II, combination of materials which resulted in problems related to production and stability of air void system (AVS) were studied. Based on the literature review, low alkali cements and class F fly ash materials (with high carbon content) were identified as the major binder associated causes for incompatibility problems affecting the AVS. Cement C1, with lowest (0.29%) total alkali content, along with class F ash and four chemical admixtures (W1, W2, A1 and A2) were used for this study. Both plain and fly ash cementitious systems (20 and 60% replacement of cement by fly ash by weight) were considered for the study. Determination of air content in mortars, foam index and foam drainage experiments were performed on 18 different mixture combinations. Air content in mortar samples was

Table S3.3. Selection of the 9-mixture design selected for the hypothetical case study.

Number of 2-Level Factors	Number of 3-Level Factors							
	0	1	2	3	4	5	6	7
0		3	9	9	9	16	18	18
1	2	8	9	9	16	18	18	18
2	4	8	9	16	16	18	18	>18
3	4	8	16	16	16	18	>18	>18
4	8	8	16	16	18	>18	>18	>18
5	8	16	16	16	>18	>18	>18	>18
6	8	16	16	16	>18	>18	>18	>18
7	8	16	16	>18	>18	>18	>18	>18
8	12	16	16	>18	>18	>18	>18	>18
9	12	16	16	>18	>18	>18	>18	>18
10	12	16	>18	>18	>18	>18	>18	>18
11	12	16	>18	>18	>18	>18	>18	>18
12	16	16	>18	>18	>18	>18	>18	>18
13	16	>18	>18	>18	>18	>18	>18	>18
14	16	>18	>18	>18	>18	>18	>18	>18
15	16	>18	>18	>18	>18	>18	>18	>18

Figure B.9 Design chart used to select number of mixes (*61*).

A 16-mixture design matrix for two three-level factors and three to nine two-level factors.

Mixture	Factor 1 (3-Level)	Factor 2 (3-Level)	Factor 3 (2-Level)	Factor 4 (2-Level)	Factor 5 (2-Level)	Factor 6 (2-Level)	Factor 7 (2-Level)	Factor 8 (2-Level)	Factor 9 (2-Level)	Factor 10 (2-Level)	Factor 11 (2-Level)
1	1	1	2	2	1	1	2	2	1	2	1
2	**2**	1	1	2	1	2	1	2	2	1	2
3	**2**	1	2	1	2	1	2	1	2	1	2
4	3	1	1	1	2	2	1	1	1	2	1
5	1	**2**	2	1	2	2	1	2	1	1	2
6	**2**	**2**	1	1	2	1	2	2	2	2	1
7	**2**	**2**	2	2	1	2	1	1	2	2	1
8	3	**2**	1	2	1	1	2	1	1	1	2
9	1	**2**	1	2	2	2	2	1	2	1	1
10	**2**	**2**	2	2	2	1	1	1	1	2	2
11	**2**	**2**	1	1	1	2	2	2	1	2	2
12	3	**2**	2	1	1	1	1	2	2	1	1
13	1	3	1	1	1	1	1	1	2	2	2
14	**2**	3	2	1	1	2	2	1	1	1	1
15	**2**	3	1	2	2	1	1	2	1	1	1
16	3	3	2	2	2	2	2	2	2	2	2

If not all factors are needed, unused columns can simply be ignored. If the font is underlined and bold, the level chosen for that factor should be the one expected to produce the best result.

Figure B.10 Chart for determining composition of mixtures to be tested (*61*).

TABLE B.5
Combination of materials for mixtures selected for the HVFS study

	3 level		2 level			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	
S. No.	Cement	% replacement	Fly ash	WRA	AEA	Mix #
1	C1	30	F2	W2	A1	C1F2(30)W2A1
2	C2	30	F1	W2	A1	C2F1(30)W2A1
3	C2	30	F2	W1	A2	C2F2(30)W1A2
4	C3	30	F1	W1	A2	C3F1(30)W1A2
5	C1	50	F2	W1	A2	C1F2(50)W1A2
6	C2	50	F1	W1	A2	C2F1(50)W1A2
7	C2	50	F2	W2	A1	C2F2(50)W2A1
8	C3	50	F1	W2	A1	C3F1(50)W2A1
9	C1	50	F1	W2	A2	C1F1(50)W2A2
10	C2	50	F2	W2	A2	C2F2(50)W2A2
11	C2	50	F1	W1	A1	C2F1(50)W1A1
12	C3	50	F2	W1	A1	C3F2(50)W1A1
13	C1	70	F1	W1	A1	C1F1(70)W1A1
14	C2	70	F2	W1	A1	C2F2(70)W1A1
15	C2	70	F1	W2	A2	C2F1(70)W2A2
16	C3	70	F2	W2	A2	C3F2(70)W2A2

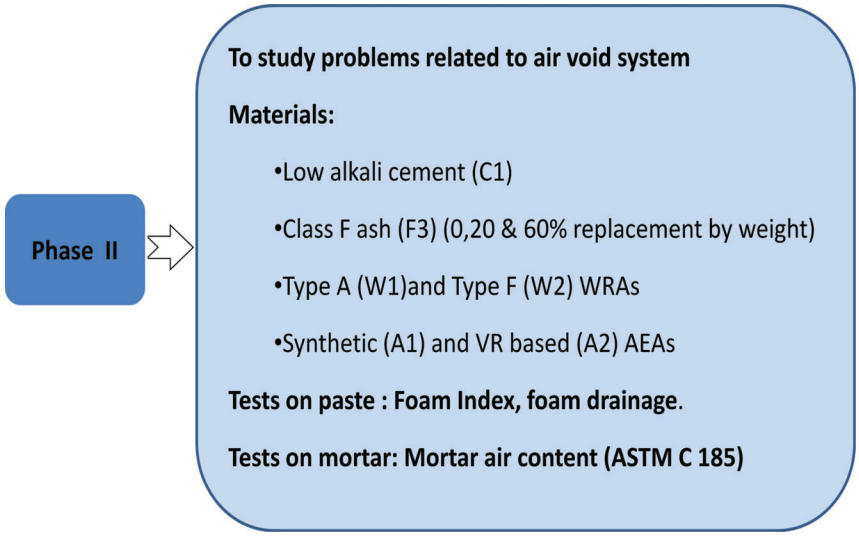

Figure B.11 Summary of Phase II experimental plan.

determined confirming to the ASTM C 185. Figure B.11 summarizes the details of Phase II testing.

B.2.3 Phase III

In this final phase of the study, few selected mixtures from Phase I and Phase II were studied to validate the results from various paste and mortar tests. In total, 10 different concrete mixtures were studied (Figure B.12).

In the subtask I of Phase III, four concrete mixtures were studied to validate the paste and mortar results from Phase I. Slump at 15, 30 and 60 minutes was measured along with semi-adiabatic temperature profile and 7 and 56 days compressive strength measurements. In the subtask II of Phase III, five of the most problematic mixtures identified based on the Phase II experiments were studied. In addition to the five mixes, one mixture was prepared at high (37°C) temperature to study the effect of high temperature on the air void system. Total air content at 15, 30 and 60 minutes along with slump, unit weight, hardened

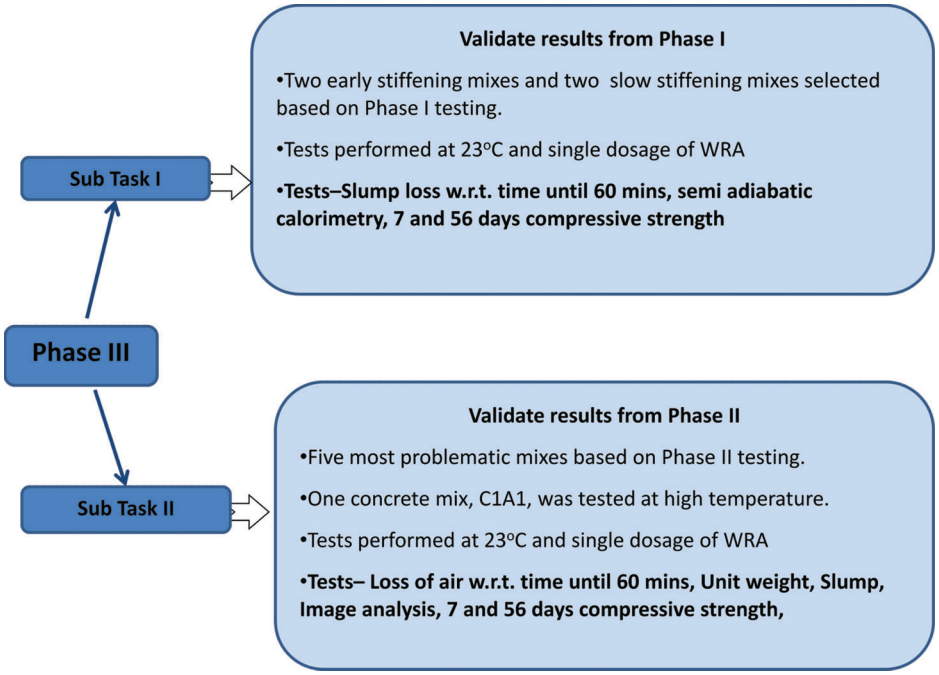

Figure B.12 Summary of Phase III concrete testing.

TABLE B.6
Nominal mix proportions of concrete mixtures

Materials	Amount (lbs/cu yd)
Binder	515
Coarse aggregate	1700
Fine aggregate	1500
Target w/binder	0.43
WRA	Maximum amount suggested by INDOT approved list
AEA	Amount required to produce 6.5 +/− 1.5% air

air content using image analysis and 7 and 56 days compressive strength measurements were made.

B.3 CONCRETE MIXTURE COMPOSITIONS

A total of ten different mixtures, selected based on the results from Phase I and Phase II, were used for concrete mixing. All concrete mixtures tested were designed to achieve target slump and air content of 2 ± 1 in. and 6.5 ± 1.5% respectively. #8 crushed limestone aggregate was used as the coarse aggregate and #23 natural sand was used as the fine aggregate. Specific gravity and absorption coefficient of coarse aggregates and fine aggregates were determined following the AASHTO T 85 (ASTM C 127-04) and AASHTO T 84 (ASTM C 128-07a) standards respectively. Coarse aggregate had a SSD specific gravity of 2.693 and an absorption coefficient of 2.7%. Fine aggregate was found to have SSD specific gravity of 2.614 and an absorption coefficient of 1.4%. Nominal mix proportions for all the concrete mixtures are listed in Table B.6.

Concrete mixtures were prepared using the AASHTO R 39 (ASTM C 192) standard. The coarse aggregates were soaked in water prior to mixing in a plastic container overnight. Approximately 3 hours prior to the actual mixing, the soaked coarse aggregates were transferred to another plastic container with perforated bottom to drain the water away. The container was then covered with plastic sheet and stored at room temperature. Fifteen minutes prior to mixing, the aggregates were manually mixed and approximately 1 lb each of coarse and fine aggregate was sampled then weighed and placed in the oven for drying. Oven drying was carried out for 10 minutes and the dry weights were measured to determine the actual moisture content of the aggregates. Thus the determined moisture content of the aggregates was used to adjust the water content in the batch.

Before the start of mixing, a part of mixing water was used for diluting the admixture solutions. The coarse and fine aggregates were placed in the open pan mixer and mixed together for 1 minute. During this 1 minute mixing, a part of mixing water was added to the aggregates, if required, to make them moist. Next, binder was added to the mixer and allowed to mix for 30 s. Then all the mixing water was added followed by addition of diluted admixture solutions over a 15 s time period. WRAs were added prior to the addition of AEAs. After adding all the ingredients, the concrete was mixed for 3 minutes, followed by a 3 minute rest period and subsequently a 2 minute final mixing.

B.4 NOMENCLATURE OF MIXTURES

Around 100 different combinations of cements, fly ashes, chemical admixtures and other miscellaneous factors were studied in this research work. The following nomenclature was used throughout this thesis to refer a particular combination. The different cements used were labeled Ci where, i ranges from 1 to 4 representing each of the four cements. Similarly the three fly ashes, the two water reducing agents and the two air entraining agents were designated by Fj, Wk and Am respectively where j ranges from 1 to 3 while k and m can take values of 1 or 2. Tables B.1 through B.3 summarize various components and their designated labels.

For instance, mixture labeled as C1F2W2 contains cement C1 (C_3A content = 9%; sulfate content = 3.2% and alkali content = 0.29%), 20% replacement of cement by class C fly ash F2 (total sulfate content = 2.13%, alkali content = 1.94%) and poly-carboxylate type superplasticizer W2. This mixture does not contain any air entraining agent.

Fly ash content in mixtures prepared with higher (>20%) replacement levels is represented by % replacement in the subscript following the fly ash variable (Fi). For example, $C2F3_{(60)}W1A1$ is a high volume fly ash cementitious system which contains cement C2, class F fly ash (F3) with 60% replacement of cement (by weight) along with lignin based WRA and synthetic type AEA.

B.5 EXPERIMENTAL METHODS

This section summarizes the various experimental methods and the corresponding limiting criteria used to identify incompatible mixtures. In total seven different test methods were performed on the pastes and mortars. Early age stiffening test, Vicat's set time, Mini slump test and the semi-adiabatic calorimetry were used to study the early stiffening behavior. Foam index, foam drainage and Air content in mortars measurements were used to study the air void related problems. Figure B.13 details the various test methods used to study various incompatibility problems.

B.5.1 Early Age Stiffening Method

Early age stiffening test method was used to test the samples for false and flash setting behaviors. This experiment was performed on mortars following the ASTM C 359 standard. Mortars were prepared using binder (cement and/or fly ash), standard 20–30 graded sand, standard sand and water required to achieve initial (at 3 minutes from the time of contact of binder with water) plunger (10 mm diameter) penetration of 46 ± 3 mm. Temperature of the mixture after initial mixing was targeted to be at 23 ± 2°C by adjusting the temperature of the mixing water. Penetration readings at 3, 5, 8 and 11 minutes after the start of mixing were measured. At the end 11 minutes, the mixture was remixed at medium speed for 1 minute and final penetration reading was measured.

B.5.1.1 Limiting Criteria

Based on the literature review, the limiting criteria to identify a potential incompatible problem using early age stiffening test experiment was established. According to the National Concrete Pavement Technology Center (NCPTC) (*63*) recommendations, a mixture is termed false setting if the penetration after remixing is greater than the 11-minute penetration. Additionally, a mixture is flash setting if the penetration depth decreases from 50 mm to approximately 10 mm at the 11-minute reading. Similar limiting criteria were used by Wang H, et al. (*44*) and Schlorholtz (*58*). Following is the list of limiting criteria used in this research to identify incompatible problems related to early age stiffening.

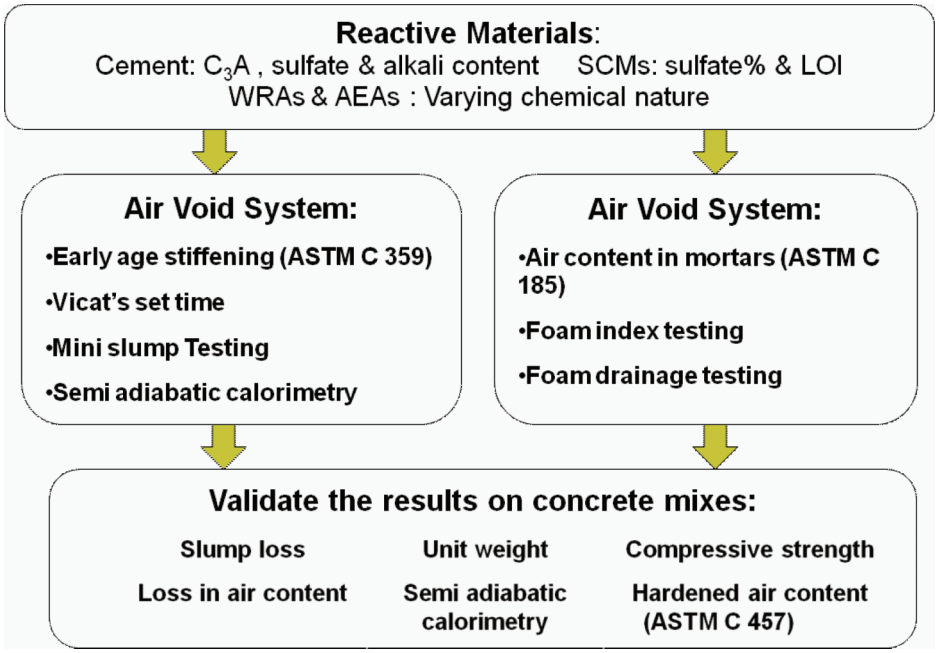

Figure B.13 Test methods used to study incompatibility problems.

1. If the penetration difference between 3 minutes and 11 minutes is greater than 40 mm, then it indicates early stiffening characteristics of a mix.
2. Penetration after remixing is used to quantify false set or flash setting characteristics of a mix. Mix which satisfied criterion 1 and regained its fluidity after remixing was classified as false setting mix whereas, a mix that satisfied criterion 1 and had a low (≤10 mm) remix penetration was considered as flash setting mix

Figure B.14 illustrates the criteria adopted for identifying potential setting incompatibilities of mixtures using ASTM C 359.

B.5.2 Mini Slump Test

Mini slump cone tests were performed to monitor the loss of workability of pastes by measuring the spread (pat) diameter over time. This test was performed following the AASHTO TP54 with minor modifications. A hand blender having both the capabilities of high intensity (11,000 rpm) mixing and low (4,000 rpm) intensity mixing was used. High intensity mixing is to achieve shearing intensity similar to that caused by aggregates during concrete mixing and slow intensity mixing was used for remixing. The temperature of the mix was checked 30 seconds, after combining cement and water at the end of the first (30-seconds long) mixing period and at the end of the second (90-seconds long) mixing period and 4 minutes (after second mixing for 90 seconds) was maintained at 23 ± 3°C. This was achieved by adjusting the temperature of the mix water.

A 57 mm high mini slump cone with a top diameter of 19 mm and a bottom diameter of 37 mm was used to obtain the spreads. Paste slurries were obtained by mixing the binder and water with appropriate admixture dosages. Mini slump test was performed on mixtures with constant w/c ratio of 0.43. The dosages of

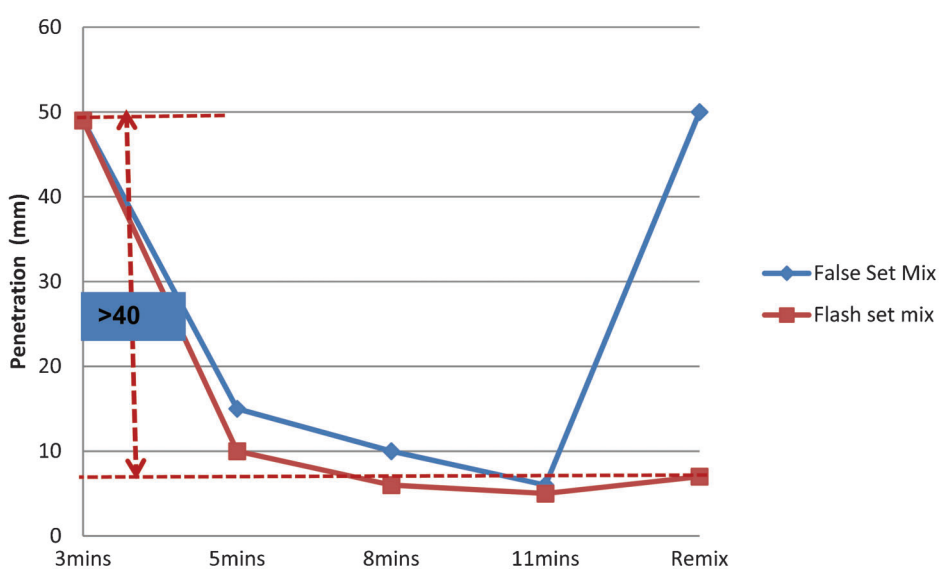

Figure B.14 Criteria for identifying false and flash setting behaviors of mixtures using ASTM C359.

admixtures were fixed at the maximum amount suggested in the Indiana approved list of materials. Mixing water was placed in the mixing jar and appropriate amounts of admixtures were added followed by addition of binder. After the initial 30 s mixing at high speed, the slump cone was filled with the sample and lifted after 2 minutes from the time of contact of water and binder. The diameter of the spread was measured and the remaining slurry was again mixed for 90 s at high speed and sampled for a measurement at 5 minutes. Similar measurements of the pat diameter were made at 15, 30 and 45 minutes after remixing for 1 minute at slow speed.

AASHTO TP54 defined two parameters—false set index and % area reduction to characterize the stiffening behavior of a mix. False set index, calculated as ($100*Area_{5\ min}/Area_{2\ min}$), greater than 120 indicated false setting behavior while % area reduction, calculated as $Area_{45\ min}/Area_{5\ min}$, greater than 50% indicated early stiffening behavior.

However, interpretation of the % area reduction criterion leads to contradicting conclusions. According to the definition of % area reduction criterion, $area_{45\ min}$ increases as the % area reduction value increases for a given $area_{5\ min}$. This actually implies that the fluidity of a mix increases with increase in % reduction area value. According to this logic, mixtures with % reduction in area values greater than 50% are more fluid and not early stiffening.

B.5.2.1 Limiting Criteria

Limiting criteria to identify incompatible combinations were established based on the literature review. Taylor et al. (*10*) and Tang and Bhattacharja (*3*) calculated stiffening index and false set index based on the areas of spreads measured at different times. Stiffening index was calculated as the ratio of area of spread at 30 minutes to that of the area at 5 minutes. False set index, calculated as the ratio of area of spread at 5 minutes to that of the spread at 2 minutes. Limiting criteria to identify a potential incompatibility problem using mini slump cone testing were established as follows:

- False setting index (F.S.I.) greater than 1.3 indicates potential problem with placement, especially when the concrete is mixed only for a short time.
- Stiffening index (S.I.) when calculated to be less than 0.8 implies the problem of rapid stiffening.

B.5.3 Set Time

Initial set time of paste samples were determined using manual Vicat's set time equipment following the ASTM C 191 standard. Paste samples of normal consistency were prepared following the ASTM C 187 after which, they were placed in the curing room (23°C and 100% relative humidity) for 30 minutes. At the end of the 30 minute period, samples were transferred to a chamber maintained at 23°C and 50% relative humidity until the end of the test. This experiment was performed on all the Phase I mixtures. While testing the fly ash cementitious mixtures, cement and fly ash were hand mixed prior to wet mixing to attain homogeneity.

B.5.3.1 Limiting Criteria

In the present research, a change in initial set time greater than 60 minutes with respect to the base mix indicate potential incompatibility problems. Also mixtures with initial set time less than 45 minutes or greater than 375 minutes were considered as incompatible combinations. These criteria were based on the specifications listed in ASTM C 150 and recommendations by Taylor et al. (*52*). It is required that all the cements confirming to ASTM C 150 must have initial set time less than 375 minutes and greater than 45 minutes. It was suggested that change in initial set time by 60 min or more w.r.t. base mixture is significant and can be an indication of potential incompatibility.

B.5.4 Semi-Adiabatic Calorimetry

Hydration of cement is an exothermic process and as a result, temperature of the sample increases as the degree of hydration increases. Semi-adiabatic calorimetry was used to monitor the temperature of a mix over time under semi-adiabatic conditions. Temperature profile of the mix with respect to time was monitored to identify changes in hydration reaction due to problematic interactions between various components.

This test was performed on all the Phase I and Phase III mixtures. Mortar mixtures of Phase I were made with binder, chemical admixtures, water and oven dried natural sand. Mixing was performed confirming to the ASTM C 305 mixing sequence. Mix proportions of the mortar samples tested in Phase I are shown in Table B.7. All the mortar samples tested have the same binder content (by weight) and the same w/binder ratio. Samples of concrete mixtures, 2000 g in weight, which were studied in Phase III, were also collected to monitor the temperature profile w.r.t. time. The semi-adiabatic temperature profile was monitored for 2 days for each mix.

B.5.4.1 Limiting Criteria

Based on the recommendations from Taylor et al. (*52*), the following limiting criteria were used to identify the incompatible combinations.

- Changes in the time of occurrence of the maximum peak temperature being greater than 60 minutes w.r.t. the base mix indicates a potential incompatibility.
- Change in the maximum peak temperature by 6°C (10°F) or more was considered significant.
- Development of secondary peaks indicates that something significant has changed in concrete composition.

B.5.5 Foam Index Testing

Foam index test was used to study the effect of supplementary cementitious materials and complex interactions between various components of the mixture on the production of stable air void system. In this test method, the amount of air entraining agent (AEA) dosage required to form a stable uniform layer of foam on

TABLE B.7
Mixture proportions of Phase I mixtures tested using semi-adiabatic calorimetry

Materials	0% fly ash system	20% fly ash system
Cement (g)	672.0	537.5
Fly ash (g)	0	134.5
w/binder	0.43	0.43
Sand	1656.4	1656.4
Weight of the sample tested (g)	2106.5	2079
Volume of the sample tested (ml)	~425	~425
Admixture dosages	Maximum dosage allowed by INDOT approved list	

the liquid surface was estimated. Abnormal changes in the required dosage of AEA w.r.t base mix indicate potential incompatibility problem. This test was performed on all the mixtures of Phase II.

20 grams of binder and 50 ml water were used to prepare paste slurries. In addition to plain cementitious systems, fly ash cementitious systems at three different levels-20, 40 & 60% (by weight) were studied. Admixture solutions were diluted to a ratio of 1:8 (by volume) by adding de-ionized water. In case of some of the mixtures, the diluted AEA solutions were further diluted to 1:5 (by volume). The procedure used for making the paste slurries is explained below.

50 ml of water along with WRA, if any, was placed in a 500 ml cylindrical glass jar to which 20 g of binder was added. Immediately after the addition of binder, the opening of the jar was closed and the mix was vigorously, albeit manually, for 15 s to form a homogenous system. A known volume of diluted AEA was then added and the mixture was further shaken for 15 s followed by a 45 s rest period. During the 45 s, the mix was left undisturbed to let the foam stabilize on the surface of the slurry. The process of addition of diluted AEA was continued until stable foam appeared on the liquid surface. Once a rough estimate of AEA dosage required was obtained from the first trial, the above process was repeated with new raw materials to reduce the number of AEA dosage additions. This was done until the actual dosage of AEA required was obtained in the first attempt.

B.5.5.1 Limiting Criteria

Recommendations by Taylor et al. (*52*) were used to establish the limiting criterion. A change in the amount of air-entraining admixture required to achieve a stable and complete coverage of foam of more than 30% w.r.t base mix was considered significant.

B.5.6 Air Content in Mortars

Determination of air content in mortars was performed according to ASTM C 185 standard. This test was performed to evaluate the effect of various mixture components on production of stable air voids in mortar samples. This experiment was performed on all the mixtures of Phase II to estimate the amount of AEA required to achieve18 $\pm$ 2% air content in mortar samples. 350 grams of binder, 1400 grams of 20–30 standard graded sand, chemical admixtures and water needed to obtain a flow of 87.5 $\pm$ 7.5% were used to prepare the mortar samples. Mixing of mortar was performed according to ASTM C 305. Thus prepared mortar samples were then placed and compacted in a 400 ml brass cup. The weight of 400 ml mortar sample was measured to calculate the air content in mortars using the specific gravity and mixture composition information. In addition to plain cementitious systems, fly ash cementitious mixtures at two different dosages—20% & 60% (by weight) of fly ashes were studied.

B.5.6.1 Limiting Criteria

In this present study, a change in the amount of air-entraining admixture required to achieve 18 $\pm$ 2% air (in the mortars) of more than 20% compared to previous tests was considered to be an indication of potential incompatibility. Significance of 18% air content in mortars was established based on the ASTM C 618 standard. Optional uniformity specifications mentioned in ASTM C 618 require that the amount of AEA needed to produce 18% air in mortar samples shall not vary from the preceding tests by 20%. Lashley (*47*) reported that a good correlation was found correlation between AEA dosage required to attain 18% air mortars and 6.5% air in fresh concrete.

B.5.7 Foam Drainage Test

Foam drainage test was performed to study the stability of air voids generated in paste slurries. This test was performed on all the mixtures of Phase II. 5 grams of binder and 300 ml of water were used to produce the paste slurries. The mix proportions used for foam drainage testing are summarized in Table B.8. A hand blender operating at medium speed (7000 rpm) was used to produce the foam. This experiment was performed according to the draft standard recommended by Taylor et al. (*10*). Brief explanation of the experimental procedure is described below.

Measured amount of water was added to a cylindrical jar of 500 ml capacity. WRA, if any, was added followed by addition of AEA. Immediately after the addition of AEA, 5 g of binder was added and the mixture was blended for 10 s at medium speed. The resultant foamed mixture was transferred to 1000 ml graduated cylinder and the level of foam-liquid interface (V_d) was monitored with respect to time for 60 minutes.

V_0, ($-1/k$) and % drainage values were the three parameters that were determined from the foam drainage experiment. A linear equation was fitted to the data of instantaneous foam level and inverse of time. V_0 and (1/k) were determined using the following equation:

$$V_d = V_0 - (1/k) * (1/t)$$

Where,

V_d is the instantaneous level of liquiD foam interface,

t is time in minutes and 1/k is a constant w.r.t. to mixture,

V_0 and $-1/k$ were determined from linear plot of foam- liquid level versus 1/time where, V_0 is the intercept on y axis and $-1/k$ is the slope of the line.

V_0 represents the amount of liquid drained from the foam after a long time (at time t = infinity). $-1/k$ represent the rate of drainage of liquid from foam. Foams with higher values of V_0 are less stable than those with lower V_0 value. Similarly, lower the value of -1/k, lower is the stability of foam. % foam drainage was calculated differently from what Taylor et al. (*10*) used. In their work, % foam drainage was calculated according to the following formula:

$$\%\ \text{drainage} = 100 - [100 * (310 - V_0)/310]$$

They proposed that foams with high % drainage values, calculated based on the above formula, are less stable. But this formula fails to differentiate between foam systems which have different initial foam contents. For instance consider two foam systems with initial foam-liquid level ($(V_d)_{initial}$) at 200 and 300 and final levels (V_0) at 308 each. According to the formula used by Taylor et al. (*10*) each of the two systems has same % drainage value which is equal to 99.41% which is not correct.

Therefore, in this present study, % foam drainage is calculated as:

$$\%\ \text{foam drainage} = 100 * [V_0 - (V_d)_{initial}]/]300 - (V_d)_{initial}]$$

Where, $(V_d)_{initial}$ is the foam-liquid level at the beginning of the experiment.

B.5.7.1 Limiting Criteria

Mixtures were ranked based on the values of % foam drainage and 1/K where a low value of 1/k in combination with high value of % foam drainage represents a mix with potentially unstable air void system. Five of the most unstable foam systems were chosen for further concrete testing.

TABLE B.8
Mixture proportions used for foam index testing

Materials	Mixtures with no WRA	Mixtures with WRA
Binder (g)	5	5
WRA (ml)	0	50
Water (g)	300	250
AEA (ml)	10	10

B.5.8 Concrete Slump Test

Slump of the fresh concrete was measured on all the mixtures of Phase III following the AASHTO T 119 (ASTM C 143) standard. For Mixtures in the subtask I of Phase III, slump was measured at 10, 30 and 60 minutes after the beginning of mixing. Immediately after the concrete mixing of concrete mixtures, fresh concrete was molded in to three slump cones. The slump cones were covered with plastic rag and were left undisturbed until they were lifted at the designated times.

A mix was considered to be rapid stiffening if the loss of slump between 10 and 60 minutes is greater than 50 mm (*52*).

B.5.9 Loss of Air Content in Concrete Mixtures

Measurement of the air content was performed on all the Phase III concrete mixtures following the AASHTO T 172 (ASTM C 152) standard. For this thesis, a Type B air meter was used to measure the % air content of fresh concrete. For the mixtures in subtask II of Phase III, air content of the mixtures was measured 15, 30 and 60 minutes. The concrete mixture was remixed for 1 minute before measuring the % air contents at 30 and 60 minutes respectively. A mix was considered to have an unstable air void system if the loss in air content between 15 and 60 minutes is greater than 30%.

B.5.10 Modified Hardened Air Content Using Image Analysis

Although the preparation of all specimens needed for this analysis was completed, the experiment itself could not be performed by the deadline for the submittal of this report due to problems with the equipment. However, a short description of the proposed approach is provided below for both, the completeness and in order to indicate how the image analysis method can be used to confirm potential deficiencies in the air-void system of the hardened concrete that may be the result of incompatibilities between admixtures.

The proposed method can used to measure total air content, specific surface area and the spacing factor of air void system in hardened concrete samples. A total of six mixtures were prepared in the subtask II of Phase III to be evaluated for abnormalities in the air void system. The 4×8 in.^{2} concrete specimens were cut, lapped and polished in to 4×4 in.^{2} samples following the ASTM C 457 standard. The surfaces of thus prepared samples were painted in black using black markers and then a white barium sulfate powder was applied to help to distinguish the air voids form the rest of the concrete. The surfaces of the specimens prepared by this procedure were then scanned (using the high resolution scanner) giving the digital representation of the microstructure. The resulting data file can, in turn, be used as input into the image analysis software (this task was not completed due to technical difficulties) which can automatically calculate the parameters of interest. It is generally accepted (*5*) that for proper protection from frost damage the air void system should have a spacing factor lower than 0.008 in. and specific area greater than 600 in^2/in^3.

The intend of the above described procedure was to demonstrate how the proposed image analysis method can be used to identify those combinations of admixtures which may result in deficient (with respect to base mixture) values of such parameters as the spacing factor and void ratio despite assuring total air content ($6 \pm 1\%$) comparable to that of a base mixture. In addition, the proposed method can also be used to identify those mixtures which may fall short of meeting the previously mentioned commonly accepted criteria for ensuring the frost protection of hardened concrete (i.e., spacing factor not higher than 0.008 in. and specific area greater than 600 in.^{2}/in.^{3}).

B.5.11 Compressive Strength

The compressive strengths of 4 in. *X* 8 in. concrete samples were tested using the AASHTO T 22 (ASTM C 39) standard after 7, 28 and 56 days of moist curing. Compressive strength of concrete samples was tested at 7 and 56 days to allow time for the activation of fly ash, especially in the high volume (60% by weight) fly ash cementitious systems. A general strength requirement for a newly constructed roadway to traffic is 3000 Psi (*63*). Therefore 7 day compressive strength of 3000 psi was taken as the benchmark to categorize concrete mixtures.

APPENDIX C. RESULTS OF EXPERIMENTS PERFORMED ON PASTE AND MORTAR SYSTEMS

This appendix presents the results of the experiments performed on paste and mortars tested in phases I and II of the research. This chapter is divided in to two major sections summarizing the Phase I and Phase II results respectively. The organization of the chapter is as follows. Section C.1 summarizes the results of experiments performed in the subtask I of Phase I. Section C.C.2 describes the methodology used to select mixtures for subsequent testing. Section C.C.3 presents the results of experiments performed in the subtask II of Phase I followed by summary of Phase II experiment results in Section C.C.4.

C.1 RESULTS OF EXPERIMENTS PERFORMED IN SUBTASK I OF PHASE I

C.1.1 Results of Experiments Performed on Mixtures Containing Cement C1

This section summarizes the results of experiments performed on plain and fly ash cementitious systems containing cement C1 and class C ashes (F1 and F2). The section is organized as follows. Section C.1.1.1 describes the results of early stiffening test. Sections C.1.1.2 and C.1.1.3 contain the results of the mini slump test and Vicat's set time experiments respectively. The results of semi-adiabatic calorimetry are discussed in Section C.1.1.4. A summary of results, with incompatible mixtures identified, is presented in the tables in each subsection.

C.1.1.1 Results of Early Age Stiffening Test

In this section, the results of early age stiffening test performed on mortars following the ASTM C 359 are discussed. The results of the experiments on mixtures containing C1F1 fly ash cementitious systems and the plain cementitious mixtures are tabulated in Table C.1 Values in columns A, B, C, D, and E correspond to penetration values of a 10 mm plunger at 3, 5, 8, and 11 and after remixing respectively. Values identified in **boldface** indicate potential incompatibilities in mixtures identified through the early age stiffening testing. In general, a majority of the mixtures exhibited false setting characteristics while some mixtures containing C1 and C2 (low (<0.3%) total alkali and moderately high (>9%) C_3A content) exhibited flash setting.

It was observed (Table C.1) that addition of fly ash or either of the WRAs, W1 or W2, to plain cement C1 (0.29% total alkalis, 3.2% sulfates and 9% C_3A content) resulted in false setting. In particulate, the C1W1 mixture exhibited partial flash setting characteristics. However addition of lignin based water reducing agent (W1) to the fly ash cementitious system resulted in false setting behavior.

All the tested fly ash cementitious mixtures containing C1 and F1 exhibited false setting behavior. Addition of air entraining agents (A1 or A2) along with W1 to the C1F1 system resulted in both false setting and partial flash setting behaviors. The early age stiffening test results of plain cementitious (C1) and C1F1 fly ash cementitious systems are presented in Figures C.1 and C.2 respectively.

Table C.2 and Figure C.3 summarize the results obtained from early age stiffening test performed on standard mortar mixtures containing C1 cement and F2 class C ash. It was observed that all mixes containing C1F2 fly ash cementitious system exhibited false set characteristics except for C1F2W1A2 mix which exhibited normal stiffening behavior. Thus the partial false setting characteristics of C1F1W1A2 mixture were eliminated by changing the fly ash source to F2. Also, it was found that addition of air entraining agents (A1 or A2) along with W1 to the C1F2 system reduced the early stiffening characteristics (lower early age stiffening rate compared to C1F2W1).

C.1.1.2 Results of Mini Slump Testing

In this section, the results of mini slump test performed on mixtures containing cement C1 are presented. Values identified in **boldface** indicate potential incompatible mixes identified based on the limiting criteria (Section B.5.2.6). Stiffening index (S.I.) and false setting index (F.S.I.) were calculated as recommended by Taylor et al. (*10*). Average pat area was calculated by taking the average of area of spreads measured at 2, 5, 15 and 30 minutes. Time at which area of spread was measured is represented by a number in the subscript. For example, values in the column under the heading $(Ar)_{30}$ represent area of spread measured at 30 minutes from the initial contact of binder with water. Table C.3 and Table C.4 summarize the results obtained from mini slump cone testing on plain and fly ash cementitious systems containing cement C1.

Based on the limiting criteria previously established for mini slump testing, three mixes-C1W1, C1F1W1A1, and C1F1W1A2-were identified as potentially incompatible mixes because of low stiffening index value (S.I. <0.85). Results of these early stiffening mixes were identified in **boldface** in Table C.3. Thus addition of lignin based WRA (W1) to plain cementitious system resulted in early stiffening behavior. Similar results were observed when W1 was added along with either of the air entraining agents (synthetic type (A1) or VR based (A2)) to the C1F1 fly ash cementitious system.

Table C.4 summarizes the results obtained from mini slump cone testing performed on C1+F2 fly ash cementitious system. It was observed that addition of lignin (W1) to C1+F2 fly ash cementitious systems resulted in early stiffening behavior

TABLE C.1
Results of early age stiffening test performed on mixes containing cement C1 and F1 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)*					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C1	185	43	7	4	3	50	40	6.4
C1F1	168.8	49	4	2	1	50	**48**	7.8
C1W1	174	46	8	3	2	19	**44**	7.0
C1W2	177.5	45	3	1	1	50	**44**	7.2
C1F1W1	161	47	15	6	4	50	**43**	6.6
C1F1W2	160	48	4	1	1	50	**47**	7.7
C1F1W1A1	159.5	45	9	4	1	36	**44**	6.9
C1F1W1A2	160	44	22	9	3	36	**41**	5.8
C1F1W2A1	164	47	3	1	0	50	**47**	7.7
C1F1W2A2	160.2	48	6	1	1	50	**47**	7.6

NOTE: Values shown in **boldface** indicate potential incompatibilities in mixtures identified through the early age stiffening testing.

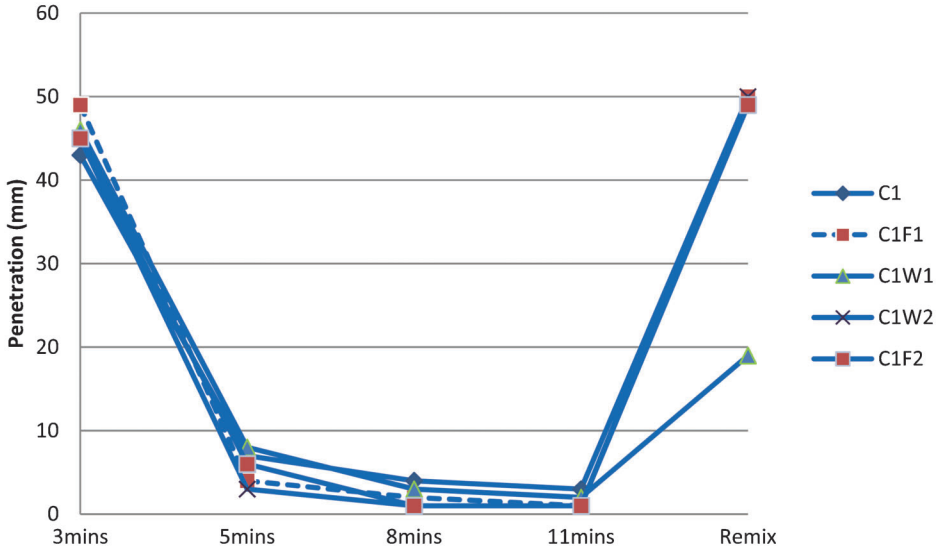

Figure C.1 Early age stiffening test results of mixtures containing C1.

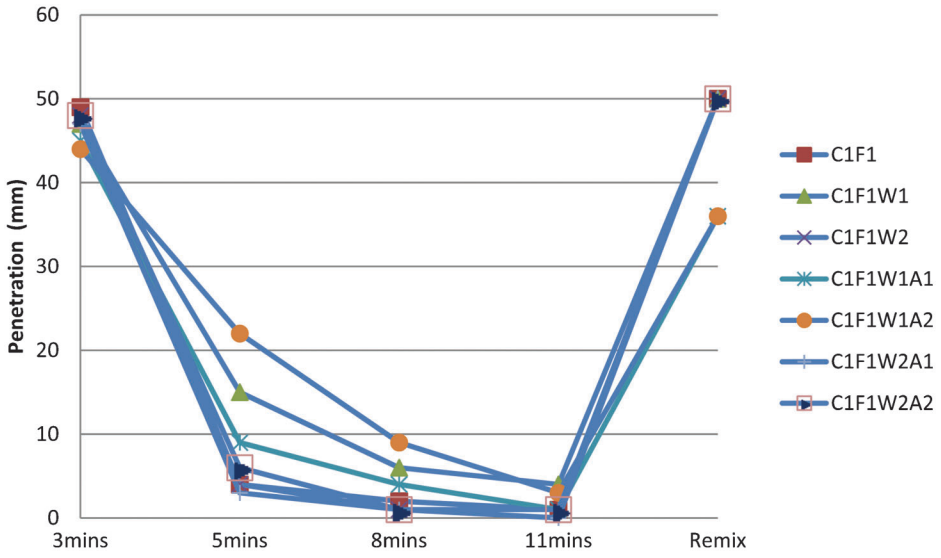

Figure C.2 Early age stiffening behavior of mixtures containing C1F1 system.

TABLE C.2
Results of early age stiffening test performed on mixes containing cement C1 and F2 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)*					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C1	185	43	7	4	3	50	40	6.4
C1F2	168	45	6	1	1	49	**44**	7.1
C1F2W1	163.1	48	13	3	2	49	**46**	7.1
C1F2W2	157	47	4	1	1	50	**46**	7.5
C1F2W1A1	158.7	48	15	6	4	42	**44**	6.7
C1F2W1A2	159.2	44	22	8	4	49	40	5.7
C1F2W2A1	157.5	47	6	1	1	50	**46**	7.4
C1F2W2A2	158.4	46	3	1	0	50	**46**	7.5

NOTE: Values shown in **boldface** indicate potential incompatibilities in mixtures identified through the early age stiffening testing.

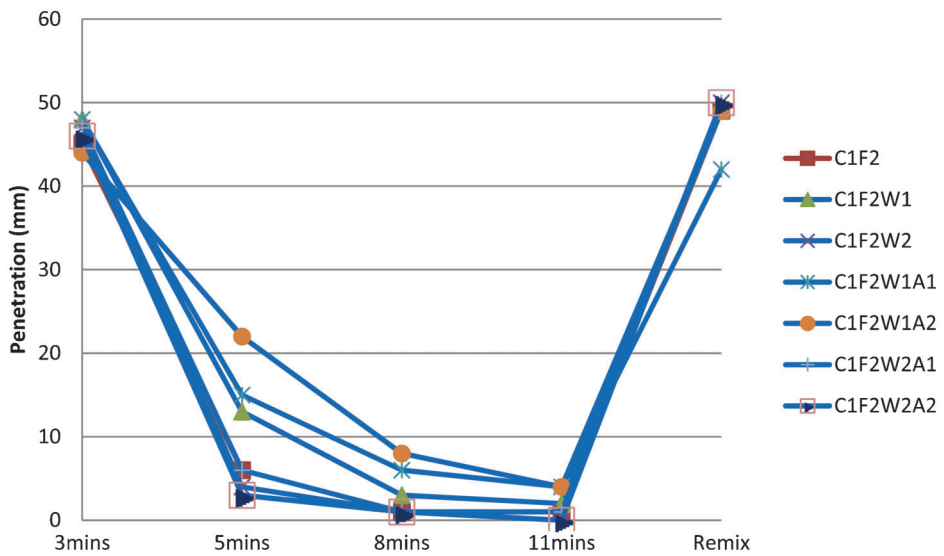

Figure C.3 Early age stiffening test results of mixtures containing C1F2.

TABLE C.3
Results of mini slump test performed on mixes containing cement C1 and F1 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C1	32.8	37.7	40.7	39.6	32.5	1.05	1.15	39.33
C1W1	75.9	56.7	40.3	37.0	35.2	**0.65**	0.75	44.68
C1W2	60.3	58.1	62.2	57.6	58.5	0.99	0.96	59.28
C1F1	55.0	55.4	56.7	49.8	43.4	0.90	1.01	53.98
C1F1W1	78.5	84.4	78.5	93.3	66.0	1.11	1.07	85.38
C1F1W2	105.6	95.0	109.9	83.3	73.4	0.88	0.90	96.06
C1F1W1A1	80.6	85.5	84.9	67.4	65.5	**0.79**	1.06	79.26
C1F1W1A2	73.9	72.8	56.7	55.0	47.8	**0.75**	0.99	61.51
C1F1W2A1	76.9	73.9	79.6	77.5	66.9	1.05	0.96	76.96
C1F1W2A2	84.4	72.3	82.7	72.8	57.2	1.01	0.86	75.98

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

TABLE C.4
Results of mini slump test performed on mixes containing cement C1 and F2 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C1	32.8	37.7	40.7	39.6	32.5	1.05	1.15	39.33
C1F2	50.7	51.1	53.6	48.6	45.3	0.95	1.01	51.10
C1F2W1	76.9	100.8	77.5	70.8	62.2	**0.70**	**1.31**	83.04
C1F2W2	100.8	143.8	106.8	120.1	113.7	0.84	**1.43**	123.56
C1F2W1A1	72.8	78.5	63.1	60.3	52.8	**0.77**	1.08	67.32
C1F2W1A2	74.4	70.8	64.5	56.3	55.0	**0.79**	0.95	63.88
C1F2W2A1	99.1	93.8	96.1	102.0	69.9	1.09	0.95	97.33
C1F2W2A2	105.0	103.2	103.2	79.0	92.1	**0.77**	0.98	95.15

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

(shown by **boldface** values in Table C.4). Similar results were obtained when W1 plasticizer was added along with either of the AEAs. However addition of W2 to C1F2 system resulted in false setting characteristics. W2 when used along with VR based AEA (A2) aggravated the problem and resulted in early stiffening behavior.

C.1.1.3 Results of Vicat's Initial Set Time Experiments

The results of the initial set time testing of plain and fly ash cementitious (20% replacement by weight) mixtures are reported in this section. Initial set time was determined following the ASTM C 191 and the change in the initial set time w.r.t. the base mixture was summarized. Base mixture is defined as the cementitious system without any admixtures. In the case of simple fly ash cementitious systems, plain cementitious system is used as base mixture for comparison. For example, C3 is the base mixture for C3F1 mixture and similarly C2F1 is the base mixture for combinations like C2F1W1A2.

Table C.5 and Table C.6 summarize the set time behavior of both plain and fly ash cementitious mixtures containing cement C1. Figures C.4 and C.5 depict a graphical representation of the initial set time results. Blue and red boxes in the figures represent the 60 minute compatibility window w.r.t. base mix. Combinations which have initial set time beyond these zones are deemed to be incompatible.

The replacement of cement by either of the fly ashes (F1 or F2) delayed the initial set, though, the change was not remarkable (≤60 mins) compared to the base mixture, C1. Also, addition of poly-carboxylate type superplasticizer (W2) to C1F1 system delayed the initial set time when compared to that of the base mix, C1F1. W2 when added along with A2 (C1F1W2A2) resulted in severe retardation of initial set. Addition of W1 slightly (≤60 min) accelerated the set time, though, when used along with either of the air entraining agents exhibited set behavior very similar to that of the base mixture.

Table C.6 summarizes the results of Vicat's set time measurement performed on C1F2 fly ash cementitious systems. The addition of lignin based W1 resulted in the acceleration of set time, however, this effect was found to be of significance (≥60 mins) only in C1F2W1 and C1F2W1A1 mixes (Figure C.5). Addition of PC type W2 alone or along with either of the air entraining admixtures did not show any marked acceleration or retardation effects w.r.t. to base mix C1F2. However, addition of synthetic type AEA (A1) along with W2 always (in both C1F1 and C1F2 systems) reduced the slight delaying effect observed when W2 alone was used.

C.1.1.4 Results of Semi-Adiabatic Calorimetry

From the semi-adiabatic calorimetry results tabulated in Table C.7, it was inferred that addition of either of the plasticizers (W1 or W2) to plain cementitious system resulted in an increase in the maximum peak temperature and also accelerated the time of occurrence of maximum peak temperature. However, the increase in the peak temperature for both combinations was less than the significant level of 10F (one of the limiting criteria) and the acceleration of maximum peak time was significant (≥60 mins) only in the case of C1W2 mixture (see Figure C.6). This Figure also contains the curves for fly ash mixtures (C1F1 and C1F2) which were added for comparative purposes.

Figure C.7 presents the semi-adiabatic calorimetric curves for C1F1 fly ash cementitious system. It can be seen that the addition of lignin based WRA (W1) to C1+F1 fly ash cementitious mixes significantly delayed the time of maximum peak occurrence. Similar results were observed when either of the air entraining agents (AEA), synthetic (A1) or VR based (A2), were added along with W1.

The results of semi-adiabatic calorimetry performed on C1F2 fly ash cementitious system are summarized in Table C.8 and are

TABLE C.5
Results of Vicat's initial set time test performed on mixes containing cement C1 and F1 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (mins)	Change w.r.t. base mix (mins)
C1	27.1	140	—
C1W1	26.2	155	+15
C1W2	26.2	160	+20
C1F1	24.9	180	+40
C1F1W1	23.5	145	−35
C1F1W2	23.8	**240**	+60
C1F1W1A1	23.3	180	0
C1F1W1A2	23.2	185	+5
C1F1W2A1	23.4	215	+35
C1F1W2A2	23.3	**285**	+105

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

TABLE C.6
Results of Vicat's initial set time test performed on mixes containing cement C1 and F2 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (mins)	Change w.r.t. base mix (mins)
C1	27.1	140	—
C1F2	24.8	175	+35
C1F2W1	23.5	**85**	−90
C1F2W1A1	23.4	**90**	−85
C1F2W1A2	23.2	120	−55
C1F2W2	23.6	205	+30
C1F2W2A1	23.2	180	+5
C1F2W2A2	23.2	160	−15

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

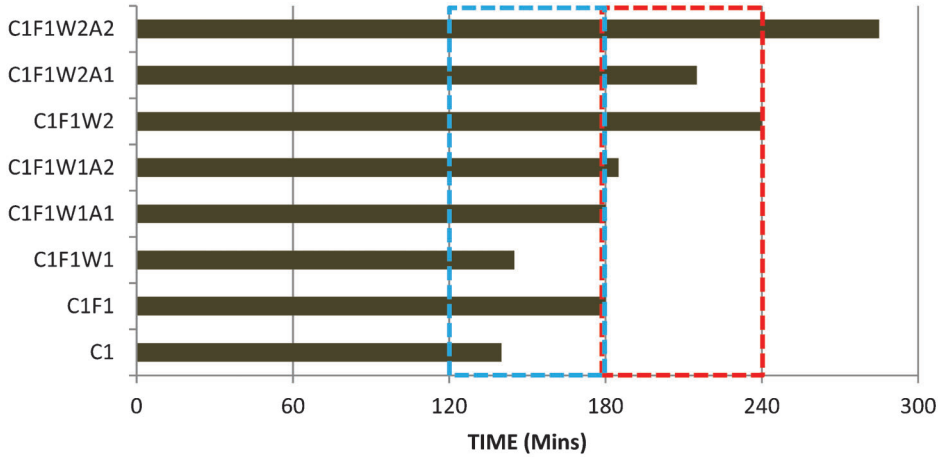

Figure C.4 Set time behavior of mixes containing C1 and F1.

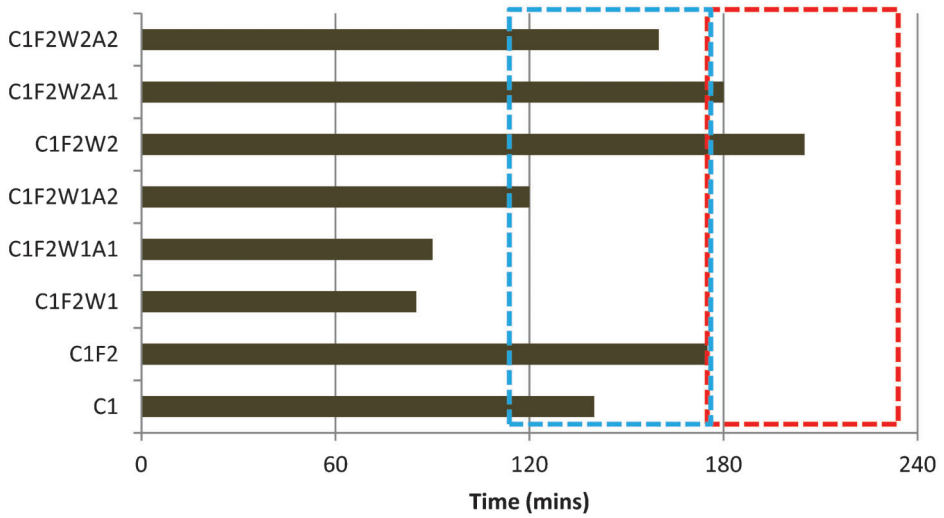

Figure C.5 Initial set time behavior of mixtures containing C1 and F2.

TABLE C.7
Summary of semi-adiabatic calorimetry results of pastes containing cement C1 and F1 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C1	104.2	812	No
C1W1	112.72	771	No
C1W2	112.05	674	No
C1F1	99.86	830	No
C1F1W1	105.14	**1011**	No
C1F1W1A1	101.56	**1069**	No
C1F1W1A2	102.01	**1068**	No
C1F1W2	103.69	803	No
C1F1W2A1	103.33	834	No
C1F1W2A2	102.67	871	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

TABLE C.8
Summary of semi-adiabatic calorimetry results of mortars containing cement C1 and F2 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C1	104.2	812	No
C1F2	97.5	952	No
C1F2W1	105.08	936	No
C1F2W1A1	101.31	**1045**	No
C1F2W1A2	100.81	**1189**	No
C1F2W2	103.23	**815**	No
C1F2W2A1	100.26	976	No
C1F2W2A2	101.06	**876**	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

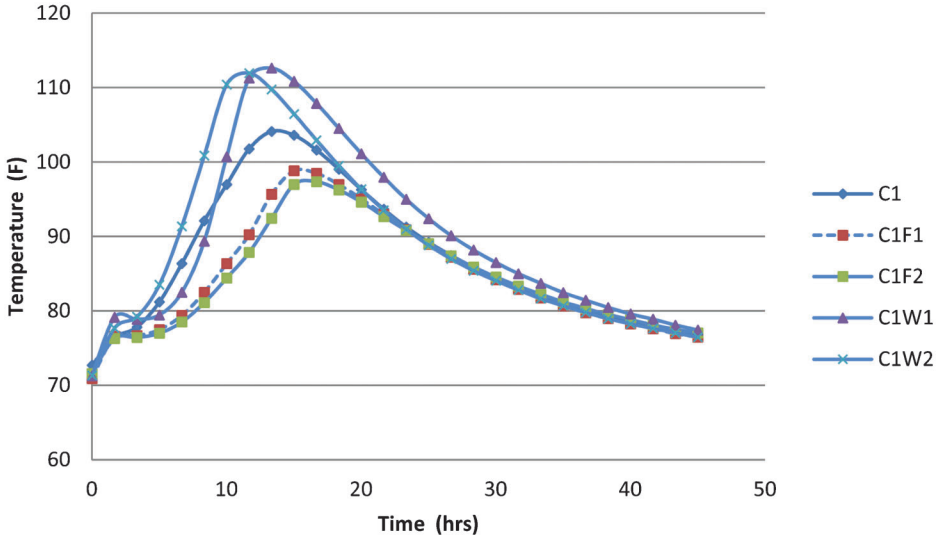

Figure C.6 Semi-adiabatic calorimetry curves of mortars containing cement C1.

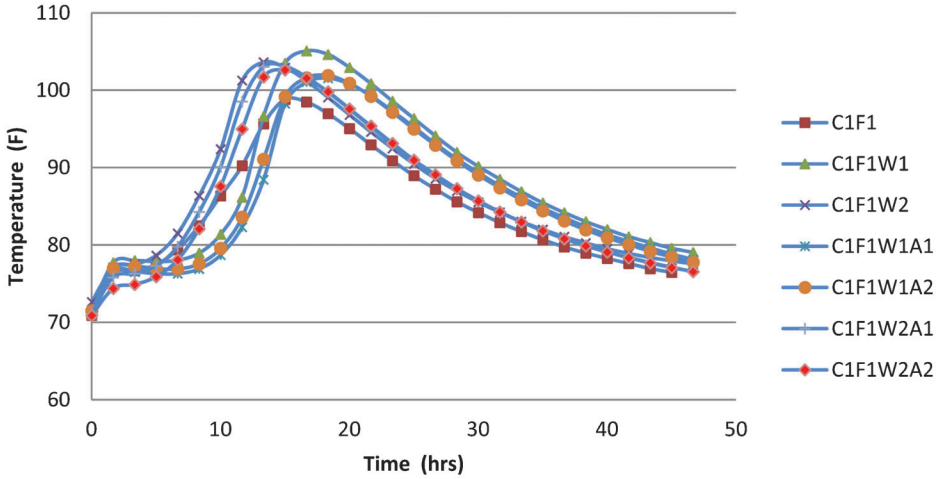

Figure C.7 Semi-adiabatic calorimetry curves of mortars containing cement C1 and F1 class C ash (20% replacement by weight).

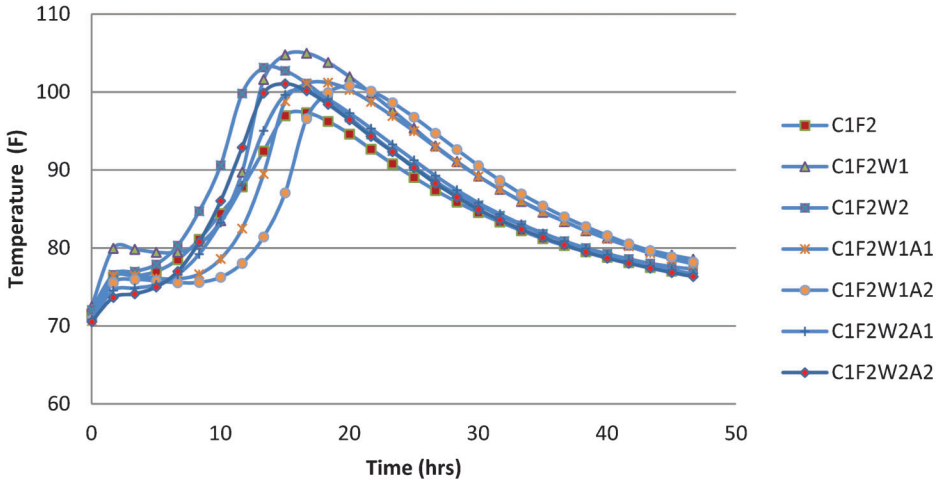

Figure C.8 Semi-adiabatic calorimetry curves of mortars containing cement C1 and F2 class C ash (20% replacement by weight).

presented graphically in Figure C.8. It was identified that addition of lignin based WRA (W1) along with A1 or A2 to C1F2 fly ash cementitious system delayed the occurrence of the peak. However, no such retardation effect was found when W1 alone was added to the C1F2 system. Addition of poly-carboxylate type superplasticizer (W2) to the C1F2 fly ash cementitious system accelerated the occurrence of the peak. Similar results were obtained when W2 plasticizer was added along with VR based AEA (A2).

C.1.2 Results of Experiments Performed on Mixtures Containing Cement C2

This section summarizes the results of experiments performed on plain and fly ash cementitious (20% replacement of cement by weight) systems containing cement C1 and class C ashes (F1 and F2). This section is subdivided in to four parts. Section C.1.2.1 summarizes the results of early stiffening test performed on mortars. Section C.1.2.2 illustrates the results of mini slump testing. Results of Vicat's initial set time are presented in Section C.1.2.3, followed by summary of semi-adiabatic calorimetry results in Section C.1.2.4.

C.1.2.1 Results of Early Age Stiffening Test

Table C.9 and Table C.10 present the early age stiffening test results of mixtures containing cement C2 (low (0.3%) alkalis, low (2.4%) sulfates and high (10.1%) C_3A content. All the plain and fly ash cementitious mixtures containing C2 exhibited early stiffening behavior in the testing. It was also observed that C2F2 mix exhibited flash setting behavior while C2F2W1 and C2F2W1A2 mixtures exhibited partial flash setting behavior. Figures C.9 through C.11 present the graphical representation of early stiffening test results of plain cementitious mixtures, C2F1 and C2F2 fly ash cementitious systems respectively.

C.1.2.2 Results of Mini Slump Testing

The results of mini slump test performed on paste mixtures containing cement C2 are presented in Table C.11 and Table C.12. Mini slump test results of mixtures were which identified as early stiffening are identified in **boldface**. It was observed that addition of W1 or W2 alone to plain cementitious systems resulted in early stiffening behavior because of a low (≤0.8) stiffening index (S.I.) value (Table C.11). Addition of W2 alone or along with A2 to C2F1 system resulted in rapid stiffening behavior. Similar behavior was exhibited when W1 was added along with either of the air entraining agents (A1 or A2) while no such behavior was observed when W1 alone was added to C2F1 system.

From Table C.12 it can be observed that addition of W1 (alone or along with either of the AEAs) to C2F2 fly ash cementitious systems resulted in early stiffening behavior (the results of the incompatible mixes are identified in **boldface**). Addition of Superplasticizer (W2) to C2F2 system did not exhibit any stiffening problems except when added along with A1. C2F2W2A1 mixture was identified as early stiffening mixtures

TABLE C.9
Results of early age stiffening test performed on mixes containing cement C2 and F1 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)*					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C2	201.8	48	4	1	0	32	**48**	7.8
C2F1	185	49	5	1	0	50	**49**	7.9
C2W1	195	46	6	4	2	50	**44**	7.1
C2W2	186	48	3	1	0	50	**48**	7.8
C2F1W1	185	45	4	5	1	50	**44**	6.1
C2F1W1A1	189.5	48	3	1	0	50	**48**	7.8
C2F1W1A2	183	49	7	4	1	50	**48**	7.7
C2F1W2	162.5	47	7	2	0	50	**47**	7.4
C2F1W2A1	165	48	7	2	1	50	**47**	7.5
C2F1W2A2	161	48	6	2	1	49	**47**	7.6

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

TABLE C.10
Results of early age stiffening test performed on mixes containing cement C2 and F2 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)*					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C2	201.8	48	4	1	0	32	**48**	7.8
C2F2	187.1	47	2	1	1	12	**46**	7.6
C2F2W1	167.5	48	3	2	1	38	**47**	7.7
C2F2W1A2	175	46	1	0	0	39	**46**	7.6
C2F2W1A1	173.5	48	2	1	0	48	**48**	7.9
C2F2W2	168.4	45	3	3	0	50	**45**	7.3
C2F2W2A1	173	47	5	1	0	50	**47**	7.6
C2F2W2A2	170	47	3	0	0	50	**47**	7.7

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

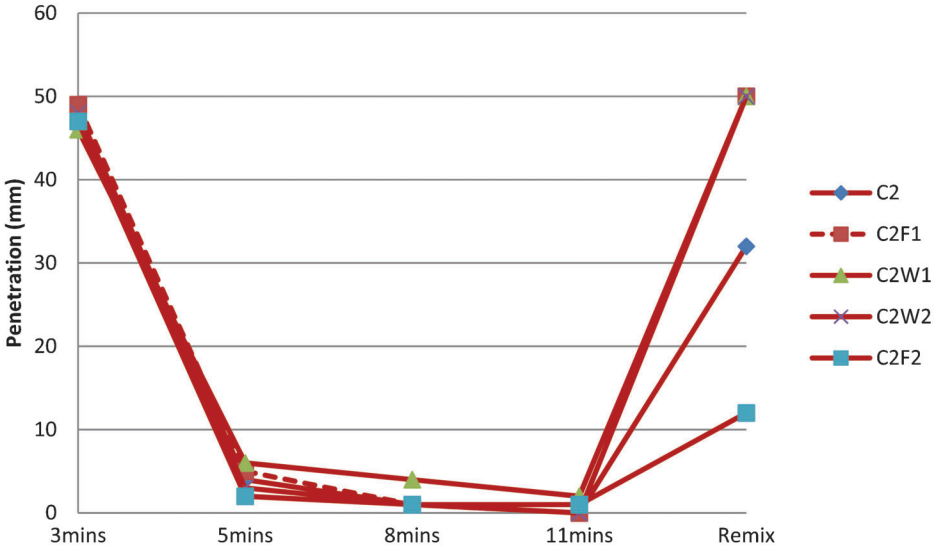

Figure C.9 Early age stiffening test results of mixtures containing cement C2.

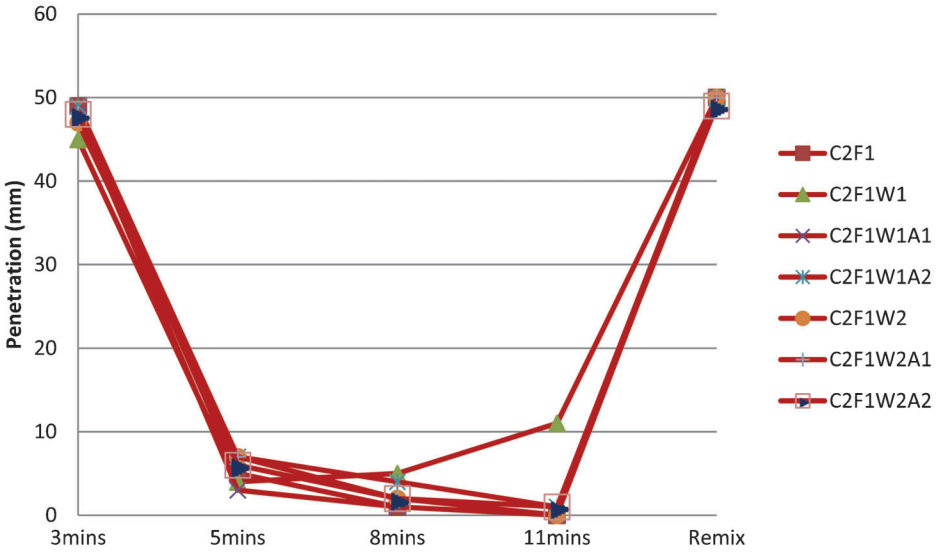

Figure C.10 Early age stiffening test results of mixtures containing cement C2F1.

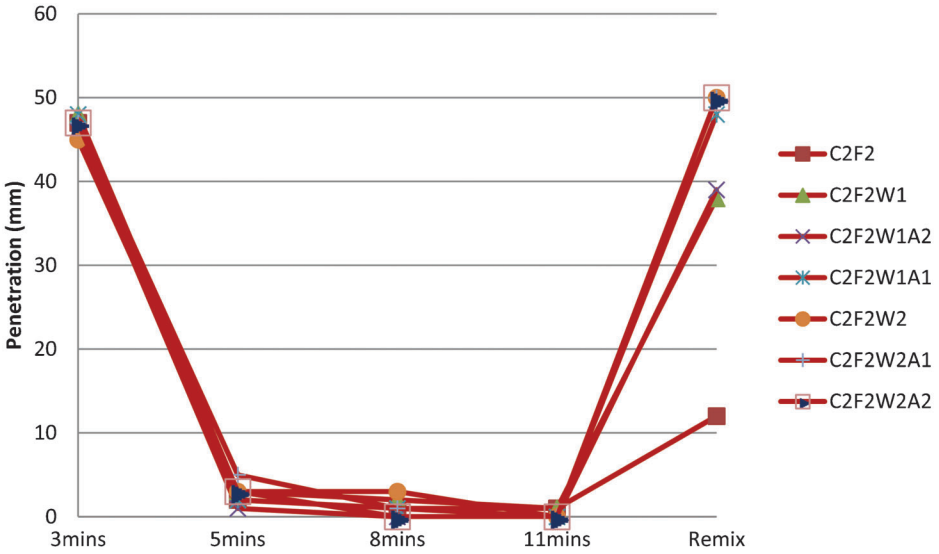

Figure C.11 Early age stiffening test results of mixtures containing cement C2F2.

TABLE C.11
Results of mini slump test performed on mixes containing cement C2 and F1 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C2	17.6	18.6	21.5	22.6	21.0	1.22	1.06	20.90
C2W1	13.6	27.3	22.1	21.8	21.8	**0.80**	**2.01**	23.72
C2W2	46.1	41.5	36.3	31.5	29.2	**0.76**	0.90	36.41
C2F1	14.3	21.2	21.5	20.7	19.4	0.97	**1.49**	21.14
C2F1W1	37.7	38.5	36.3	32.8	29.5	0.85	1.02	35.86
C2F1W2	40.3	60.8	50.7	43.4	40.3	**0.71**	**1.51**	51.61
C21F1W1A1	14.1	38.8	33.2	31.2	28.6	**0.80**	**2.76**	34.39
C2F1W1A2	13.6	46.5	40.7	35.6	29.9	**0.76**	**3.42**	40.94
C2F1W2A1	45.3	47.4	46.5	42.6	37.7	0.90	1.04	45.50
C2F1W2A2	40.3	44.9	39.2	35.6	34.9	**0.79**	1.11	39.91

NOTE: Mixtures identified as early stiffening are shown in **boldface**.

TABLE C.12
Results of mini slump test performed on mixes containing cement C2 and F2 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C2	17.6	18.6	21.5	22.6	21.0	1.22	1.06	20.90
C2F2	19.4	22.1	22.6	22.1	21.2	1.00	1.14	22.24
C2F2W1	14.3	38.5	29.2	25.5	19.9	**0.66**	**2.69**	31.06
C2F2W2	44.5	42.2	39.2	36.3	34.9	0.86	0.95	39.24
C2F2W1A1	18.3	39.2	30.8	27.3	21.0	**0.70**	**2.14**	32.45
C2F2W1A2	13.6	43.0	32.8	32.8	28.3	**0.76**	**3.15**	36.21
C2F2W2A1	40.3	46.9	37.4	35.6	34.2	**0.76**	1.16	39.97
C2F2W2A2	37.4	42.2	39.2	35.6	34.9	0.84	1.13	39.00

NOTE: Mixtures identified as early stiffening are shown in **boldface**.

because of a low S.I. value.Thus by changing the fly ash source from F1 to F2, early stiffening behavior observed when W2 was added was eliminated. At the same time, two mixtures—C2F2W1 and C2F2W2A1—that were compatible when F1 was used turned out to be early stiffening when F2 class C ash was used.

C.1.2.3 Results of Vicat's Initial Set Time Test

Table C.13 and Table C.14 summarize the set time behavior of both plain and fly ash cementitious mixtures containing cement C2. Figure C.12 and Figure C.13 summarize the results of Vicat's set time results for fly ash cementitious system containing C2F1 and C2F2 respectively. Replacing 20% of C2 with F1 class C ash delayed the initial set time (similar to the behavior of C1 mixtures) while replacing 20% of C2 by F2 resulted in acceleration in initial set time.

From Figure C.12, it can be observed that addition of chemical admixtures in general accelerated the initial set time w.r.t. base mix C2F1. Addition of lignin based WRA (W1) to C2F1 system resulted in serious acceleration of set. Also W1, when added along with either of the air entraining agents, resulted in significant accelerating effect. Similarly addition of PC type WRA (W2) also significantly accelerated the set. Addition of synthetic air entrainer (A1)or VR based air entrainer (A2) along with W2 exhibited similar effect.

Table C.14 and Figure C.13 summarize the results of Vicat's initial set time experiment performed on C2F2 system. Accelerating effect of W1 and W2 was found to be pronounced in case of mixes containing C2 and F2. The acceleration of initial

TABLE C.13
Results of Vicat's initial set time test performed on mixes containing cement C2 and F1 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (mins)	Change w.r.t. base mix (mins)
C2	s	175	—
C2F1	27.4	230	+55
C2F1W1	24.4	**140**	−90
C2F1W2	24.0	**155**	−75
C2F1W1A1	26.2	**110**	−120
C2F1W1A2	26.4	**135**	−95
C2F1W2A1	23.8	**157**	−73
C2F1W2A2	2.3	**170**	−60

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

TABLE C.14
Results of Vicat's initial set time test performed on mixes containing cement C2 and F2 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (mins)	Change w.r.t. base mix (mins)
C2	30.0	175	—
C2F2	27.2	115	−60
C2F2W1	24.5	**25**	−90
C2F2W2	23.6	**45**	−70
C2F2W1A1	24.4	**20**	−95
C2F2W1A2	24.1	**40**	−75
C2F2W2A1	23.5	**55**	−60
C2F2W2A2	23.3	**50**	−65

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

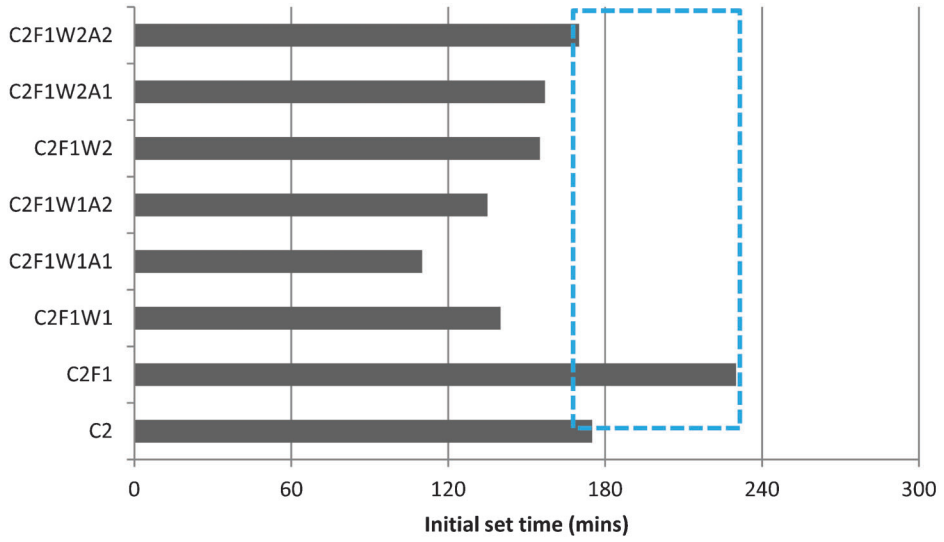

Figure C.12 Set time behavior of mixes containing C2 and F1.

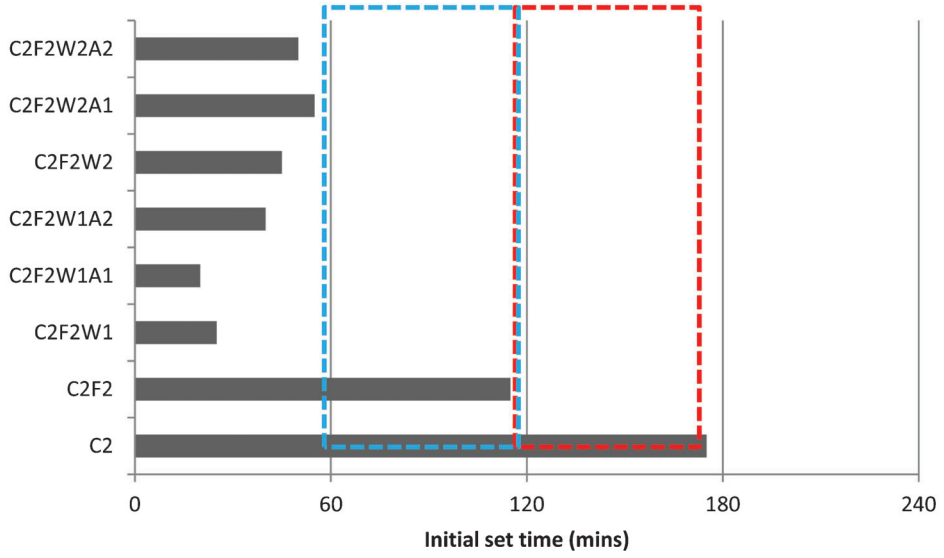

Figure C.13 Set time behavior of mixes containing C2 and F2.

TABLE C.15
Summary of semi-adiabatic calorimetry results of pastes containing cement C2 and F1 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C2	113.39	620	No
C2W1	108.51	**861**	No
C2W2	112.61	628	No
C2F1	**99.71**	**699**	No
C2F1W1	92.2	**521**	**Yes**
C2F1W1A1	93.47	**473**	**Yes**
C2F1W1A2	92.53	**531**	**Yes**
C2F1W2	100.36	**774**	No
C2F1W2A1	102.06	**767**	No
C2F1W2A2	102.32	**824**	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

set time was also found to be significant (≥60 mins) when W1 or W2 were added along with either of the AEAs to the C2F2 system.

C.1.2.4 Results of Semi-Adiabatic Calorimetry

Results of semi-adiabatic calorimeter experiment performed on C2 plain and C2F1 fly ash cementious systems are presented in Table C.15 and in Figures C.14 and C.15. The replacement of cement by F1 class C ash, reduced the maximum peak temperature and delayed the occurrence of maximum peak. It was also observed that addition of W1 to C2F1 fly ash cementitious systems accelerated the occurrence of peak (w.r.t. base mix C2F1) and also resulted in development of secondary peaks. Similar results were obtained when either of the AEAs were added along with W1 to the C2F1 system. However, addition of W2 (alone or along with either of the AEAs) to C2F1 fly ash cementitious system delayed occurrence of peak and no significant secondary peaks were observed. Development of secondary peaks due to addition of W1 to C2F1 system can be clearly seen in Figure C.15.

Table C.16 and Figure C.16 summarize the results of semi-adiabatic calorimeter test performed on the C2F2 fly ash cementitious systems. It was observed that addition of W1 to C2F2 fly ash cementitious system resulted in development of

TABLE C.16
Summary of semi-adiabatic calorimetry results of pastes containing cement C2 and F2 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C2	113.39	620	No
C2F2	**100.21**	668	No
C2F2W1	89.82	613	**Yes**
C2F2W1A1	87.57	650	**Yes**
C2F2W1A2	87.12	693	**Yes**
C2F2W2	100.56	**728**	No
C2F2W2A1	99.07	**764**	No
C2F2W2A2	98.58	**749**	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

significant secondary peaks. Similar results were observed when either of the AEAs were added along with W1 to the C2+F2 system. No such behavior was observed in mixes with W2 alone. However, addition of W2 along with either of the AEAs delayed the occurrence of the primary peak.

C.1.3 Results of Experiments Performed on Mixtures Containing Cement C3

This section summarizes the results of experiments performed on plain and fly ash cementitious (20% replacement of cement by weight) systems containing cement C3 and class C ashes (F1 and F2). Section C.1.3.1 reports the results of early stiffening test while Section C.1.3.2 summarizes the results of mini slump testing. Results of Vicat's initial set time are presented in Section C.1.3.3 followed by semi-adiabatic calorimetry results in Section C.1.3.4.

C.1.3.1 Results of Early Age Stiffening Test

Early age stiffening results of mortar samples containing cement C3 (high (1.06%) alkalis, high (3.6%) sulfates and high (10%) C_3A content) are summarized in Tables C.17 (for C3F1 system) and C.18 (for C3F2 system).

Mixtures containing cement C3 exhibited very few cases of incompatibility and hence turned out to be the most robust. Only

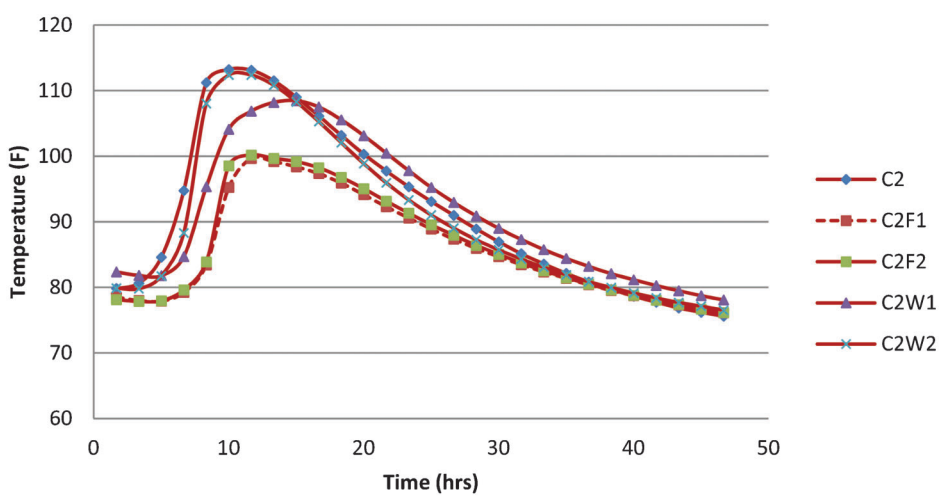

Figure C.14 Semi-adiabatic calorimetry curves of mortars containing cement C2.

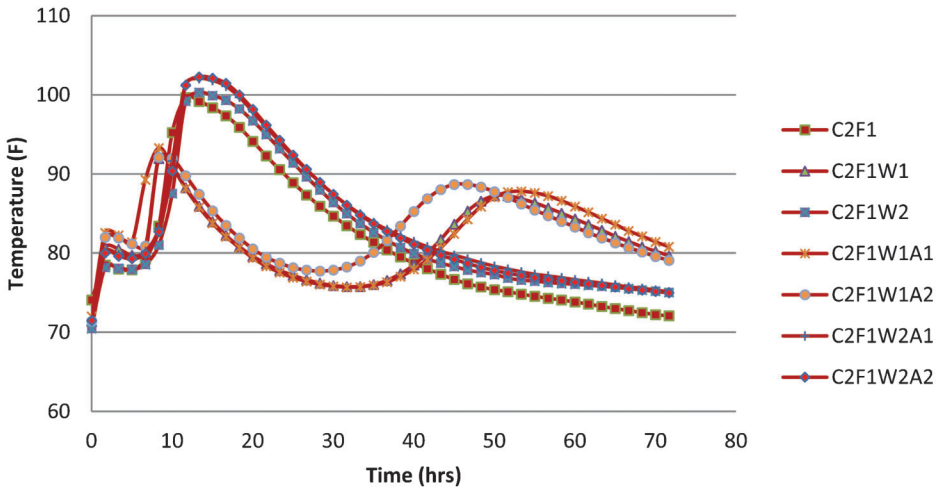

Figure C.15 Semi-adiabatic calorimetry curves of mortars containing cement C2 and F1 class C ash (20% replacement by weight).

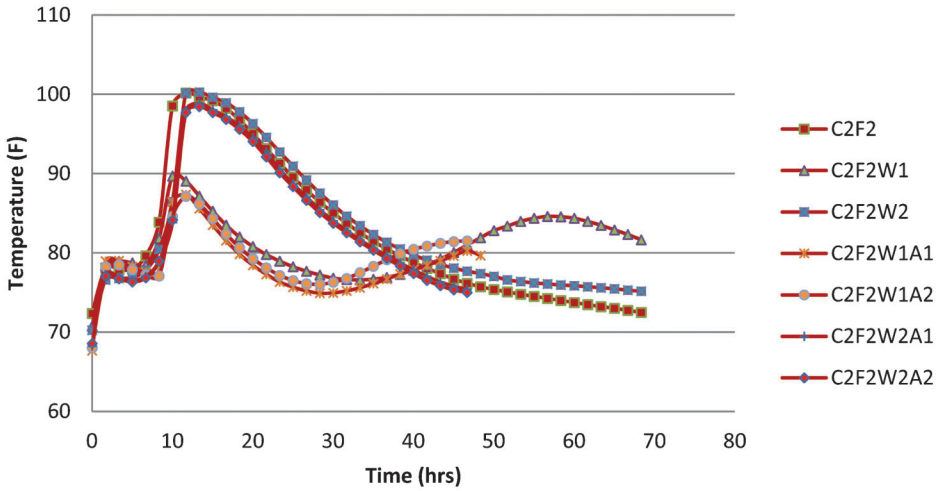

Figure C.16 Semi-adiabatic calorimetry curves of mortars containing cement C2 and F2 class C ash (20% replacement by weight).

TABLE C.17
Results of early age stiffening test performed on mixes containing cement C3 and F1 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C3	200.2	44	29	20	14	50	30	4.17
C3W1	204.5	46	24	19	7	50	39	5.56
C3W2	188.2	47	40	34	27	50	20	2.61
C3F1	181	49	48	25	12	50	37	4.17
C3F1W1	177.2	47	13	5	3	50	**44**	6.78
C3F1W2	166.7	48	40	22	20	49	28	3.56
C3F1W1A1	182.6	49	48	26	10	50	39	4.39
C3F1W1A2	180.1	44	33	32	6	50	38	4.83
C3F1W2A1	174	49	30	10	10	50	39	5.39
C3F1W2A2	170	49	43	31	28	50	21	2.67

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

TABLE C.18
Results of early age stiffening test performed on mixes containing cement C3 and F2 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C3	200.2	44	29	20	14	50	30	4.17
C3F2	179.4	49	47	10	9	50	40	4.56
C3F2W1	180.2	49	7	4	3	50	**46**	7.44
C3F2W2	171.6	45	34	12	8	50	37	4.72
C3F2W1A1	180.2	48	26	13	6	50	**42**	5.9
C3F2W1A2	179.9	48	35	13	8	50	40	5.2
C3F2W2A1	172.8	45	34	10	9	50	36	4.6
C3F2W2A2	172	48	38	24	13	50	35	4.4

NOTE: Values shown in **boldface** indicate potential incompatible mixes identified based on the limiting criteria.

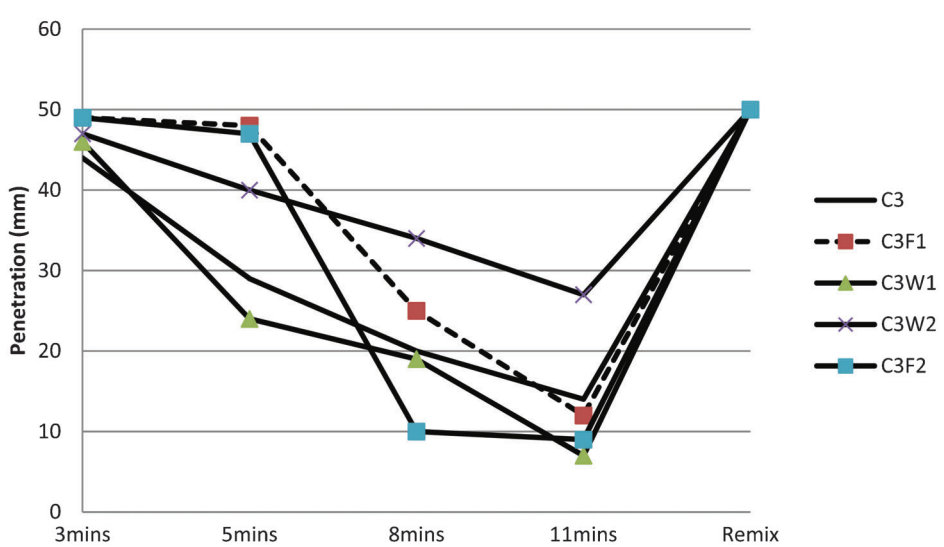

Figure C.17 Early age stiffening test results of mixtures containing cement C3.

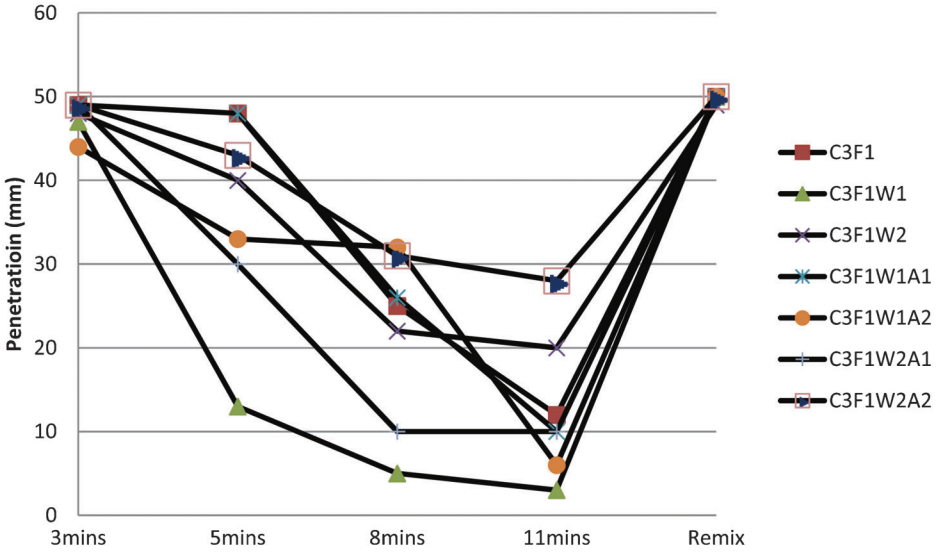

Figure C.18 Early age stiffening test results of mixtures containing cement C3F1.

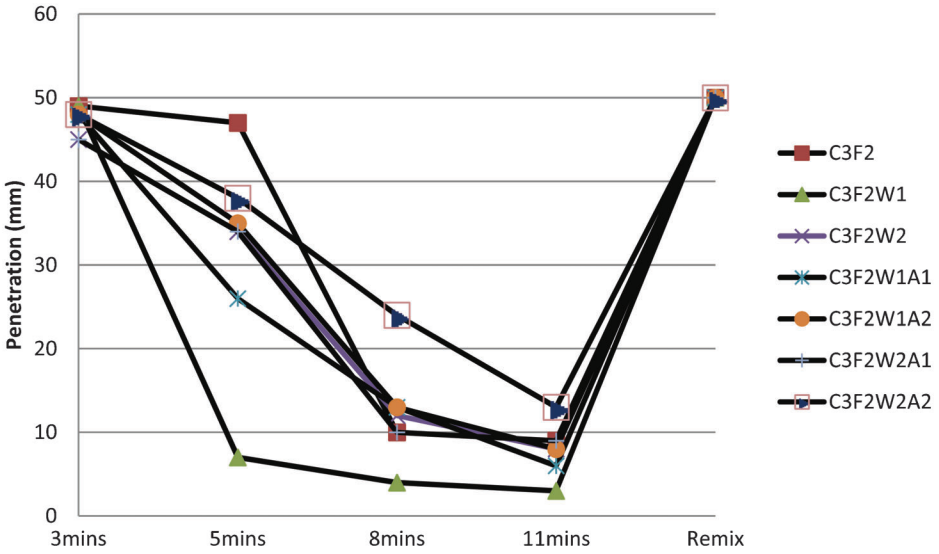

Figure C.19 Early age stiffening test results of mixes containing C3F2.

three mixtures (C3F1W1, C3F2W1 and C3F2W1A1) out of the 17 mixtures tested exhibited early stiffening behavior when tested using ASTM C 359 (early age stiffening test on mortars). The three incompatible mixtures were found to exhibit false setting behavior.

Thus addition of lignin type WRA (W1) to the fly ash cementitious (both C3F1 and C3F2) mixtures resulted in false setting behavior. On the other hand, addition of poly-carboxylate type superplasticizer (W2) to plain or to fly ash cementitious systems did not result in early stiffening behavior. Figures C.17 through C.19 summarize the early stiffening results of mixtures containing cement C3.

C.1.3.2 Results of Mini Slump Testing

Table C.19 and Table C.20 summarize the mini slump test results of plain and fly ash cementitious mixtures containing cement C3. The plain system (C3) by itself was found to exhibit false setting behavior (F.S.I. > 1.3). 20% replacement of cement C3 by either of the class C ashes slightly reduced the FSI. However, F.S.I. of the mixtures C3F1 and C3F2 were found to be large enough (>1.3) and hence were classified as false setting mixtures. Addition of lignin based WRA (W1) to C3 eliminated the problem of false setting. Addition of poly-carboxylate type SP (W2) along with VR based AEA (A2) to C3F1 system resulted in false setting characteristics. In general, mixtures with C3F1 system (Table 3.19) registered lower incompatibility problems when compared to those with C3F2 system (Table 3.20). All mixtures with C3F2 system exhibited false setting behavior except for C3F2W2A1 mixture. C3F2W1A2 mixture in particular, was found to show both early stiffening and false setting characteristics.

C.1.3.3 Results of Vicat's Initial Set

Table C.21 and Figure C.20 summarize the results from setting time experiment performed on the plain cementitious and C3F1 fly ash cementitious systems. Addition of lignin based WRA W1 or PC based superplasticizer (W2) to plain cementitious system significantly (≥60 mins) delayed the initial set time w.r.t. base mixture C3. However no significant retardation was observed when either of these plasticizers were added to C3F1 fly ash cementitious system. It was also observed that addition of W2

TABLE C.19
Results of mini slump test performed on mixes containing cement C3 and F1 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C3	30.2	44.2	41.5	38.5	36.7	0.87	**1.46**	41.36
C3W1	15.4	17.8	36.3	38.1	36.3	2.14	1.16	30.74
C3W2	29.9	41.1	42.2	41.5	41.1	1.01	**1.38**	41.58
C3F1	41.5	55.0	49.0	44.2	39.6	**0.80**	**1.33**	49.37
C3F1W1	49.4	56.3	53.2	51.9	50.2	0.92	1.14	53.80
C3F1W2	55.4	62.2	56.7	56.7	53.2	0.91	1.12	58.54
C31F1W1A1	54.1	48.6	51.1	48.6	45.3	1.00	0.90	49.41
C3F1W1A2	82.2	50.2	56.3	70.3	43.4	1.40	0.61	58.95
C3F1W2A1	51.5	55.0	51.1	45.3	41.1	0.83	1.07	50.46
C3F1W2A2	28.3	39.6	34.9	35.2	32.2	0.89	**1.40**	36.57

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.20
Results of mini slump test performed on mixes containing cement C3 and F2 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C3	30.2	44.2	41.5	38.5	36.7	0.87	**1.46**	41.36
C3F2	25.8	35.2	30.5	30.8	28.9	0.87	**1.37**	32.19
C3F2W1	13.8	33.5	31.8	30.2	38.5	0.90	**2.42**	31.83
C3F2W2	39.6	61.7	55.4	50.7	49.8	0.82	**1.56**	55.92
C3F2W1A1	12.4	42.2	36.3	36.6	34.5	0.87	**3.42**	38.38
C3F2W1A2	19.6	43.4	38.5	34.5	34.9	**0.80**	**2.21**	38.79
C3F2W2A1	51.9	64.1	61.7	57.2	52.8	0.89	1.23	60.98
C3F2W2A2	38.1	59.0	57.6	51.5	51.9	0.87	**1.55**	56.03

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.21
Summary of setting time results of pastes containing cement C3 and F1 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (min)	Change w.r.t. base mix (min)
C3	28.5	190	—
C3W1	30.1	280	**+90**
C3W2	27.8	258	**+68**
C3F1	26	190	0
C3F1W1	27.8	175	−15
C3F1W2	25.8	200	+10
C3F1W1A1	28	220	+30
C3F1W1A2	26.9	235	+45
C3F1W2A1	25.9	275	**+85**
C3F1W2A2	25.9	250	**+60**

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

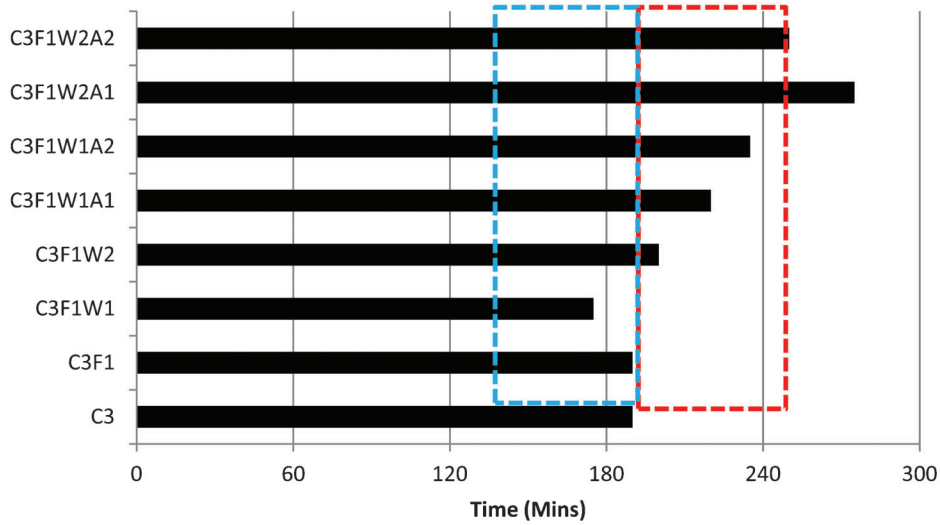

Figure C.20 Vicat's intial set test performed on mixtures containing C3F1 systems.

along with either of the AEAs resulted in significant delay of the initial set time.

Table C.22 and Figure C.21 summarize the initial set time results of C3F2 fly ash cementitious systems. All of C3F2 series mixtures, except for C3F2W1A1, were found to have initial set time within the compatibility window of 60 minutes w.r.t. base mix (C3F2). Acceleration of the initial set was observed in C3F2W1A1 mix.

TABLE C.22
Summary of setting time results of pastes containing cement C3 and F2 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (min)	Change w.r.t. base mix (min)
C3	28.5	190	—
C3F2	26.9	248	+58
C3F2W1	26.2	197	−51
C3F2W2	24.2	295	+47
C3F2W1A1	27.7	**180**	−68
C3F2W2A1	25.2	285	+37
C3F2W1A2	27.0	200	−48

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

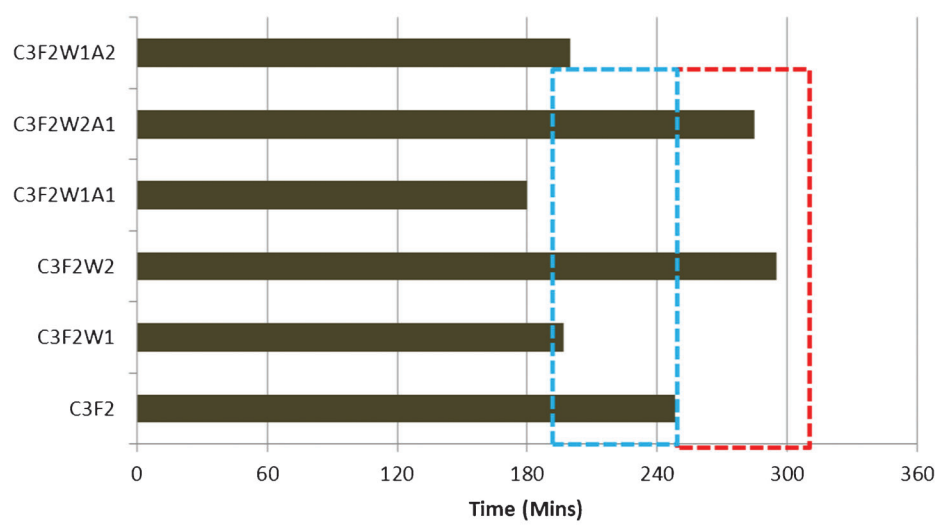

Figure C.21 Vicat's intial set test performed on mixtures containing C3F2 systems.

TABLE C.23
Summary of semi-adiabatic calorimetry results of pastes containing cement C3 and F1 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C3	118.83	634	No
C3W1	120.76	**707**	No
C3W2	119.07	654	No
C3F1	110.4	**829**	No
C3F1W1	111.06	**922**	No
C3F1W1A1	112.22	**989**	No
C3F1W1A2	110.51	**1009**	No
C3F1W2	113.28	835	No
C3F1W2A1	112.27	843	No
C3F1W2A2	112.44	867	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

C.1.3.4 Results of Semi-Adiabatic Calorimetry

Results of the semi-adiabatic calorimetry performed on plain and C3F1 fly ash cementitious systems are presented in Table C.23 and in Figures C.22 and C.23, respectively. Replacement of cement by either of the class C ashes, resulted in delay of the time of maximum peak occurrence and a minor (<10F) decrease in maximum peak temperature. Tests also indicated that addition of lignin based WRA (W1) alone or along with either of the AEAs to C3F1 fly ash cementitious systems significantly delayed the occurrence of maximum temperature peak.

Table C.24 and Figure C.24 summarize the results of semi-adiabatic calorimetry performed on C3F2 fly ash cementitious mixtures. It was observed that addition of lignin based WRA (W1) alone or along with either of the AEAs to C3F2 fly ash cementitious systems significantly delayed (>60 mins) the occurrence of peak.

C.1.4 Results of Experiments Performed on Mixtures Containing Cement C4

This section summarizes the results of experiments performed on plain and fly ash cementitious (20% replacement of cement by weight) systems containing cement C4 (7.7% C_3A, 3.6% SO_3 and 0.96% total alkalis) and class C ashes (F1 and F2). This section is subdivided in to four parts. Section C.1.4.1 summarizes early stiffening test while Section C.1.4.2 summarizes the results of mini slump testing. Results of Vicat's initial set time are presented in Section C.1.4.3 followed by semi-adiabatic calorimetry results in Section C.1.4.4.

C.1.4.1 Results of Early Age Stiffening Test

This section comprises of a summary of the results of early age stiffening experiments performed on mortar samples containing cement C4.10 out of the 17 mixtures containing cement C4 were found to exhibit false setting behavior. Table C.25 and Table C.26 summarize the early stiffening results of plain C4 cementitious and either C4F1 systems or C4F2 fly ash cementitious mixtures, respectively. Figures C.25 to C.27 are the graphical representation of the results tabulated in these tables.

Plain cement C4 mixture, without any admixtures, was found to exhibit false setting behavior. However 20% replacement by F2 fly ash eliminated the false setting characteristics. Addition of lignin based WRA (W1) to plain or fly ash cementitious systems (both C4F1 and C4F2) resulted in false setting. Addition of AEAs did not alleviate the false setting characteristics of C4F1W1.

Table C.26 and Figure C.27 present the results of early age stiffening test performed on C4F2 fly ash cementitious mixtures. Addition of lignin based WRA (W1) or poly-carboxylate type superplasticizer (W2) to the C4F2 fly ash cementitious systems

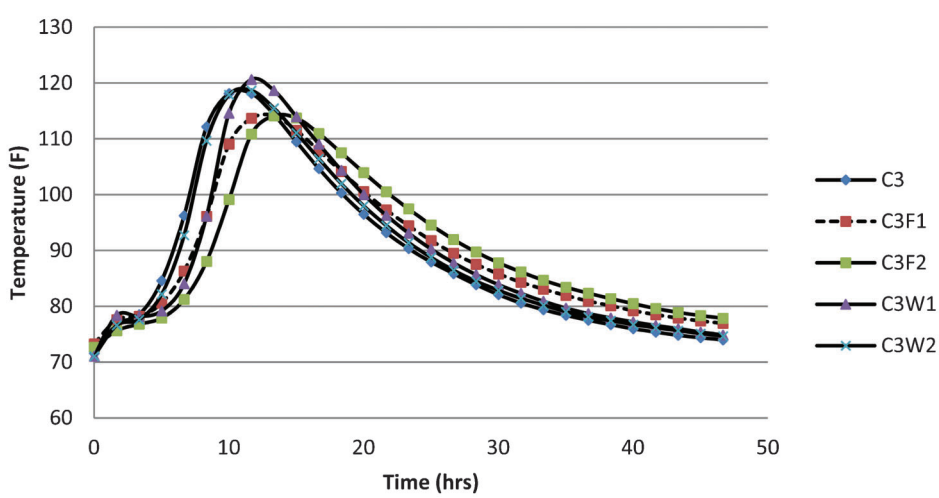

Figure C.22 Semi-adiabatic calorimetry curves of mortars containing cement C3.

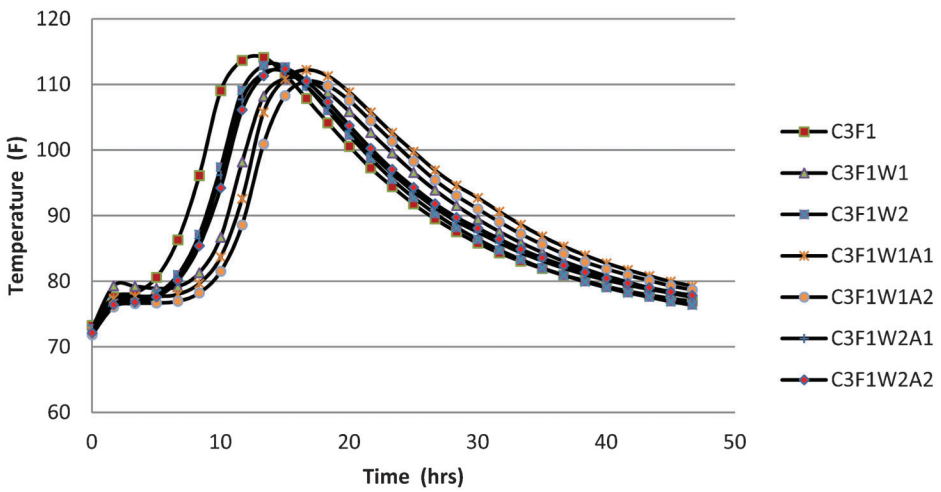

Figure C.23 Semi-adiabatic calorimetry curves of mortars containing cement C3 and F1 class C ash (20% replacement by weight).

TABLE C.24
Summary of semi-adiabatic calorimetry results of pastes containing cement C3 and F2 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C3	118.83	634	No
C3F2	114.41	**825**	No
C3F2W1	110.45	**925**	No
C3F2W1A1	113.11	**945**	No
C3F2W1A2	111.06	**969**	No
C3F2W2	111.99	840	No
C3F2W2A1	113.84	785	No
C3F2W2A2	114.24	813	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

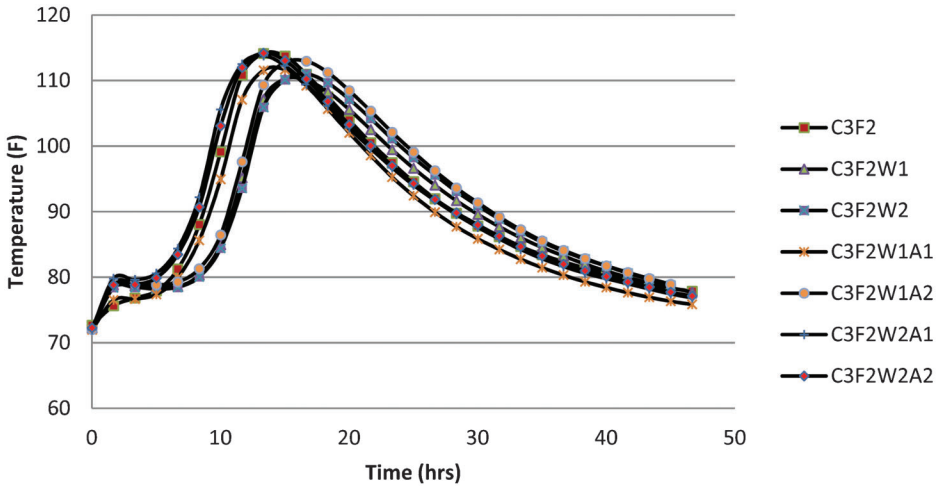

Figure C.24 Semi-adiabatic calorimetry curves of mortars containing cement C3 and F2 class C ash (20% replacement by weight).

TABLE C.25
Results of early age stiffening test performed on mixes containing cement C4 and F1 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)*					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C4	205.1	46	9	4	3	50	**43**	6.83
C4W1	193.6	45	6	4	3	50	**42**	6.83
C4W2	194	48	11	6	6	50	**42**	6.72
C4F1	184.7	48	19	5	3	50	**45**	6.61
C4F1W1	168.9	49	20	3	1	50	**48**	6.94
C4F1W2	166.3	46	6	5	6	50	40	6.67
C4F1W1A1	168.9	49	16	3	2	43	**47**	7.06
C4F1W1A2	163	48	18	7	2	49	**46**	6.78
C4F1W2A1	174	49	47	35	25	50	24	2.78
C4F1W2A2	167.6	46	20	7	7	50	39	5.78

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.26
Results of early age stiffening test performed on mixes containing cement C4 and F2 class C ash (20% replacement by weight)

Mix #	Water required (g)	Penetration depth (mm)					Early age stiffening amount (mm)	Average early age stiffening rate (mm/min)
		A	B	C	D	E		
C4	205.1	46	9	4	3	50	43	6.83
C4F2	178.7	49	29	25	12	50	37	5.22
C4F2W1	171.9	48	8	3	1	50	**47**	7.44
C4F2W2	171.2	49	32	6	4	50	**45**	5.94
C4F2W1A1	167	45	12	5	2	50	**43**	6.6
C4F2W1A2	166.9	48	35	11	8	50	40	5.2
C4F2W2A1	168.3	44	20	17	9	50	35	5.2
C4F2W2A2	164.4	45	15	9	7	50	38	5.9

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

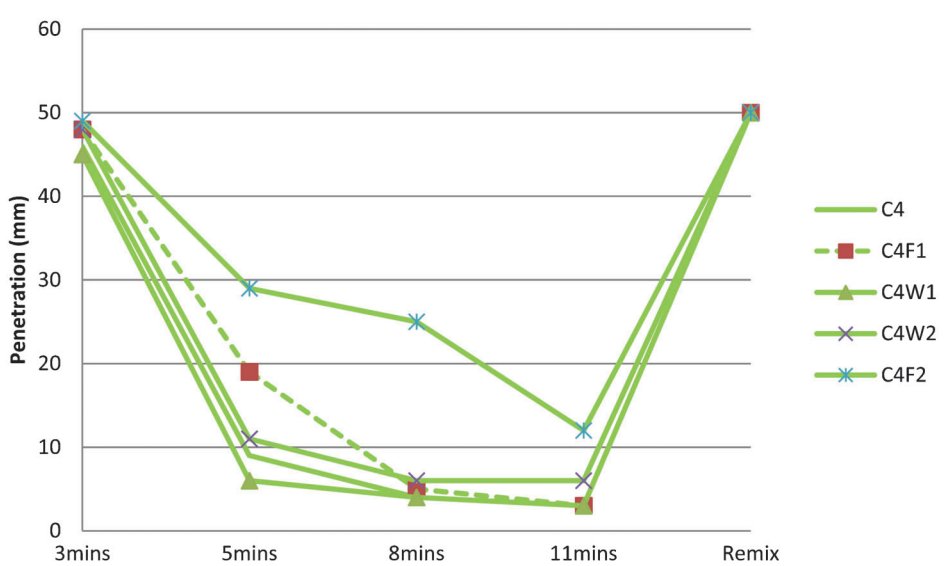

Figure C.25 Early age stiffening test results of mixes containing C4.

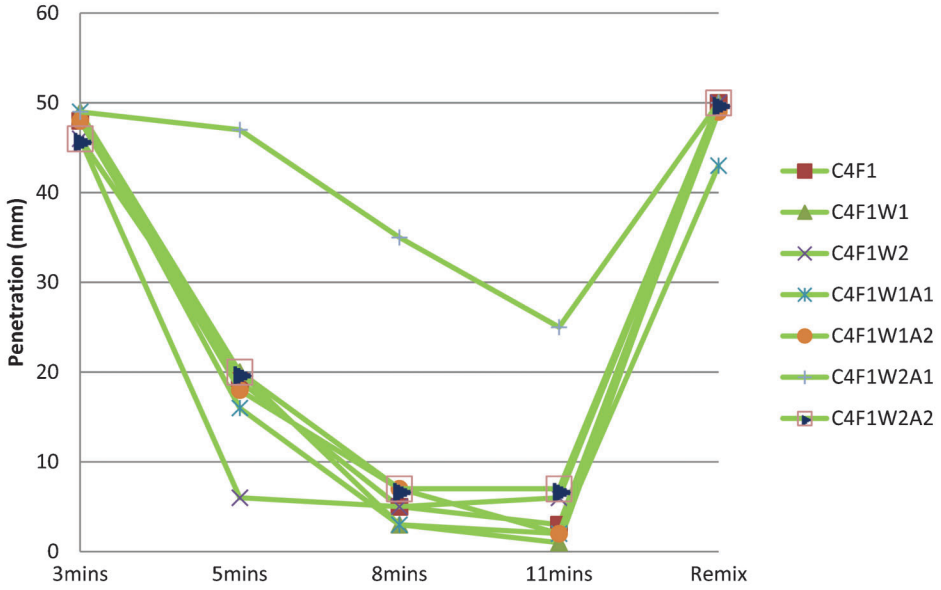

Figure C.26 Early age stiffening test results of mixes containing C4F1.

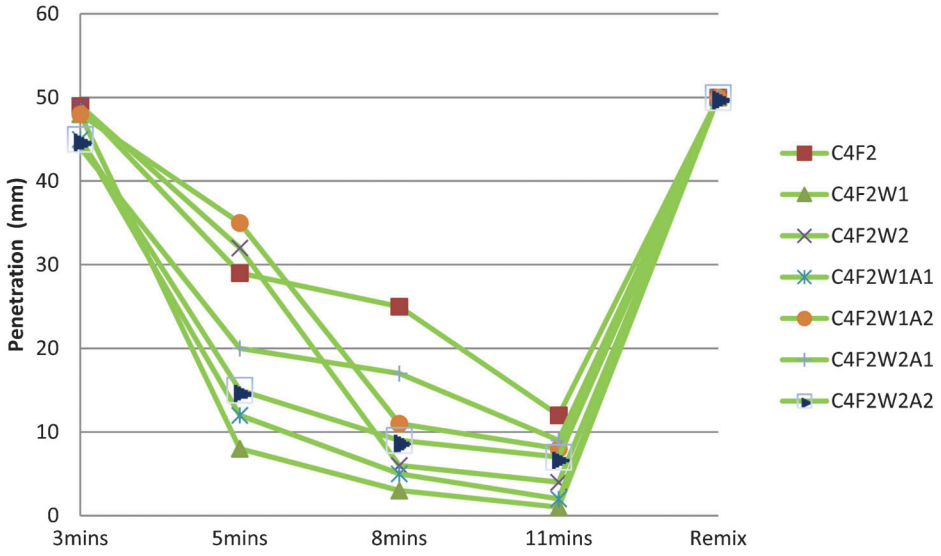

Figure C.27 Early age stiffening test results of mixes containing C4F2.

resulted in false setting behavior. However, no such effect was observed when W2 was added along with either of the AEAs (A1 or A2) to the C4F2 system.

C.1.4.2 Results of Mini Slump Test

Table C.27 and Table C.28 summarize the mini slump test results of plain and fly ash cementitious mixtures containing cement C4. It was observed that plain cementitious mixture (C4), without any admixtures, was identified as early stiffening mixture. Addition of lignin based WRA (W1) to the plain cementitious mixture aggravated the early stiffening behavior (lower S.I. value). 20% replacement of cement F1 class C ash or addition of W2 eliminated the early stiffening behavior.

It was also found out that addition of lignin based WRA (W1) to plain or C4F1 fly ash cementitious systems decreased the S.I value and hence resulted in more severe early stiffening behavior. However, no such behavior was observed with poly-carboxylate type SP (W2).

Table C.28 summarizes the results of mini slump cone test performed on C4F2 fly ash cementitious systems. It must be noted that the addition of lignin based WRA (W1) to C4F2 fly ash cementitious system, unlike in the case of C4F1 system, resulted in a compatible mixture. However, W1 when added along with along either of the entraining agents (A1 or A2) resulted in false setting behavior. Addition of W2 did not have any significant effect on the stiffening characteristics of the plain and fly ash cementitious mixtures containing cement C4.

C.1.4.3 Results of Vicat's Initial Set Time

Table C.29 and Figure C.28 summarize the results of set time experiment performed on the plain and C4F1 fly ash cementitious mixtures. It was observed that addition of either of the class C ashes delayed the initial set time slightly (< 60 mins w.r.t. base mixture C4). Addition of W1 or W2 to plain or C4F1 fly ash cementitious mixtures resulted in significant delay of the initial set

TABLE C.27
Results of mini slump test performed on mixes containing cement C4 and F1 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C4	48.2	58.1	43.0	46.1	46.9	**0.79**	1.21	49.06
C4W1	81.7	60.3	38.8	39.6	43.8	**0.66**	0.74	46.24
C4W2	58.5	53.2	58.5	61.3	60.3	1.15	0.91	57.66
C4F1	49.8	52.4	62.6	57.2	55.8	1.09	1.05	57.39
C4F1W1	95.0	80.6	59.0	52.8	51.9	**0.65**	0.85	64.12
C4F1W2	71.8	86.0	87.6	71.8	71.8	0.84	1.20	81.83
C41F1W1A1	84.9	64.5	63.6	54.1	55.0	0.84	0.76	60.73
C4F1W1A2	73.4	56.3	52.4	48.2	48.2	0.86	0.77	52.27
C4F1W2A1	60.3	68.9	76.9	73.4	76.4	1.07	1.14	73.05
C4F1W2A2	59.9	75.9	68.9	64.1	64.1	0.84	1.27	69.61

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.28
Results of mini slump test performed on mixes containing cement C4 and F2 class C ash (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
C4	48.2	58.1	43.0	46.1	46.9	**0.79**	1.21	49.06
C4F2	45.3	69.4	58.1	57.6	52.8	0.83	**1.53**	61.68
C4F2W1	55.4	66.4	67.9	65.5	59.4	0.99	1.20	66.61
C4F2W2	67.9	73.9	76.9	79.0	67.9	1.07	1.09	76.61
C4F2W1A1	43.0	63.1	58.1	57.2	55.4	0.91	**1.47**	59.45
C4F2W1A2	32.5	48.2	56.3	53.2	56.7	1.10	**1.48**	52.55
C4F2W2A1	59.4	67.4	75.9	81.7	88.8	1.21	1.13	75.00
C4F2W2A2	61.6	65.5	74.4	80.6	75.9	1.23	1.06	73.49

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.29
Summary of setting time results of pastes containing cement C4 and F1 class C ash (20% replacement by weight)

Mix #	Water of normal consistency (%)	Initial set time (min)	Change w.r.t. base mix (min)
C4	27.6	220	—
C4W1	28.6	**380**	+160
C4W2	27	**305**	+85
C4F1	25.1	235	+15
C4F1W1	25.2	**320**	+85
C4F1W2	24.2	**335**	+100
C4F1W1A1	25.1	230	−5
C4F1W1A2	24.6	**320**	+85
C4F1W2A1	24.2	280	+45
C4F1W2A2	23.8	275	+40

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

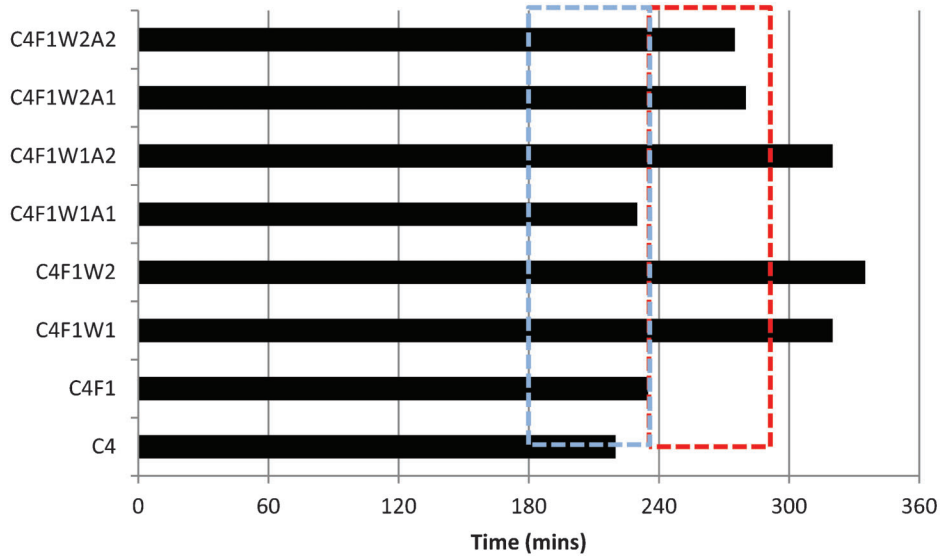

Figure C.28 Intial set behavior of mixtures containing C4F1.

time. Similar effects were observed when W1 was added along with VR based AEA (A2).

Table C.30 summarizes the Vicat's initial set time measurements performed on C4F2 fly ash cementitious system. The same results are plotted in Figure C.29. It was observed that addition of chemical admixtures in general delayed the initial set time. However retardation was significant only in 3 mixes: C4F2W2, C4F2W1 and C4F2W2A2.

C.1.4.4 Results of Semi-Adiabatic Calorimetry

This section presents the results of semi-adiabatic calorimetry performed on plain and fly ash cementitious mixtures containing cement C4. Table C.31 summarizes the results of plain and C4F1 fly ash cementitious mixtures (plotted, respectively, in Figure C.30 and Figure C.31). Addition of lignin based (W1) or polycarboxylate SP (W2) to C4F1 fly ash cementitious system delayed the occurrence of the peak. Similar results were obtained when synthetic or VR based AEAs were added along with either of the plasticizers except for the C4F1W2A1 mix which did not show significant retardation.

Table C.32 and Figure C.32 present the semi-adiabatic calorimetry results performed on C4F2 fly ash cementitious mixtures. It was observed that addition of lignin based (W1) alone or along with either of the AEAs (A1 or A2) to C4F2 fly ash cementitious systems delayed the occurrence of peak. Similar results were obtained when synthetic/VR based AEAs were added along with W1.

C.2 SELECTION OF MIXTURES FOR FURTHER TESTING

This section summarizes the procedure adopted for selecting the mixtures used to study the effect of miscellaneous factors on early age stiffening and setting behavior. The selected mixtures were thereby studied to evaluate the effect of the following miscellaneous factors on the stiffening related incompatibility problems:

- Effect of double dosage of water reducing agent
- Effect of low and high temperature
- Effect of delayed addition of chemical admixtures

Various mixtures used for this study were identified as discussed below.

Initial set time values obtained from the Vicat's setting time experiment and the stiffening index value (S.I.) obtained from mini slump experiments were used to identify various early, normal behaving and slow stiffening/setting mixtures. Mixes were ranked separately based on their stiffening behaviors (S.I. value) and the change in the initial set time w.r.t. the base mixture. Combined rank was calculated as the sum of the ranks from setting and stiffening behavior. Mixes were again ranked based on the combined rank and thus obtained final ranks were used to identify various mixes for subsequent testing.

Table C.33 lists various mixtures arranged in the increasing order of their combined ranks. Mixes identified in **boldface** are the three mixes which have the highest tendency for early stiffening/setting characteristics. Similarly, those identified in *italics* are the slow

TABLE C.30
Summary of setting time results of pastes containing cement C4 and F2 class C ash

Mix #	Water of normal consistency (%)	Initial set time (min)	Change w.r.t. base mix (min)
C4	27.6	220	—
C4F2	25.4	278	+58
C4F2W1	25.5	**370**	+92
C4F2W2	26.2	**368**	+90
C4F2W1A2	24.5	330	+52
C4F2W2A2	23.8	**415**	+137
C4F2W2A1	23.6	320	+42

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

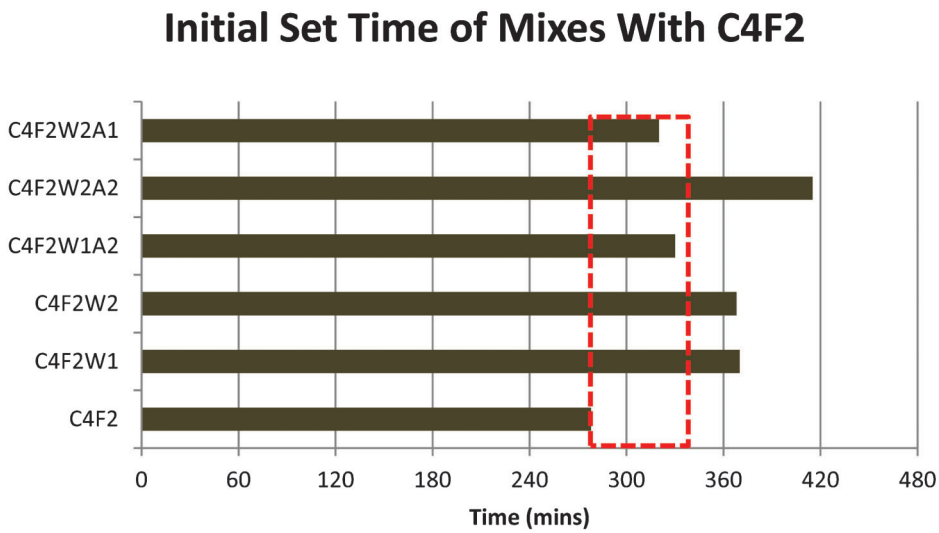

Figure C.29 Intial set behavior of mixtures containing C4F2.

TABLE C.31
Summary of semi-adiabatic calorimetry results of pastes containing cement C4 and F1 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C4	118.53	651	No
C4W1	120.09	**822**	No
C4W2	114.69	681	No
C4F1	104.67	**764**	No
C4F1W1	101.71	**1065**	No
C4F1W1A1	110.35	**1017**	No
C4F1W1A2	108.62	**1050**	No
C4F1W2	106.91	**843**	No
C4F1W2A1	109.42	785	No
C4F1W2A2	109.64	**821**	No

NOTE: Values identified in **boldface** indicate potential incompatible mixes.

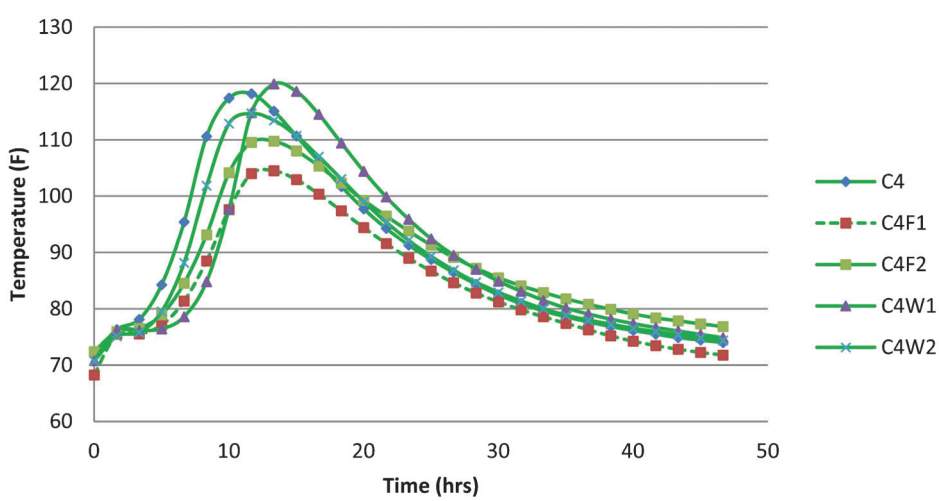

Figure C.30 Semi-adiabatic calorimetry curves of mortars containing cement C4.

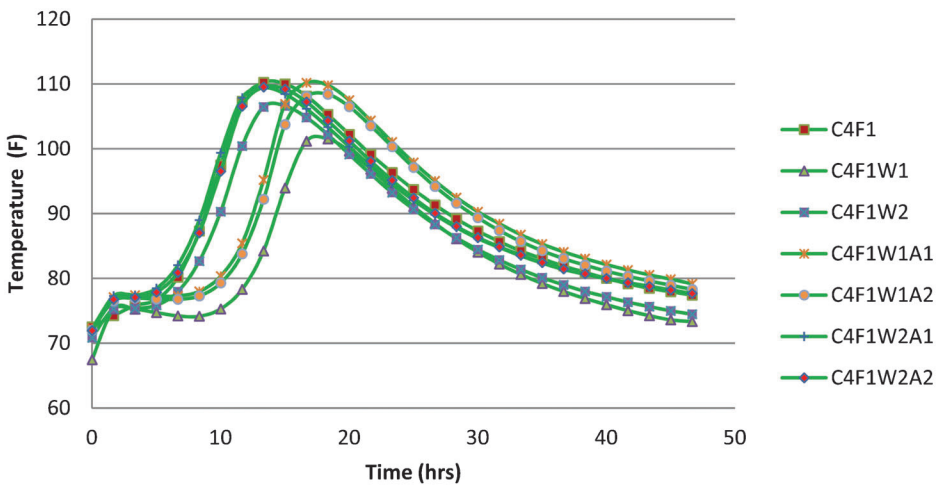

Figure C.31 Semi-adiabatic calorimetry curves of mortars containing cement C4 and F1 class C ash (20% replacement by weight).

TABLE C.32
Summary of semi-adiabatic calorimetry results of pastes containing cement C4 and F2 class C ash (20% replacement by weight)

Mix #	Peak temp (F)	Time of peak (min)	Secondary peaks
C4	118.53	**651**	No
C4F2	109.96	**750**	No
C4F2W1	105.45	**996**	No
C4F2W1A1	109.15	**928**	No
C4F2W1A2	107.6	**957**	No
C4F2W2	110.89	773	No
C4F2W2A1	108.94	762	No
C4F2W2A2	110.89	783	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

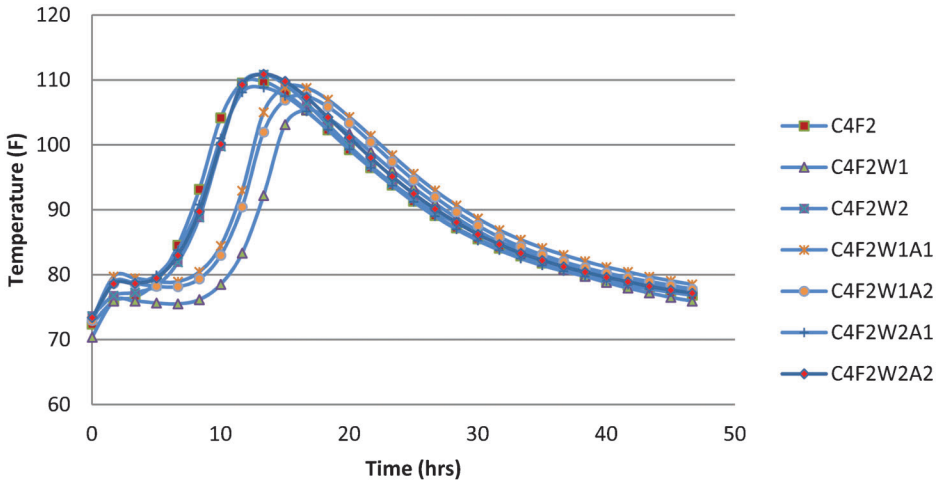

Figure C.32 Semi-adiabatic calorimetry curves of mortars containing cement C4 and F2 class C ash (20% replacement by weight).

TABLE C.33
Ranking of mixtures based on set time and mini slump results

Mix #	Set time experiment			Mini slump testing			Rank set + rank S.I.	Ranking of combined rank
	Initial set (min)	Change	Rank set*	FSI	SI	Rank S.I.**		
C2F1W1A1	110	120	2	1.51	0.71	7	9	1
C2F2W1	**25**	**90**	**7**	**2.69**	**0.66**	**4**	**11**	**2**
C1F2W1	**85**	**90**	**5**	**1.31**	**0.70**	**6**	**11**	**3**
C2F2W1A2	40	75	11	2.14	0.70	5	16	4
C2W1	25	150	1	2.01	0.80	19	20	5
C2F1W2	155	75	10	3.42	0.76	12	22	6
C2F1W1A2	135	95	3	2.76	0.80	20	23	7
C2F2W2	45	70	13	3.15	0.76	11	24	8
C2F2W2A1	55	60	18	1.16	0.76	9	27	9
C1W1	**155**	**−15**	**30**	**0.75**	**0.65**	**1**	**31**	**10**
C2F1W2A2	170	60	16	1.11	0.79	16	32	11
C1F2W1A2	120	55	19	1.08	0.77	14	33	12
C1F2W1A1	90	85	9	1.43	0.84	25	34	13
C1F2W2A2	160	15	22	0.98	0.77	13	35	14
C3F2W1A1	180	68	14	1.56	0.82	22	36	15
C2F1W1	140	90	6	1.02	0.85	30	36	16
C2F2W1A1	20	95	4	0.95	0.86	32	36	17
C3F2W1A2	160	88	8	3.42	0.87	33	41	18
C1F1W1A2	185	−5	27	1.06	0.79	15	42	19
C2F2W2A2	50	65	15	1.13	0.84	28	43	20
C3F1	190	0	26	1.33	0.80	21	47	21
C1F2W2	205	−30	33	0.95	0.79	17	50	22
C4F1W1A1	230	5	24	1.20	0.84	26	50	23
C2F1W2A1	157	73	12	1.04	0.90	40	52	24
C4F1W1	320	−85	55	0.85	0.65	2	57	25
C1F1W2	240	−60	49	0.99	0.75	8	57	26
C2W2	235	−60	50	0.90	0.76	10	60	27
C1F1W1A1	***180***	***0***	***25***	***0.90***	***0.88***	***36***	***61***	***28***
C3F2W1	197	51	20	2.42	0.90	41	61	29
C3F2W2	295	−47	44	2.21	0.80	18	62	30
C4W1	335	−115	61	0.74	0.66	3	64	31
C2F2	115	60	17	1.14	1.00	49	66	32
C3F1W1	175	15	23	1.14	0.92	44	67	33
C4F1W2A2	275	−40	39	1.27	0.84	29	68	34
C4F2	278	−58	48	1.53	0.83	24	72	35
C3F2W2A2	290	−42	40	1.55	0.87	34	74	36
C3F2W2A1	285	−37	37	1.23	0.89	38	75	37
C3F1W2A1	275	−85	53	1.07	0.83	23	76	38
C1F1	180	−40	38	1.01	0.90	39	77	39
C3F1W1A1	220	−30	34	1.12	0.91	43	77	40
C1F1W1	145	35	21	1.07	1.11	58	79	41
C1W2	160	−20	32	0.96	0.99	48	80	42
C1F2	175	−35	36	1.01	0.95	45	81	43
C3F2	248	−58	47	1.37	0.87	35	82	44
C4F1W1A2	320	−85	56	0.76	0.84	27	83	45
C1F2W2A1	***180***	***−5***	***28***	***0.95***	***1.09***	***55***	***83***	***46***
C4F2W1A2	330	−52	45	1.47	0.91	42	87	47
C4F1	235	−15	31	1.05	1.09	56	87	48
C3F1W2A2	250	−60	51	1.40	0.89	37	88	49
C1F1W2A1	215	−35	35	0.96	1.05	53	88	50
C3F1W2	***200***	***−10***	***29***	***0.61***	***1.40***	***62***	***91***	***51***
C2F1	230	−55	46	1.49	0.97	46	92	52
C3F1W1A2	235	−45	42	0.90	1.00	50	92	53
C4F1W2	385	−150	63	0.77	0.86	31	94	54
C4F1W2A1	280	−45	43	1.14	1.07	54	97	55
C4F2W2A1	320	−42	41	1.13	1.21	60	101	56
C3W2	258	−68	52	1.38	1.01	52	104	57
C4F2W1	370	−92	59	1.20	0.99	47	106	58
C1F1W2A2	*285*	*−105*	*60*	*0.86*	*1.01*	*51*	*111*	*59*

TABLE
(Continued)

Mix #	Set time experiment			Mini slump testing			Rank set + rank S.I.	Ranking of combined rank
	Initial set (min)	Change	Rank set*	FSI	SI	Rank S.I.**		
C4W2	305	−85	54	0.91	1.15	59	113	60
C4F2W2	*368*	*−90*	*58*	*1.48*	*1.10*	*57*	*115*	*61*
C3W1	*280*	*−90*	*57*	*1.16*	*2.14*	*63*	*120*	*62*
C4F2W2A2	415	−137	62	1.06	1.23	61	123	63

*Rank set: Mix with rank 1 has the highest acceleration of initial set time and mix with rank 63 has the highest retardation of initial set time.
**Rank S.I.: Mix with rank 1 has the highest early stiffening characteristics (low S.I. value) and mix with rank 63 has the no or low early stiffening characteristics (high S.I. value).

NOTES:

Mixes identified in **boldface** are the three mixes which have the highest tendency for early stiffening/setting characteristics.

Mixes identified in *italics* are the slow stiffening/setting mixes.

Normally behaving mixes are identified in ***boldface italics***.

stiffening/setting mixes. Normally behaving mixes are identified in ***boldface italics***. The criteria for selecting normal stiffening mixtures were that these mixtures have change in initial set time within ± 10 minutes w.r.t. the base mix and also their corresponding S.I. values are > 0.8. All the three mixtures that were selected in each category of stiffening/setting behaviors have different combination of materials (different chemical composition).

Table C.34 lists the mixtures selected for investigating the effect of miscellaneous causes on the incompatibility. The combined rankings were also used to select four mixtures for concrete testing to validate the early age stiffening/abnormal setting results obtained from paste and mortars tests. Table C.35 lists the mixtures selected for concrete testing.

C.3 RESULTS OF EXPERIMENTS PERFORMED IN SUBTASK II OF PHASE I

This section summarizes the results of various experiments performed to study the effect of miscellaneous factors on early age stiffening and abnormal setting behavior. A total of 24 different combinations were studied to evaluate the effect of following miscellaneous factors on the mixture compatibility:

- Effect of double dosage of water reducing agent
- Effect of low and high temperature
- Effect of delayed addition of chemical admixtures

A total of six mixtures, three each of the normal and early stiffening mixtures, were used to study the effect of increased dosage of admixtures and also the effect of high temperature. Similarly, a total of six mixtures, three each of normal and slow stiffening mixtures, were used to study the effect of low (10°C) temperature and were additionally used to study the effect of delayed addition of admixtures. Mini slump experiment along with Vicat's initial set time test and semi-adiabatic calorimetry were used to determine the effect of higher dosage additions of WRAs and high (37°C) temperature on compatibility. Vicat's initial set time test and semi-adiabatic calorimetry were performed to study the effect of delayed addition of admixtures on the compatibility of a mixture.

TABLE C.34
List of mixtures identified for sub-phase II of Phase I

Mix #	Set time experiment			Mini slump testing			Combined rank	Ranking of combined rank
	Initial set (min)	Change	Rank set	F.S.I.	S.I.	Rank S.I.		
Fast stiffening/setting mixes								
C2F2W1	25	90	7	2.69	0.66	4	11	2
C1F2W1	85	90	5	1.31	0.70	6	11	3
C2F1W2	155	75	10	3.42	0.76	12	22	6
Normal stiffening mixes								
C3F1W2	200	−10	29	0.61	1.40	62	91	51
C1F1W1A1	180	0	25	0.90	0.88	36	61	28
C1F2W2A1	180	−5	28	0.95	1.09	55	83	46
Slow stiffening/setting mixes								
C3W1	280	−90	57	1.16	2.14	63	120	62
C4F2W2	415	−137	62	1.06	1.23	61	123	63
C1F1W2A2	285	−105	60	0.86	1.01	51	111	59

TABLE C.35
List of mixtures selected for Phase III-concrete mixing

Mix #	Set time experiment			Mini slump testing				
	Initial set (min)	Change	Rank set	F.S.I.	S.I.	Rank S.I.	Rank set + rank S.I.	Ranking of combined rank
Fast stiffening mixes								
C2F2W1	25	90	7	2.69	0.66	4	11	2
C1F2W1	85	90	5	1.31	0.70	6	11	3
Slow setting mixes								
C3W1	280	−90	57	1.16	2.14	63	120	62
C4F2W2	368	−90	58	1.48	1.10	57	115	61

C.3.1 Effect of Double Dosage of Water Reducing Agent on Mixture Compatibility

This section summarizes the results experiments performed on a total of six mixtures to evaluate the effect of double dosage of water reducing agents (WRA). Mini slump testing, Vicat's initial set time experiment and semi-adiabatic calorimetry were performed on three early stiffening mixtures and three normal stiffening mixtures. The results of mini slump testing, semi-adiabatic calorimetry and Vicat's initial set time experiments are summarized in Tables C.36 through C.39 respectively. Values identified in **boldface** indicate results of potentially incompatible mixtures identified based on the previously established limiting criteria.

C.3.1.1 Results of Mini Slump Cone Testing

Table C.36 summarizes the results of mini slump testing performed on the six mixtures while Table C.37 presents the comparison of mini slump test results performed with double and normal dosages of WRAs. It was observed that addition of double dosage of lignin based WRA (W1) aggravated the problem of early stiffening (lower S.I. value) in C2F2W1 mixture. Whereas addition of double dosage of poly-carboxylate type WRA (W2) reduced the early stiffening (S.I.) and false setting behavior (F.S.I.) of C2F1W2 mixture. However, increased dosage of plasticizer had no significant effect on the behavior of normal stiffening mixes. All the three normal stiffening mixtures exhibited acceptable slump loss (S.I. $>$ 0.8 and F.S.I. $<$ 1.3) in spite of the double dosage addition of WRA.

C.3.1.2 Results of Semi-Adiabatic Calorimetry

Table C.38 summarizes the results of semi-adiabatic calorimetry performed on the same six mixtures as those used for mini slump testing. The same results are shown in Figure C.33 and C.44 for, respectively, early stiffening and normal stiffening mixtures. Mixtures prepared with double dosage of WRA are suffixed by (DD) in the figures. No significant (<10F) difference was recorded in the maximum peak temperatures of the six mixtures made with double dosage of WRA w.r.t. their corresponding mixtures prepared with normal dosage of WRA. Addition of double dosage of WRA significantly (difference $>$ 60 mins) delayed the occurrence of maximum peak temperature in four (C1F2W1, C2F1W2, C3F1W2 and C1F2W1A1) out of the six mixtures when compared to that of mixtures with normal WRA dosage. However significant acceleration ($>$ 60 mins) of maximum peak temperature occurred with C2F2W1 mixture. Also slight impressions of secondary peaks were observed in semi-adiabatic calorimetric curves of C2F1W2 mixture made with double dosage of W2 while no such peaks were observed when made with normal dosage of W2.

TABLE C.36
Summary of mini slump results-effect of double dosage of plasticizer

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
Early stiffening mixtures								
C2F2W1	**88.2**	**80.1**	**33.5**	**27.6**	**23.5**	0.35	**0.91**	**47.1**
C1F2W1	**71.8**	**97.3**	**75.9**	**76.9**	**57.2**	0.79	1.35	**83.4**
C2F1W2	**67.9**	**108.1**	**146.6**	**143.1**	**144.5**	**1.32**	1.59	**132.6**
Normal stiffening mixtures								
C3F1W2	**78.5**	**98.5**	**102.0**	**125.9**	**114.3**	**1.28**	**1.25**	**108.8**
C1F1W1A1	**95.6**	**83.3**	**82.2**	**69.9**	**65.0**	**0.84**	**0.87**	**78.4**
C1F2W2A1	**151.7**	**156.8**	**161.3**	**184.6**	**186.17**	**1.18**	**1.03**	**167.5**

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.37
Comparison between mini slump test results performed with double and normal dosages of WRAs

Mix#	S.I. (30 min/5 min)		F.S.I. (5 min/2 min)	
	Double dosage	Normal dosage	Double dosage	Normal dosage
Early stiffening mixtures				
C2F2W1	0.35	0.66	**0.91**	2.69
C1F2W1	0.79	0.70	1.35	1.31
C2F1W2	**1.32**	0.76	1.59	3.42
Normal stiffening mixtures				
C3F1W2	**1.28**	**1.40**	**1.25**	**0.61**
C1F1W1A1	**0.84**	**0.88**	**0.87**	**0.90**
C1F2W2A1	**1.18**	**1.09**	**1.03**	**0.95**

NOTE: Values identified in **boldface** indicate potential incompatible mixes.

TABLE C.38
Summary of semi-adiabatic calorimetry results of mixtures used to study effect of double dosage of WRA (20% replacement by weight)

Mix #	Peak temp (F)		Time of max peak (mins)		Secondary peaks (DD)
	Double dosage (DD)	Normal dosage	Double dosage (DD)	Normal dosage	
Early stiffening mixtures					
C1F2W1	99.66	105.08	**1567**	936	No
C2F2W1	93.75	89.82	**510**	613	No
C2F1W2	102.32	100.36	**951**	774	**Yes**
Normal stiffening mixtures					
C3F1W2	111	113.28	**974**	835	No
C1F1W1A1	99.32	101.56	**1586**	1069	No
C1F2W2A1	101.61	100.26	964	976	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.39
Summary of Vicat's Initial set time results of mixtures used to study effect of double dosage of WRA

Mix #	Normal consistency % (DD)	Initial set time (mins)	
		Double dosage (DD)	Normal dosage
C2F2W1	21.9	**20**	85
C2F1W2	23.8	130	130
C1F2W1	22.6	**60**	140
C3F1W2	24.3	**440**	200
C1F1W1A1	22.9	**100**	180
C1F2W2A1	21.9	**270**	180

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

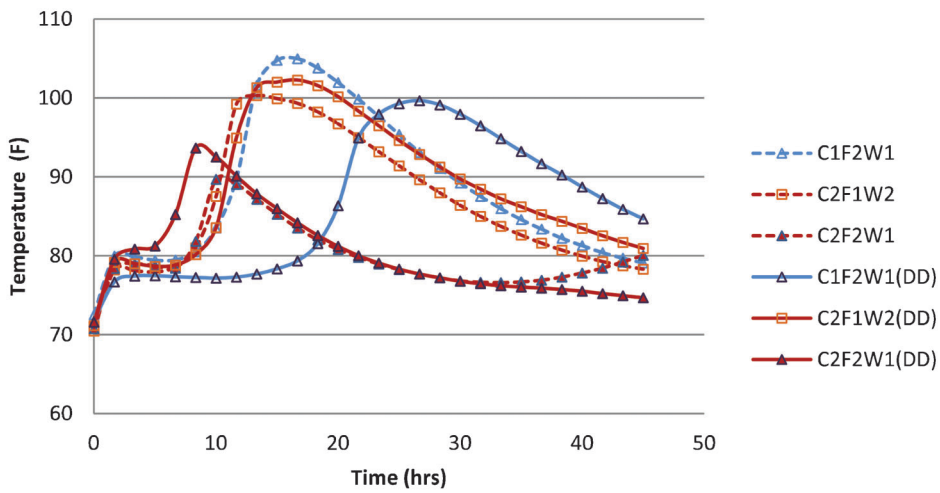

Figure C.33 Effect of double dosage of plasticizer on semi-adiabatic temperature profile of early stiffening mixes.

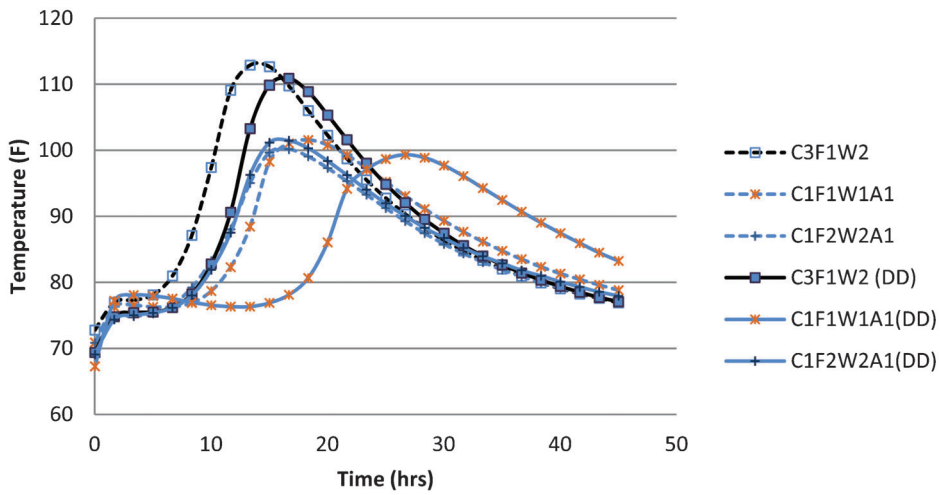

Figure C.34 Effect of double dosage of plasticizer on semi-adiabatic temperature profile of normal stiffening mixes.

C.3.1.3 Results of Vicat's Initial Set Time

Summary of initial set time results of mixtures prepared with double dosage of water reducing agents is presented in Table C.39. Double dosage of WRAs significantly modified the setting characteristics of five out of the six mixtures. In general, it was observed that double dosage of W1 severely accelerated the set time while double dosage additions of W2 retarded the set time; except for the case of C2F1W2 (no change in initial set time was observed).

C.3.2 Effect of Low and High temperature on Mixture Compatibility

The results of mini slump testing, Vicat's initial set time experiment and semi-adiabatic calorimetry performed to study the effect of temperature on compatibility of a mixture are presented in this section. Early stiffening and normal stiffening mixtures were used for the high (37°C) temperature study, while the low (10°C) temperature study was performed on slow and normal stiffening mixtures. All the materials used for testing were stored at respective temperature (10°C or 37°C) for at least 5 hours before the start of mixing. All the samples were transferred immediately, after mixing, to the respective chambers maintained at specific temperatures (10°C or 37°C).

C.3.2.1 Results of Mini Slump Cone Testing

Table C.40 summarizes the results of mini slump testing performed to study the effect of low temperature while Table C.41 presents the comparison between results obtained from low and room (23°C) temperature testing. It was observed that all the slow stiffening mixtures exhibited normal stiffening behavior when tested at low temperature. However, two normal stiffening mixtures, C3F1W2 and C1F2W1A1, exhibited false setting behavior (F.S.I.>1.3) when tested at low temperature.

Table C.42 summarizes the results of mini slump testing performed at high (37°C) temperature. Table C.43 presents the comparison between results of mini slump cone test performed at 37°C and room (23°C) temperature. It was observed that all the mixtures, except for one, C1F2W1, exhibited early stiffening characteristics (S.I. <0.8) when tested at high temperature. Early stiffening characteristics of C1F2W1 mixture were eliminated (S.I. > 0.8 and F.S.I. < 1.3) when tested at high temperature.

TABLE C.40
Summary of Mini slump results of mixtures used to study effect of low (10°C) temperature (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
Slow stiffening mixtures								
C3W1	57.2	64.5	46.5	61.7	44.9	0.96	1.13	57.6
C4F2W2	117.5	147.3	104.4	134.0	141.7	0.91	1.25	128.6
C1F1W2A2	74.4	86.0	88.8	87.6	78.0	1.02	1.16	87.5
Normal stiffening mixtures								
C3F1W2	55.0	117.5	132.7	129.6	132.7	1.10	**2.14**	126.6
C1F1W1A1	99.1	136.1	137.5	145.9	115.6	1.07	**1.37**	139.8
C1F2W2A1	102.0	116.8	120.1	118.8	99.6	1.02	1.15	118.6

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.41
Comparison between mini slump test results performed at 10°C temperature and room temperature

Mix #	S.I. (30 min/5 min)		F.S.I. (5 min/2 min)	
	Low temp (LT)	Room temp	Low temp (LT)	Room temp
Slow stiffening mixtures				
C3W1	0.96	2.14	1.13	1.16
C4F2W2	0.91	1.10	1.25	**1.48**
C1F1W2A2	1.02	1.01	1.16	0.86
Normal stiffening mixtures				
C3F1W2	1.10	1.40	**2.14**	0.61
C1F1W1A1	1.07	0.88	**1.37**	0.90
C1F2W2A1	1.02	1.09	1.15	0.95

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.42
Summary of mini slump test results of mixtures used to study effect of high temperature (20% replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
Early stiffening mixtures								
C2F2W1 (HT)	16.4	26.4	27.0	19.9	21.0	**0.75**	**1.61**	24.4
C1F2W1 (HT)	58.1	28.3	31.2	26.1	22.3	0.92	0.49	28.5
C2F1W2 (HT)	25.8	62.6	46.5	37.0	31.5	**0.6**	**2.4**	48.7
Normal stiffening mixtures								
C3F1W2 (HT)	18.6	39.2	31.2	24.3	28.6	**0.62**	**2.11**	31.6
C1F1W1A1 (HT)	44.9	44.9	40.7	34.2	26.1	**0.76**	1.00	39.9
C1F2W2A1 (HT)	32.5	75.9	49.8	39.9	38.8	**0.53**	**2.34**	55.2

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.43
Comparison between mini slump test results performed at 37°C temperature and room temperature

Mix #	S.I. (30 min/5 min)		F.S.I. (5 min/2 min)	
	High temp (HT)	Room temp	High temp (HT)	Room temp
		Early stiffening mixtures		
C2F2W1	**0.75**	**0.66**	**1.61**	**2.69**
C1F2W1	0.92	**0.70**	0.49	**1.31**
C2F1W2	**0.6**	**0.76**	**2.4**	**3.42**
		Normal stiffening mixtures		
C3F1W2	**0.62**	1.40	**2.11**	0.61
C1F1W1A1	**0.76**	0.88	1.00	0.90
C1F2W2A1	**0.53**	1.09	**2.34**	0.95

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

C.3.2.2 Results of Semi-Adiabatic Calorimetry

Table C.44 summarizes the results of semi-adiabatic calorimeter experiments performed on normal and slow stiffening mixtures to study the effect of low temperature. Figure C.35 and Figure C.36 present the graphical representation of semi-adiabatic calorimetric temperature profiles of the same six mixtures tested at, respectively, low and room temperatures. Semi-adiabatic calorimetry indicated very long durations of dormant zone in all the mixtures tested. Also significant (>60 mins) delay, w.r.t. mixtures prepared at room temperature, in the time of maximum peak temperature was observed in all the mixtures tested at low temperature.

Table C.45 summarizes the results of semi-adiabatic calorimetry performed at high (37°C) temperature and room (23°C) temperature respectively. Plots of semi-adiabatic calorimetric temperature profiles of mixtures prepared at high and room temperatures are provided in Figures C.37 and C.38, respectively. Time of occurrence of maximum peak temperature was significantly accelerated (>60 min) in all the normal stiffening mixtures, when tested at high temperature. However, early stiffening mixtures containing cement C2, C2F1W2 and C2F2W1, exhibited significant delay in the occurrence of maximum peak temperature when tested at high temperature. Also both these mixtures were associated with appearance of secondary peaks. Other interesting phenomenon observed was that there was no dormant zone in the mixtures tested at high temperature.

C.3.2.3 Results of Vicat's Initial Set Time Experiments

Table C.46 summarizes the results of Vicat's set time experiment performed to study the effect of temperature on compatibility of a mixture. Three slow stiffening were used to study the effect of low temperature while three fast stiffening mixtures were used to study the effect of high temperature. The results from low and high temperature testing were compared with the results of mixtures tested at room temperature (23°C). It was observed that low temperature testing delayed the initial set time though, this effect was found to be significant (≥ 60 mins) only in one of the three mixtures. However, severe acceleration of initial set time was observed in all the three mixtures tested at high temperature. Also, the initial set times of all the three high temperature mixtures were less than the 45 minutes.

C.3.3 Effect of Delayed Addition of Chemical Admixtures on Mixture Compatibility

The effect of double dosage of water reducing agents (WRA) was evaluated on a total of six mixtures. Mini slump testing, Vicat's initial set time experiment and semi-adiabatic calorimetry were performed on three early stiffening mixtures and three normal stiffening mixtures. Table C.47 and Table C.48 summarize the results of, respectively, semi-adiabatic calorimetry and Vicat's initial set time experiments performed to evaluate the effect of double dosage of water reducing agents on early age stiffening behavior of the mixtures. The values identified in **boldface** indicate results of potential incompatible mixtures identified based on the previously established limiting criteria.

C.3.3.1 Results of Semi-Adiabatic Calorimetry

Table C.47 summarizes the results of semi-adiabatic calorimetry performed to study the effect of delayed addition of chemical admixtures. Figure C.39 and Figure C.40 present the plots of semi-adiabatic calorimetric temperature profiles of, respectively, the slow stiffening and normal stiffening mixtures. Addition of chemical admixtures (air entraining agents (AEA) and water reducing agents (WRA)) was delayed by 60 seconds from the beginning of mixing. It was observed that maximum peak temperatures of mixtures made with delayed addition were similar to that of the peaks of mixtures with normal addition. Delayed addition of admixtures did not have a significant (difference w.r.t. normal addition was < 60 mins) effect on the time of occurrence of maximum peak temperature in slow stiffening mixtures. However, the time of occurrence of maximum temperature of normal stiffening mixtures was significantly delayed, except for C1F2W2A1 mixture.

C.3.3.2 Results of Vicat's Initial Set Time Experiments

Table C.48 summarizes the results of Vicat's initial set time experiments performed to study the effect of delayed addition of chemical admixtures. Delaying the addition of admixtures by 60s significantly altered the initial set time, w.r.t. mixtures prepared with simultaneous addition of admixtures, in five of the six mixtures tested. Pronounced acceleration of initial set time was observed in four of the six mixtures prepared by delayed addition of admixtures while, retardation of set time occurred in the remaining two mixtures. Thus it is thought that the effect of delayed addition depends on the chemical nature of components in the mixture.

C.3.4 Effect of Increased Fly Ash Content on the Compatibility of a Mixture

This section summarizes the results of the early age stiffening test, Vicat's set time test and semi-adiabatic calorimeter experiments performed on mixtures containing higher volumes of class C ash. Mixtures prepared with 30%, 50% and 70% replacement (by weight) of cement with class C ashes were studied. The test matrix comprised of mixtures containing cements C1, C2 and C3 along with the two class C ashes, F1 and F2. In total, 16 mixtures

TABLE C.44
Summary of semi-adiabatic calorimetry results of mixtures used to study effect of low temperature (20% replacement by weight)

Mix #	Peak temp (F)		Time of max peak (mins)		Secondary peaks (LT)
	Low temp (LT)	Room temp	Low temp (LT)	Room temp	
Slow stiffening mixtures					
C3W1	89.36	120.76	**1350**	707	No
C4F2W2	80.8	110.89	**1424**	773	No
C1F1W2A2	74.73	102.67	**1386**	871	No
Normal stiffening mixtures					
C3F1W2	80.67	113.28	**1468**	835	No
C1F1W1A1	73.08	101.56	**1953**	1069	No
C1F2W2A1	74.16	100.26	**1324**	976	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

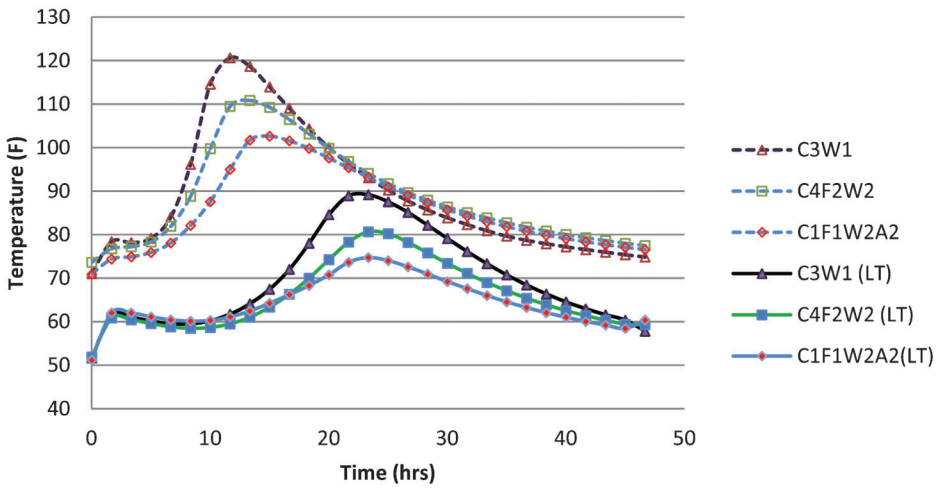

Figure C.35 Effect of low temperature on semi-adiabatic temperature profile of slow stiffening mixes.

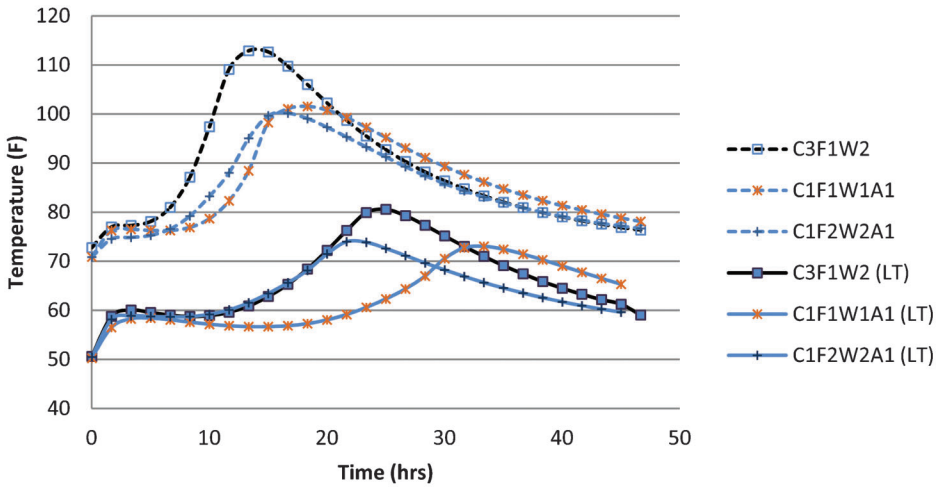

Figure C.36 Effect of low temperature on semi-adiabatic temperature profile of normal stiffening mixes.

TABLE C.45
Summary of semi-adiabatic calorimetry results of mixtures used to study effect of high temperature (20% replacement by weight)

Mix #	Peak temp (F)		Time of max peak (mins)		Secondary peaks (HT)
	High temp (HT)	Room temp	High temp (HT)	Room temp	
Early stiffening mixtures					
C1F2W1	132.92	105.08	**735**	936	No
C2F1W2	135.14	89.82	670	613	**Yes**
C2F2W1	131.87	100.36	**899**	774	**Yes**
Normal stiffening mixtures					
C3F1W2	143.66	113.28	**506**	835	No
C1F1W1A1	137.2	101.56	**733**	1069	No
C1F2W2A1	136.16	100.26	**598**	976	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

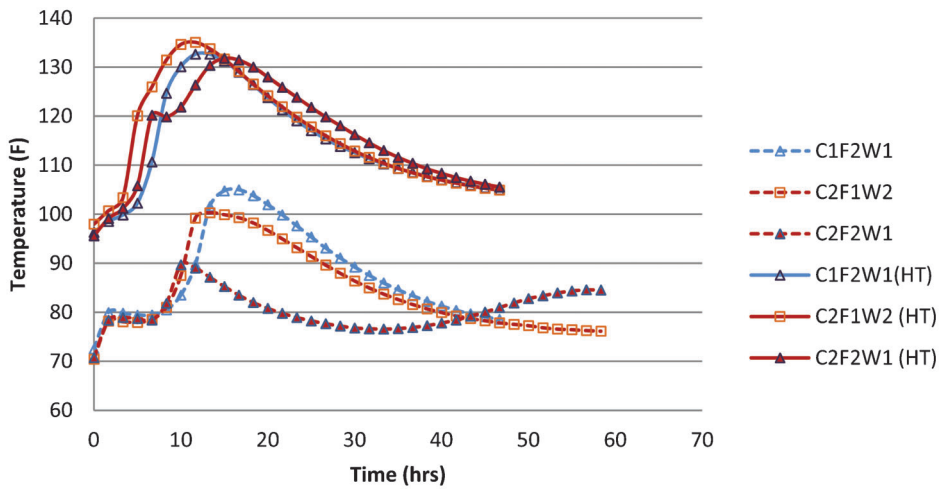

Figure C.37 Effect of high temperature on semi-adiabatic temperature profile of early stiffening mixes.

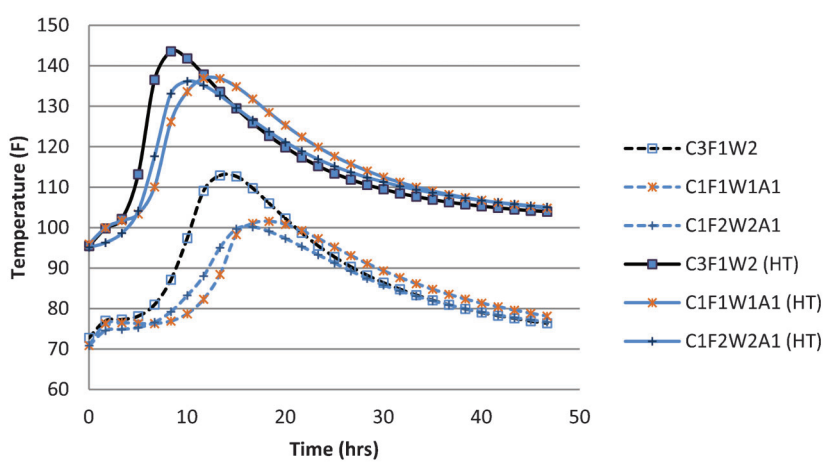

Figure C.38 Effect of high temperature on semi-adiabatic temperature profile of normal stiffening mixes.

TABLE C.46
Summary of Vicat's set time results of mixtures used to study effect of high temperature (20% replacement by weight)

Mix #	Normal consistency %	Initial set time (mins)	
		Low temp (LT)	Room temp (23C)
C3W1	28.0	320	280
C4F2W2	22.3	380	368
C1F1W2A2	23.2	**260**	160
		High temp (HT)	Room temp (23C)
C2F2W1	29.5	**45**	85
C2F1W2	27.2	**25**	130
C1F2W1	29.5	**40**	140

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.47
Summary of semi-adiabatic calorimetry results of mixtures used to study effect of delayed addition of WRA (20% replacement by weight)

Mix #	Peak temp (F)		Time of max peak (mins)		Secondary peaks
	60 sec delayed addition	Normal addition	60 sec delayed addition	Normal addition	
Slow stiffening mixtures					
C3W1	117.88	120.76	727	707	No
C4F2W2	109.42	110.89	751	773	No
C1F1W2A2	104.26	102.67	900	871	No
Normal stiffening mixtures					
C3F1W2	108.94	113.28	1114	835	No
C1F1W1A1	101.16	101.56	1118	1069	No
C1F2W2A1	99.81	100.26	887	976	No

TABLE C.48
Summary of Vicat's set time results of mixtures used to study effect of delayed addition of WRA (20% replacement by weight)

Mix #	Normal consistency % (DD)	Initial set time (mins)	
		Delayed addition (DLYD)	Normal addition
Normal stiffening mixtures			
C3F1W2	26.6	**85**	200
C1F1W1A1	23.9	**75**	180
C1F2W2A2	23.9	195	160
Slow stiffening mixtures			
C3W1	29.2	**215**	280
C4F2W2	23.8	**115**	368
C1F1W2A2	24.0	**220**	160

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

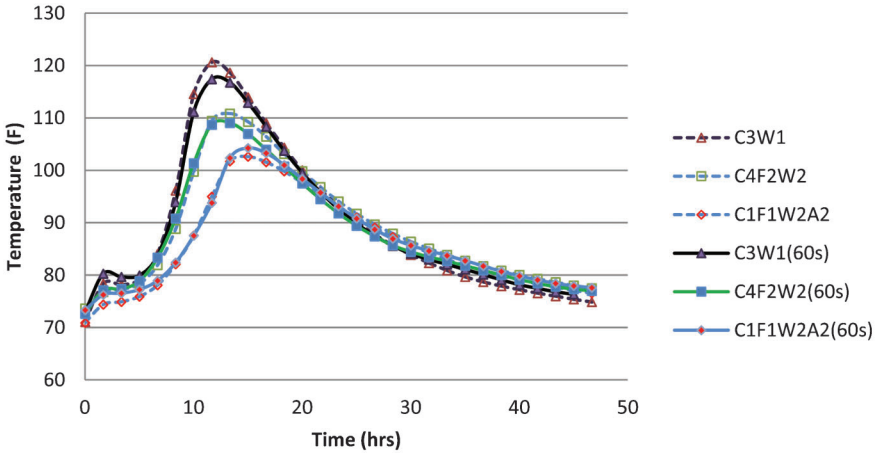

Figure C.39 Effect of delayed addition of plasticizer on semi-adiabatic temperature profile of slow stiffening mixes.

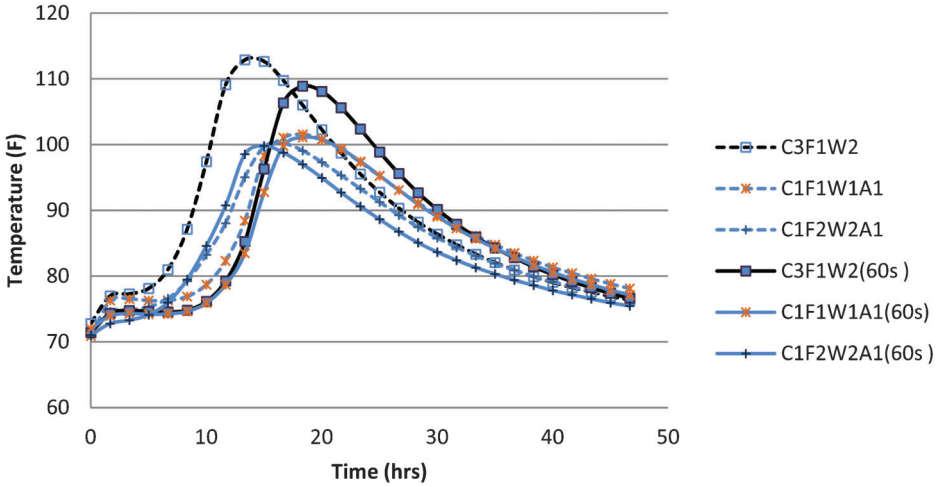

Figure C.40 Effect of delayed addition of plasticizer on semi-adiabatic temperature profile of normal stiffening mixes.

were selected using the orthogonal experiment design approach as discussed in Appendix B.

C.3.4.1 Results of Mini Slump Cone Test

Table C.49 summarizes the results of mini slump test performed on high volume fly ash cementitious mixtures. Eleven out of sixteen higher (>30%) fly ash cementitious mixtures tested exhibited abnormal stiffening (F.S.I.>1.3 or S.I. <0.8) characteristics. High volumes of class C ash induced abnormal stiffening behavior in six out of the sixteen HVFS mixtures which were found to be otherwise compatible at 20% replacement levels. A comparison between mini slump results of HVFS and 20% fly ash systems is provided in Table C.50.

C.3.4.2 Results of Semi-Adiabatic Calorimetry

Table C.51 summarizes the results of semi-adiabatic calorimetry performed on the higher volume fly ash cementitious systems. It was observed that higher (>30%) replacement of cement by class C fly ashes resulted in development of secondary peaks in nine out of the sixteen mixtures tested. This suggests that addition of class C ash in higher volumes affects the hydration process. Figures C.41 through C.44 present the graphical representation of the semi-adiabatic temperature profile of high volume fly ash mixtures along with their corresponding 20% fly ash cementitious mixtures.

Table C.52 provides the comparison between the results of semi-adiabatic calorimetry performed on the higher volume fly ash cementitious systems to that of the 20% fly ash cementitious mixtures. It was observed that replacement of cement by higher volume of class C fly ashes significantly affected the time of occurrence of maximum peak temperature w.r.t. to the corresponding mixtures prepared with 20% replacement. Significant acceleration of the time of maximum peak was observed in six mixtures whereas maximum peak time was delayed significantly in eight of the remaining ten mixtures. Also, pronounced reduction in the maximum peak temperature was observed in three out of the four 70% fly ash cementitious mixtures. Similar phenomenon was also observed in four of the eight 50% fly cementitious mixture.

C.3.4.3 Results of Vicat's Initial Set Time

Effect of higher volumes of class C ashes on early stiffening and abnormal setting related incompatibility problems was studied on few selected mixtures. Table C.53 compares the results of set time experiments performed on the sixteen mixtures selected for the high volume fly ash study (HVFS) with the results obtained for 20% fly ash mixtures. It was observed that all the higher (>30%) volume fly ash cementitious mixtures significantly accelerated the initial set time w.r.t. to the corresponding 20% fly ash cementitious mixtures except for one mixture ($C1F2_{(30)}W2A1$). Also eleven out of the sixteen higher volume fly ash mixtures had initial set time less than or equal to 45 minutes.

C.4 RESULTS OF EXPERIMENTS PERFORMED IN PHASE II

This section summarizes the results of experiments performed to study the incompatibility problems related to air voids production and stability. Plain and fly ash cementitious mixtures were prepared using low alkali (0.29%) cement C1 and class F ash, F3. Fly ash cementitious mixtures with both 20% and 60% replacement of cement by class F ash were evaluated for air void related incompatibility problems. Foam index testing, determination of air content in mortars (ASTM C 185) and foam drainage experiments were performed on 18 different mixtures. Results of foam index testing and air content in mortar experiments are summarized in Section C.4.1.while the results of foam drainage tests are presented in Section C.4.2.

TABLE C.49
Summary of mini slump results of mixtures with higher volumes of class C ash (replacement by weight)

Mix #	Pat area (cm^2)					S.I.	F.S.I.	Avg pat area (cm^2)
	$(Ar)_2$	$(Ar)_5$	$(Ar)_{15}$	$(Ar)_{30}$	$(Ar)_{45}$			
30% replacement of cement by fly ash								
$C1F2_{(30)}W2A1$	116.2	122.7	93.8	52.4	67.9	**0.43**	1.06	89.6
$C2F1_{(30)}W2A1$	57.2	82.7	78.5	89.9	66.0	1.09	**1.45**	83.7
$C2F2_{(30)}W1A2$	28.3	51.1	50.2	51.5	45.7	1.01	**1.81**	50.9
$C3F1_{(30)}W1A2$	12.4	59.4	59.0	55.4	49.8	0.93	**4.81**	57.9
50% replacement of cement by fly ash								
$C1F1_{(50)}W2A2$	71.3	141.7	137.5	134.7	113.0	0.95	**1.99**	137.9
$C1F2_{(50)}W1A2$	39.2	32.2	44.5	52.8	66.9	1.64	0.82	43.2
$C2F1_{(50)}W1A2$	35.9	34.9	81.1	72.8	63.6	2.09	0.97	63.0
$C2F1_{(50)}W1A1$	67.9	61.7	103.2	100.2	95.0	1.62	0.91	88.4
$C2F2_{(50)}W2A1$	44.2	118.1	105.6	90.4	75.9	**0.77**	**2.68**	104.7
$C2F2_{(50)}W2A2$	54.1	113.7	93.3	87.1	74.4	**0.77**	**2.10**	98.0
$C3F1_{(50)}W2A1$	113.0	120.7	105.0	63.1	103.2	**0.52**	1.07	96.3
$C3F2_{(50)}W1A1$	28.6	65.5	44.9	42.6	38.5	**0.65**	**2.29**	51.0
70% replacement of cement by fly ash								
$C1F1_{(70)}W1A1$	79.0	133.3	132.0	175.8	75.9	1.32	**1.69**	147.1
$C2F1_{(70)}W2A2$	76.4	59.4	71.3	66.4	71.8	1.12	0.78	65.7
$C2F2_{(70)}W1A1$	153.1	130.0	103.2	74.4	61.7	**0.57**	0.85	102.5
$C3F2_{(70)}W2A2$	69.4	56.1	79.6	86.0	68.9	1.53	0.81	73.9

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.50
Comparison of mini slump results of mixtures with high volumes of class C ash (replacement by weight) and 20% fly ash mixtures

High volume fly ash systems				20% fly ash cementitious mixtures			
Mix #	**S.I.**	**F.S.I.**	**Avg pat area (cm^2)**	**Mix #**	**S.I.**	**F.S.I.**	**Avg pat area (cm^2)**
30% replacement of cement by fly ash							
C1F2(30)W2A1	**0.43**	1.06	89.6	C1F2W2A1	1.09	0.95	97.33
C2F1(30)W2A1	1.09	**1.45**	83.7	C2F1W2A1	0.90	1.04	45.50
C2F2(30)W1A2	1.01	**1.81**	50.9	C2F2W1A2	**0.76**	**3.15**	36.21
C3F1(30)W1A2	0.93	**4.81**	57.9	C3F1W1A2	1.40	0.61	58.95
50% replacement of cement by fly ash							
C1F1(50)W2A2	0.95	**1.99**	137.9	C1F1W2A2	1.01	0.86	75.98
C1F2(50)W1A2	1.64	0.82	43.2	C1F2W1A2	**0.79**	0.95	63.88
C2F1(50)W1A2	2.09	0.97	63.0	C2F1W1A2	**0.76**	**3.42**	40.94
C2F1(50)W1A1	1.62	0.91	88.4	C2F1W1A1	**0.80**	**2.76**	34.39
C2F2(50)W2A1	**0.77**	**2.68**	104.7	C2F2W2A1	**0.76**	1.16	39.97
C2F2(50)W2A2	**0.77**	**2.10**	98.0	C2F2W2A2	0.84	1.13	39.00
C3F1(50)W2A1	**0.52**	1.07	96.3	C3F1W2A1	0.83	1.07	50.46
C3F2(50)W1A1	**0.65**	**2.29**	51.0	C3F2W1A1	0.87	**3.42**	38.38
70% replacement of cement by fly ash							
C1F1(70)W1A1	1.32	**1.69**	147.1	C1F1W1A1	**0.79**	1.06	79.26
C2F1(70)W2A2	1.12	0.78	65.7	C2F1W2A2	**0.79**	1.11	39.91
C2F2(70)W1A1	**0.57**	0.85	102.5	C2F2W1A1	**0.70**	**2.14**	32.45
C3F2(70)W2A2	1.53	0.81	73.9	C3F2W2A2	0.87	**1.55**	56.03

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.51
Summary of semi-adiabatic calorimetry results of mixtures with higher volumes of class C ash (replacement by weight)

Mix #	Max peak temp (F)	Time of max peak (mins)	Secondary peaks
C1 Mixes			
$C1F2_{(30)}W2A1$	98.04	856	No
$C1F2_{(50)}W1A2$	84.41	1171	**Yes**
$C1F1_{(50)}W2A2$	89.55	1026	No
$C1F1_{(70)}W1A1$	81.73	523	No
C2 Mixes			
$C2F1_{(30)}W2A1$	94.47	1077	**Yes**
$C2F1_{(50)}W1A2$	92.1	203	No
$C2F1_{(50)}W1A1$	91.87	176	**Yes**
$C2F1_{(70)}W2A2$	83.33	384	**Yes**
$C2F2_{(30)}W1A2$	91.64	841	**Yes**
$C2F2_{(50)}W2A1$	89.45	834	**Yes**
$C2F2_{(50)}W2A2$	91.64	749	**Yes**
$C2F2_{(70)}W1A1$	86.71	716	**Yes**
C3 Mixes			
$C3F1_{(30)}W1A2$	101.96	1080	No
$C3F1_{(50)}W2A1$	96.92	1016	No
$C3F2_{(50)}W1A1$	90.38	831	**Yes**
$C3F2_{(70)}W2A2$	87.66	874	No

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

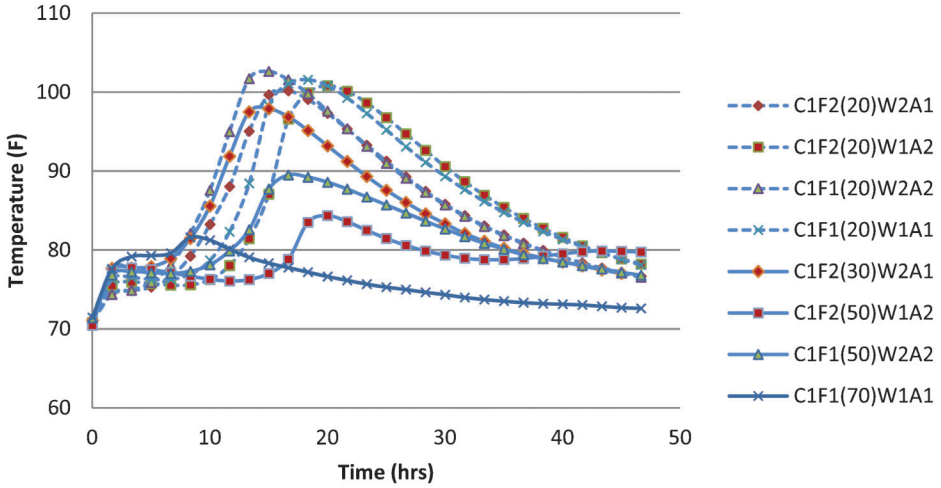

Figure C.41 Effect of higher volume of class C ash semi-adiabatic temperature profile of mixtures containing cement C1.

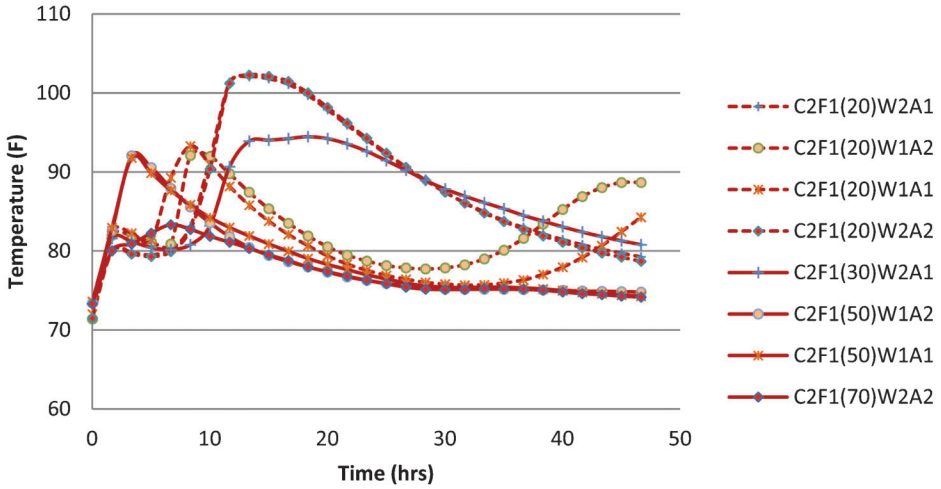

Figure C.42 Effect of higher volume of class C ash semi-adiabatic temperature profile of mixtures containing C2F1 fly ash cementitious system.

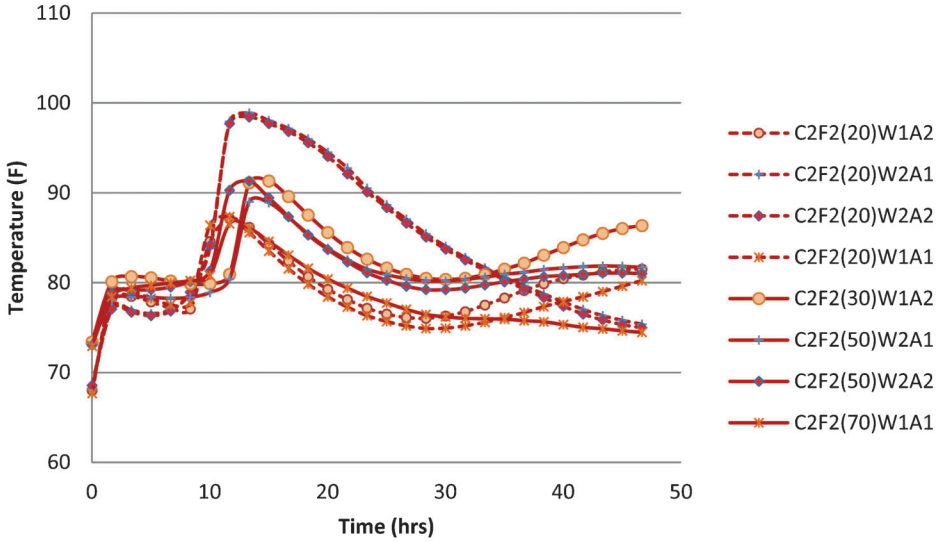

Figure C.43 Effect of higher volume of class C ash semi-adiabatic temperature profile of mixtures containing C2F2 fly ash cementitious system.

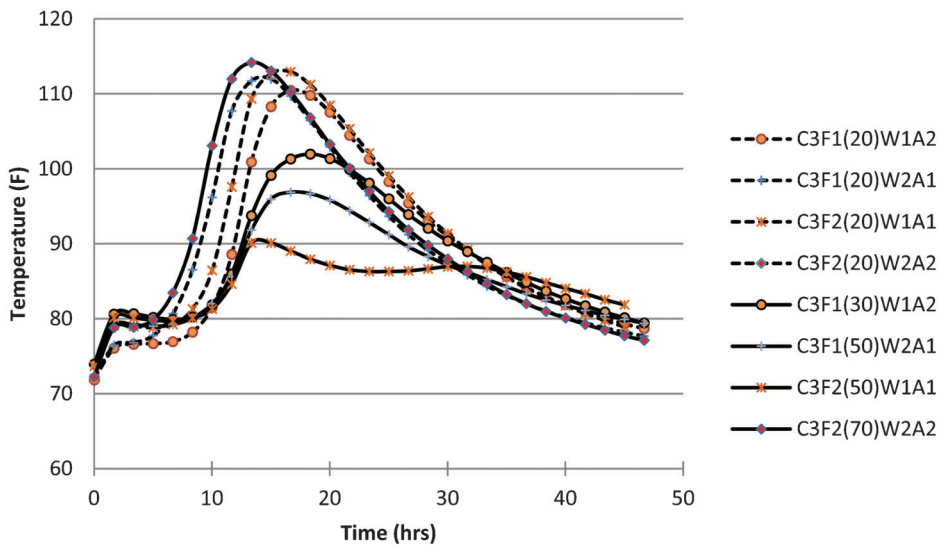

Figure C.44 Effect of higher volume of class C ash semi-adiabatic temperature profile of mixtures containing cement C3.

TABLE C.52
Comparison between semi-adiabatic calorimetry results of mixtures with higher volumes of class C ash and 20% fly ash cementitious mixtures

	High volume fly ash systems		20% fly ash cementitious mixtures	
Mix #	**Max peak temp (F)**	**Time of max peak (mins)**	**Max peak temp (F)**	**Time of max peak (mins)**
		30% replacement of cement by fly ash		
$C1F2_{(30)}W2A1$	98.04	**856**	100.26	976
$C2F1_{(30)}W2A1$	94.47	**1077**	102.06	767
$C2F2_{(30)}W1A2$	91.64	**841**	87.12	693
$C3F1_{(30)}W1A2$	101.96	**1080**	110.51	1009
		50% replacement of cement by fly ash		
$C1F1_{(50)}W2A2$	**89.55**	**1026**	102.67	871
$C1F2_{(50)}W1A2$	**84.41**	1171	100.81	1189
$C2F1_{(50)}W1A2$	92.1	**203**	92.53	531
$C2F2_{(50)}W2A1$	89.45	**834**	99.07	764
$C2F1_{(50)}W1A1$	91.87	**176**	93.47	473
$C2F2_{(50)}W2A2$	91.64	749	98.58	749
$C3F1_{(50)}W2A1$	**96.92**	**1016**	112.27	843
$C3F2_{(50)}W1A1$	**90.38**	**831**	113.11	945
		70% replacement of cement by fly ash		
$C1F1_{(70)}W1A1$	**81.73**	**523**	101.56	1069
$C2F1_{(70)}W2A2$	**83.33**	**384**	102.32	824
$C2F2_{(70)}W1A1$	86.71	**716**	87.57	650
$C3F2_{(70)}W2A2$	**87.66**	**874**	114.24	813

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

TABLE C.53
Comparison of Vicat's set time experiment results performed on mixtures with higher volumes of class C ash (replacement by weight) and 20% fly ash mixtures

Mix #	Normal consistency % (HVFS)	Initial set time (mins)	
		HVFS	20% fly ash mixtures
$C1F2_{(30)}W2A1$	22.0	160	180
$C1F2_{(50)}W1A2$	20.4	**40**	120
$C1F1_{(50)}W2A2$	19.9	**20**	285
$C1F1_{(70)}W1A1$	18.8	**35**	180
$C2F1_{(30)}W2A2$	23.8	**55**	170
$C2F2_{(30)}W1A2$	23.1	**25**	40
$C2F2_{(50)}W2A1$	20.6	**20**	55
$C2F2_{(50)}W2A2$	20.7	**20**	50
$C2F1_{(50)}W1A2$	23.0	**60**	135
$C2F2_{(70)}W1A1$	20.1	**13**	20
$C2F1_{(70)}W2A2$	18.7	**25**	170
$C2F1_{(50)}W1A1$	23.2	**35**	110
$C3F1_{(30)}W1A2$	26.3	**75**	235
$C3F1_{(50)}W2A1$	21.7	**140**	275
$C3F2_{(50)}W1A1$	25.1	**45**	480
$C3F2_{(70)}W2A2$	19.2	**25**	255

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

C.4.1 Results of Foam Index and Air Content in Mortar

Foam index testing was performed according to draft procedure outlined by Taylor et al. (*52*) to find out the amount of air entraining agent (AEA) required for producing a stable foam layer in paste slurries. ASTM C 185 was used to determine the amount of AEA dosage required to obtain 18 ± 2% air content in mortars. Table C.54 summarizes the results obtained from foam index testing and ASTM C 185 testing on plain and fly ash cementitious systems (20% and 60% replacement by weight). AEA requirements of various combinations were compared with that of the base mixture and the mixtures with significant (30% for

TABLE C.54
Summary of results obtained from foam index and ASTM C 185 testing

Mix #	Foam index results		ASTM C 185 results (air content in mortars)			
	AEA dosage ml/ 100 kg	% change w.r.t. base mix	AEA dosage ml/ 100 kg	Flow %	Air content %	% change w.r.t. base mix
Plain cementitious mixtures						
C1A1	122.2	—	342.9	80	17.4	—
C1A2	44.4	—	128.6	85	18.6	—
C1W1A1	194.4	**59**	2.9	82.5	20.6	**−99**
C1W1A2	4.6	**−90**	5.7	75	19.5	**−96**
C1W2A1	88.9	27	42.9	80	17.6	**−88**
C1W2A2	27.8	**−38**	142.9	82.5	19.9	11
20% fly ash mixtures						
$C1F3_{20}A1$	150.0	23	400.0	87.5	18.6	17
$C1F3_{20}A2$	94.4	**113**	200.0	80	19.1	**56**
$C1F3_{20}W1A1$	188.9	26	28.6	80	18.9	**−86**
$C1F3_{20}W1A2$	13.9	**−85**	28.6	80	19.5	**−93**
$C1F3_{20}W2A1$	16.7	**−89**	57.1	85	19.2	**−79**
$C1F3_{20}W2A2$	27.8	**−71**	142.9	81.25	18.5	**−29**
60% fly ash mixtures						
$C1F3_{60}A1$	405.6	**232**	571.4	85	18.2	**67**
$C1F3_{60}A2$	255.6	**475**	400.0	82.5	18.2	**211**
$C1F3_{60}W1A1$	294.4	−27	128.6	87.5	19.02	**−71.7**
$C1F3_{60}W1A2$	33.3	**−87**	114.3	87.5	17.8	**−71**
$C1F3_{60}W2A1$	127.8	**68.5**	57.1	87.5	18.3	**−90**
$C1F3_{60}W2A2$	44.4	**−89**	157.1	87.5	19.6	**−73**

NOTE: Values shown in **boldface** indicate incompatible behavior determined based on the limiting criteria adopted.

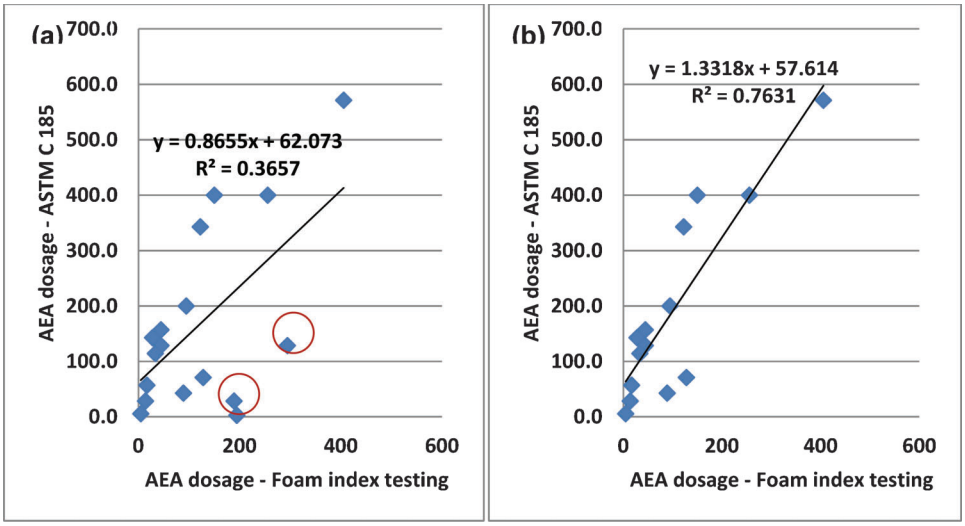

Figure C.45 Correlation between the results of ASTM C 185 test and foam index testing: (a) plot with all the data points; (b) plot with 3 data points excluded.

the foam index testing and 20% for the determination of air content in mortars experiment) difference in the AEA requirement were considered incompatible. Values identified in **boldface** in Table C.54 indicate incompatible behavior determined based on the limiting criteria adopted.

It was observed that 82% of the 22 different combinations studied were identified as incompatible based on the foam index testing. And 91% of the 22 different combinations studied were found to be incompatible based on the ASTM C 185 testing. C1W2A1, C1F3A1, C1F3_{20}W1A1 and C1F3_{60}W1A1 are the combinations that were found to be compatible when tested using the Foam index method. C1F3_{20}A1 and C1W2A2 were the only two combinations which were found to be compatible when tested using the ASTM C 185 method.

Figure C.45(a) represents the correlation between the results of both the experiments taking into consideration all the data points. Figure C.45(b) represents the same relation but without the three outliers (circled points on Figure C.45(a)).

It can be observed from Figure C.45(b) that there exists reasonably a good correlation (R^2 value of 0.76) between the results obtained from ASTM C 185 and foam Index testing. Mixtures corresponding to the three outliers are: C1W1A1, C1F3_{20}W1A1 and C1F3_{60}W1A1. In general, AEA requirement obtained from foam index testing was less than that obtained from ASTM C 185 testing with exception of three mixtures containing the W1 & A1 combination-the three outliers pointed in Figure C.45(a). It was observed during the foam index testing that W1A1 admixtures combination yielded smaller air voids compared to the other combinations. It was therefore difficult to determine if the thin layer of smaller voids was stable and if it completely covered the liquid surface. This was henceforth concluded to be the reason for the high dosage requirements and hence the deviation from the regular trends.

In general, dosage requirement of A1, as determined by foam index test, was greater than that of the A2 AEA. However, no clear trends can be observed in the results of ASTM C 185 test. Figure C.46 and Figure C.47 summarize the effect of fly ash replacement levels on the requirement of A1 and A2 air entraining agents respectively.

From the results summarized in Table C.54, Figure C.46 and Figure C.47, it can be observed that the addition of either of the

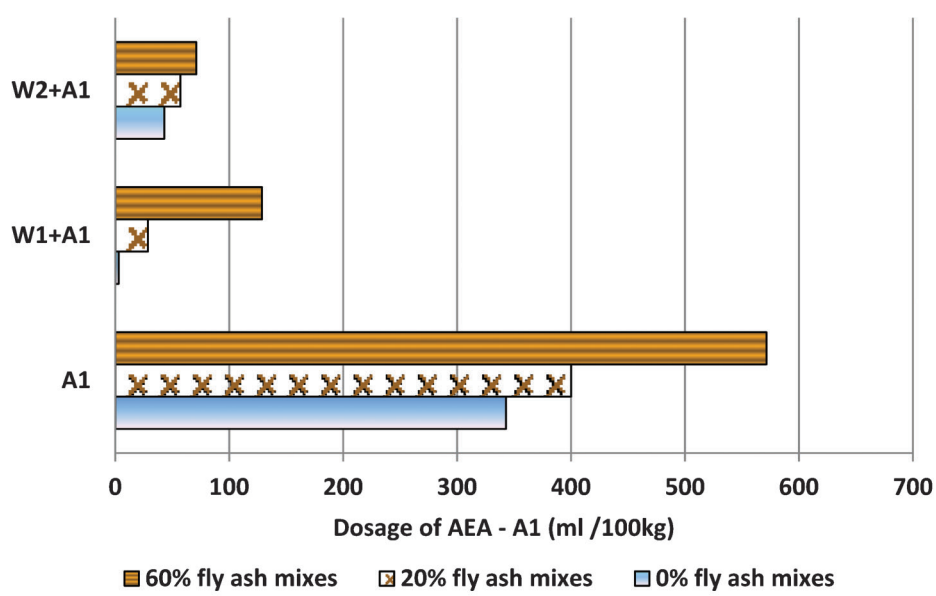

Figure C.46 Effect of fly ash content on the requirement of AEA: ASTM C 185 test results of mixtures with A1.

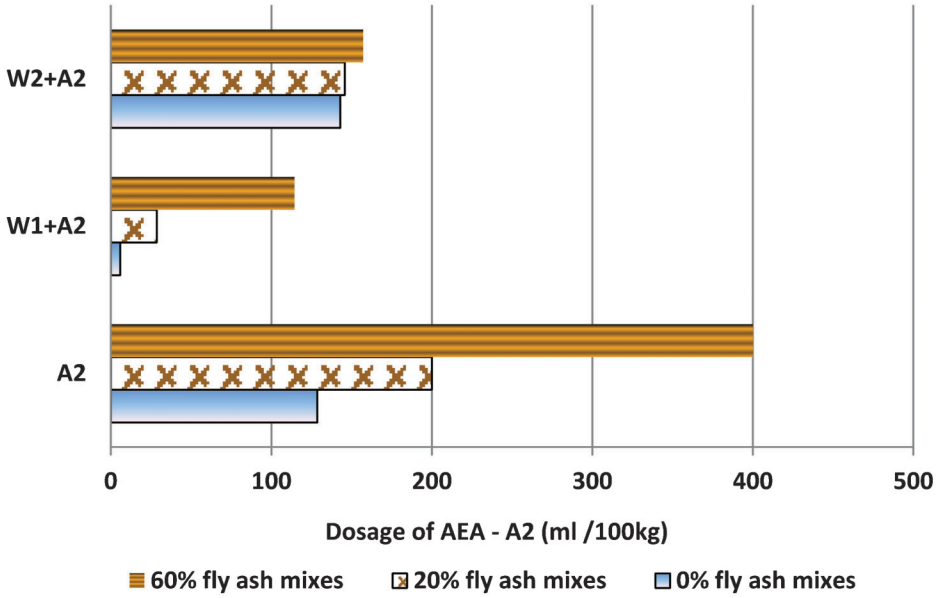

Figure C.47 Effect of fly ash content on the requirement of AEA: ASTM C 185 test results of mixtures with A2.

TABLE C.55
Foam drainage results of mixtures containing synthetic AEA, A1

			Rank		
Mix #	**1/K (1/min)**	**% foam drainage**	**1/K (1/min)**	**% foam drainage**	**Average rank**
C1W2A1	23.25	87.3	5	1	3*
C1F3W2A1 (60%)	21.3	73.64	4	2	3
C1F3W1A1 (60%)	0.88	13.33	1	6	3.5*
C1F3W1A1 (20%)	1.92	10	2	7	4.5
C1F3W2A1 (20%)	27.72	38	6	5	5.5
C1W1A1	5.28	6	3	8	5.5
C1F3A1 (20%)	38.57	70.5	8	3	6
C1A1	36.09	46.25	7	4	6

*Indicates mixes chosen for concrete testing.

TABLE C.56
Foam drainage results of mixtures containing VR based AEA, A2

			Rank		
Mix #	**1/K (1/min)**	**% foam drainage**	**1/K (1/min)**	**% foam drainage**	**Average rank**
C1W2A2	62.28	90	3	1	2.5*
$C1F3_{20}W2A2$	53. 3	80.67	2	3	3
$C1F3_{60}W2A2$	29.56	56.65	1	7	4*
C1W1A2	201.95	83.04	7	2	5*
C1A2	155.69	68.44	5	4	5
$C1F3_{20}A2$	122.22	62.58	4	6	5.5
$C1F3_{60}W1A2$	216.57	66.27	8	5	7
$C1F3_{20}W1A2$	199.55	56.48	6	8	7.5

*Indicates mixes chosen for concrete testing.

WRAs along with synthetic AEA, A1 reduced the amount of AEA, required to attain 18 ± 2% air content, when compared to the mixes without plasticizers. Similar trends were observed with lignin based WRA (W1) was added along with VR based AEA, A2. However, no such clear trends were observed in mixtures which contained poly-carboxylate type superplasticizer (W2) and A2.

It was also found out that that in mixtures with no water reducing agents, the amount of air entraining agents (both A1 and A2), required to attain 18 ± 2% air content increased with the increase in fly ash content. Similar results were also observed when either of the AEA agents were added along with lignin based WRA, W1. However, the amount of fly ash in the system did not have any significant effect on the amount of AEA required in cases of mixes with poly-carboxylate superplasticizer W2. Also, Mixtures with W1 required lower AEA (A1 or A2) dosages compared to that of mixes with W2 (exception of $C1F3_{60}W2A1$ mixture). It can be thus inferred that W1 had higher air entraining effect compared to that of W2.

C.4.2 Results of Foam Drainage Test

This section summarizes the results of foam drainage test performed on paste slurries. The values of 1/k and % foam drainage estimated from the foam drainage test were used to quantify the stability of the foam produced by the various combinations of materials. Five mixtures which exhibited poor air void stability were selected based on the foam drainage tests. Table C.55 summarizes the results of foam index results and the ranks of mixtures containing synthetic air entrainer (A1) while Table C.56 tabulates the results of mixtures containing Vinsol resin (VR) based air entrainer (A2). Mixes were ranked separately on a scale of 1 to 8 based on the 1/k and % foam drainage values.

TABLE C.57
Foam drainage parameters of mixtures selected for concrete testing

Mix #	1/K (1/min)	% foam drainage
C1W2A2	62.28	90
C1W1A2	201.95	83.04
C1W2A1	23.25	87.3
$C1F3_{60}W2A2$	29.56	56.65
$C1F3_{60}W1A1$	0.88	13.33

Rank 1 indicates a mix with most unstable air void system where as rank 8 indicates the most stable air void system. Average of the ranks was then calculated where a low value of average rank indicates potentially incompatibility.

Five most incompatible mixtures were thus identified based on these rankings for concrete testing and validation. Second criterion for selecting the mixtures for concrete testing was that matrix of the five mixtures does not have similar combination of materials. In addition to the five mixtures selected based on foam drainage testing, one more mixture C1A1 was selected for concrete testing at high temperature (37°C). This combination (C1A1T) was reported to result in low compressive strengths and improper air void system (*56*).

Table C.57 summarizes the list of mixes that were chosen for concrete testing. These mixes have all different 1/k values ranging from 0.88 to 201. Also, all these mixtures were identified as incompatible combinations from the ASTM C 185 or the foam index testing.

APPENDIX D. RESULTS OF CONCRETE TESTING (PHASE III)

Results and analysis of the Phase III concrete testing is detailed in this section. The first part of the chapter summarizes the results of experiments performed on concrete mixtures that were selected based on the Phase I early stiffening study. The second part of the chapter presents the results of experiments on concrete mixtures which were selected based on the Phase II air void system study.

D.1 TEST RESULTS OF CONCRETE MIXTURES FOR SUBTASK I (PHASE III)

Four mixtures were selected to validate the findings from paste and mortar experiments performed in Phase I. Two of the four mixtures, C2F2W1 and C1F2W1, were identified as early stiffening/setting mixtures from Phase I testing whereas the other two mixtures, C3W1 and C4F2W2, were the slow stiffening mixtures. Summary of fresh concrete properties, semi-adiabatic calorimetry and compressive strength results of the four mixes are presented in this section.

D.1.1 Fresh Concrete Properties

Table D.1 summarizes water binder ratio and variation of slump over time. Figure D.1 is the graphical representation of slump variation over time.

The two early stiffening mixes exhibited significant slump loss (> 2 in.) with in the first 60 minutes from the start of the experiment. Whereas the remaining slow stiffening mixes did not have a significant slump loss. Thus the two concrete mixtures which were identified as early stiffening through paste and mortar testing in Phase I also exhibited early stiffening behavior through rapid slump loss.

D.1.2 Results of Semi-Adiabatic Calorimetry

Table D.2 and Figures D.2 through D.5 summarize the results of semi-adiabatic calorimetry experiment performed on concrete mixtures. These figures also present the semi-adiabatic calorimetry results of mortar samples tested in Phase I. Temperature of 2 kg of concrete sample was monitored for at 48 hours under semi-adiabatic conditions. Figures D.2 through D.5 represent the actual semi-adiabatic calorimetric results of the four concrete samples, C2F2W1, C1F2W1, C3W1 and C4F2W2 respectively, obtained from semi-adiabatic monitoring. Results obtained from mortar testing were represented by the dotted line while the results from concrete testing were indicated by the solid line.

It was observed that the early stiffening mixes had lower maximum peak temperature values, when compared to the slow stiffening mixes. In general, the trends of semi-adiabatic temperature profile for all the concrete mixtures were similar to that of the results from mortar testing. Also, the occurrence of maximum peak temperature was faster in concrete samples when compared to that of the mortar samples.

Secondary peaks were observed with C2F2W1 concrete mixture which indicates that significant changes occurred in the hydration process. Similar secondary peaks were also observed when mortar samples of C2F2W1 were tested in Phase I. However, the secondary peaks in concrete sample occurred much quicker when compared to those in the mortar samples.

Major difference between mortar and concrete testing is the variation in the magnitude of temperature peaks. This difference is thought to be mainly because of different samples sizes used for testing. Temperature profile of 2 kg concrete samples was monitored whereas mortar testing was performed on ~2.080 kg sample. Therefore, the volume of paste, responsible for evolution of heat is different in both the system. Volume of paste in 2 kg concrete samples was in between 193 ml to 203 ml where the volume of paste in the 2.08 kg mortar samples was around 405 ml.

D.1.3 Compressive Strength Results

Table D.3 and Figure D.6 summarize the 7 day and 56 day compressive strength values of the four concrete mixtures. All the four mixtures had similar 7-day compressive strength with C4F2W2 and C2F2W1 mixtures having the minimum and the maximum values respectively. At the end of 7 days, all the four mixes had compressive strength greater than the critical value of 3000 psi, necessary for opening a highway to the traffic. 56 day strength values of the fly ash cementitious system were greater than that of the plain cementitious mixture.

D.2 RESULTS OF CONCRETE TESTING ON MIXTURES OF SUB-PHASE II (PHASE III)

This section summarizes the results of various tests performed on concrete mixes which were selected based on the Phase II testing. Five mixtures were selected to validate the findings from paste and mortar experiments performed in Phase II. One mixture C1A1, designated as C1A1T, was also included in the matrix to study the effect of high temperature on stability of the air void system. Summary of fresh concrete properties, image analysis and compressive strength results of the six mixtures are presented in this section.

D.2.1 Fresh Concrete Properties

Table D.4 summarizes the results of the fresh properties of concrete mixtures-water binder ratio, dosage of air entrainer required to achieve target air content, variation of slump and air content over time. 15 minute slump and air content measurements were performed after the initial concrete mixing (3 min mix-3 min rest-2 min mix cycle) whereas the 30 and 60 minutes measurements were made after remixing the concrete mixture for 1 minute.

It was observed that all the mixtures had significant (>30% w.r.t. initial air content) loss of total air content within 60 minutes from the beginning of mixing, except for C1A1T (loss of air content 28.9%). $C1F3_{60}W2A2$ mixture had the highest loss of air content while C1A1T mixture had the lowest loss. Figure D.7 is the graphical representation of % air content variation over time.

Table D.5 and Figure D.8 present the correlation between the total air content and unit weight measurements of concrete

TABLE D.1
Summary of fresh concrete properties

Mix #	w/b	Slump 15 min	Slump 30 min	Slump 60 min	Change in slump (15 to 60 min)
C2F2W1	0.43	2.5	0.7	0.3	**2.2**
C1F2W1	0.44	2.75	1.25	0.7	**2.05**
C3W1	0.44	3.25	1.75	1.6	1.65
C4F2W2	0.42	2.75	1.5	1	1.75

NOTE: Values shown in **boldface** indicate potential incompatible mixes.

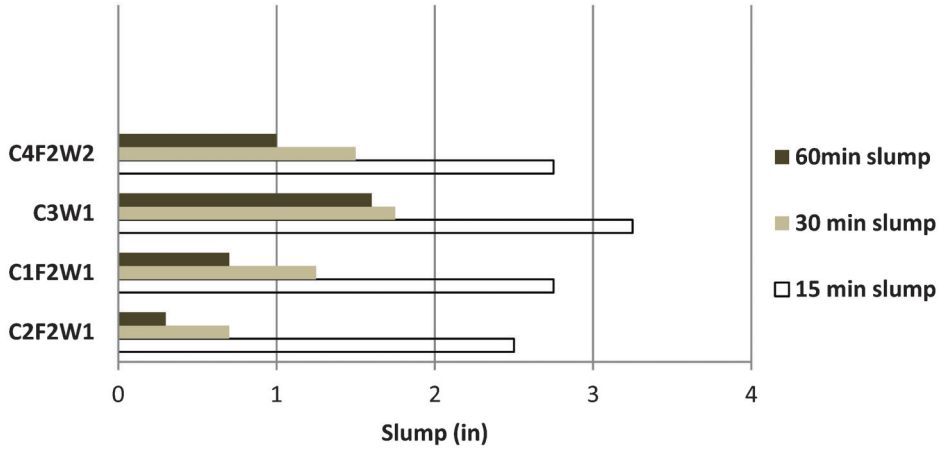

Figure D.1 Slump loss of concrete mixtures over time.

TABLE D.2
Summary of semi-adiabatic calorimetry results

Mix #	Max peak temperature (F)	Time of max peak (mins)	Secondary peaks
C2F2W1	82.7	590	Yes
C1F2W1	84.7	773	No
C3W1	92.1	687	No
C4F2W2	90.0	651	No

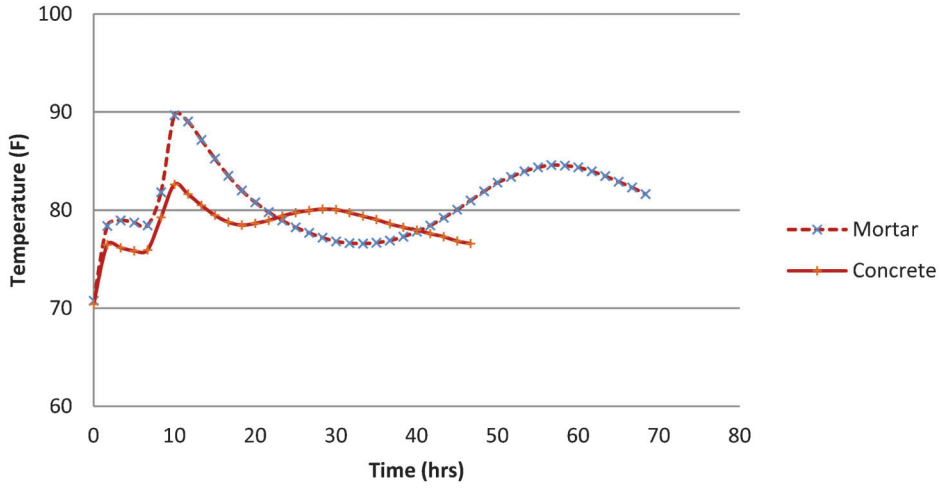

Figure D.2 Semi-adiabatic calorimetric results of C2F2W1 mixture.

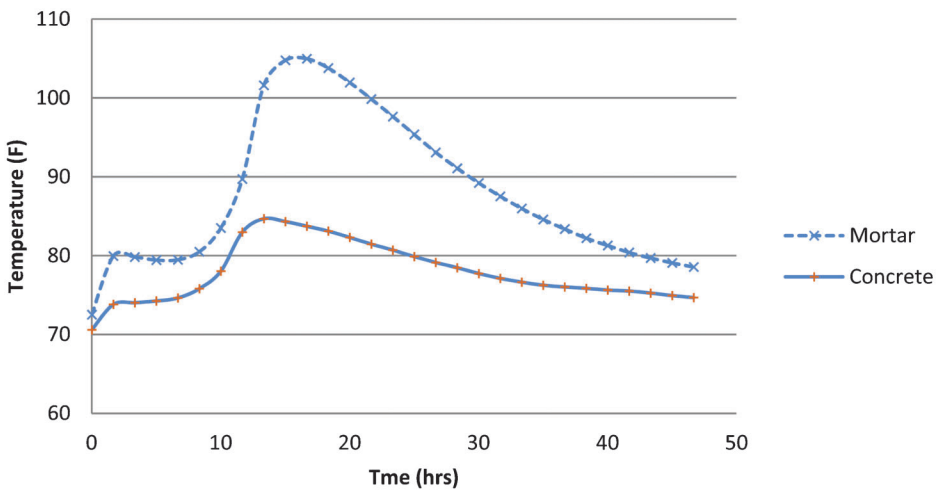

Figure D.3 Semi-adiabatic calorimetric results of C1F2W1 mixture.

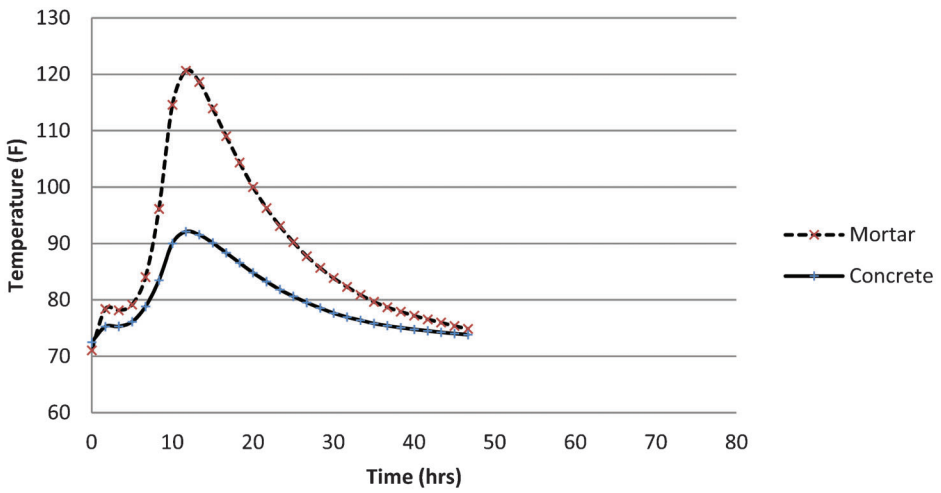

Figure D.4 Semi-adiabatic calorimetric results of C3W1 mixture.

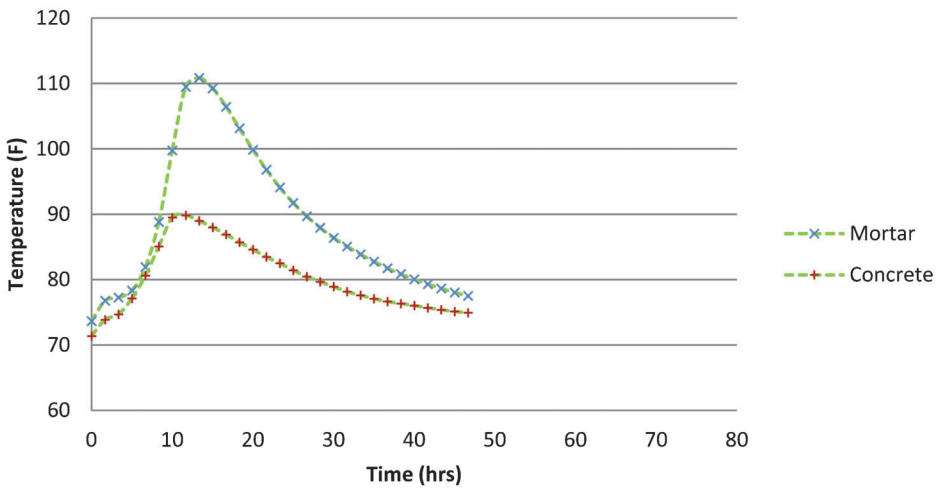

Figure D.5 Semi-adiabatic calorimetric results of C4F2W2 mixture.

TABLE D.3
7 and 56 days' compressive strength results of concrete mixtures

Mix #	7 day results		56 day results	
	Failure load (lb)	Strength (psi)	Failure load (lb)	Strength (psi)
C2F2W1	63440	5015	105840	8730
C1F2W1	62570	4935	107660	8780
C3W1	62060	4920	83750	6865
C4F2W2	59840	4680	98855	8060

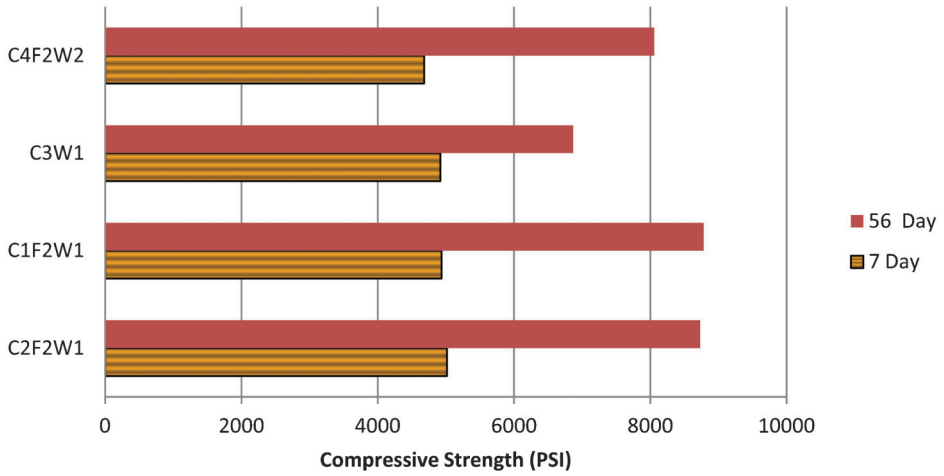

Figure D.6 7 day and 56 day compressive strength of concrete mixtures.

TABLE D.4
Summary of fresh properties of concrete mixes

Mix #	w/b	AEA dsg ml/ 100 kg	Slump (in)			Air content (%)		
			15 min	30 min	60 min	15 min	60 min after mxng	% chng
C1W1A2	0.474	35.9	2	0.75	0.25	6	3.9	35
C1W2A2	0.468	121.8	1.3	0.5	0.2	5.7	3.7	35.1
CW2A1	0.471	37.8	1.5	0.7	0.5	6.6	4	39.4
$C1F3_{60}W2A2$	0.40	130.5	1.75	0.5	0.2	7.3	3.1	57.5
$C1F3_{60}W1A1$	0.38	127.2	2	1	0.5	6	4	33.3
C1A1 T	0.44	131.4	2	1.5	0.7	7.6	5.4	28.9

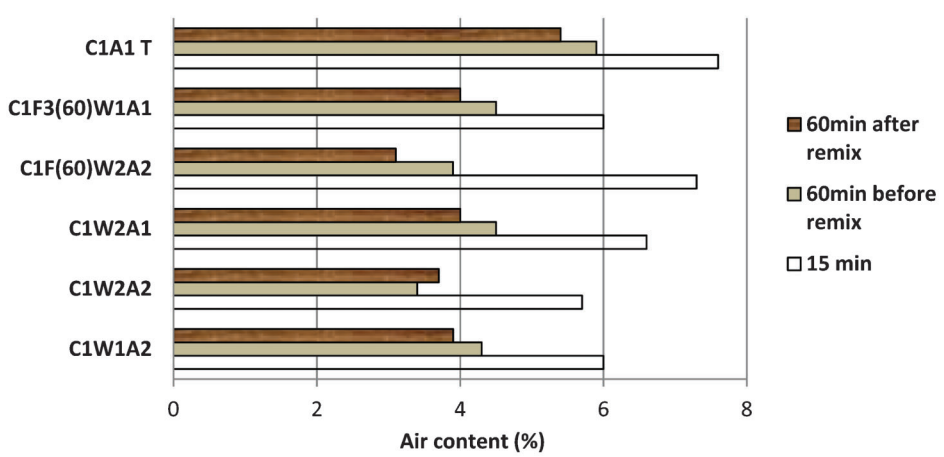

Figure D.7 Variation of total air content of concrete mixtures with time.

TABLE D.5
Correlation between total air content and corresponding unit weight measurements of concrete mixtures

	Air content (%)				Unit weight (lbs/ft^3)		
		60 min				60 min	
Mix #	15 min	Before rmxng	After rmxng	% change	15 min	Before rmxng	After rmxng
C1W1A2	6	4.3	3.9	35	146.8	149.1	149.4
C1W2A2	5.7	3.4	3.7	35.1	144.1	148.2	150.1
CW2A1	6.6	4.5	4	39.4	144.3	148.8	149.7
C1F3$_{60}$W2A2	7.3	3.9	3.1	57.5	141.8	147.8	148.8
C1F3$_{60}$W1A1	6	4.5	4	33.3	144.3	146.1	148.4
C1A1 T	7.6	5.9	5.4	28.9	141.1	143.4	144.6

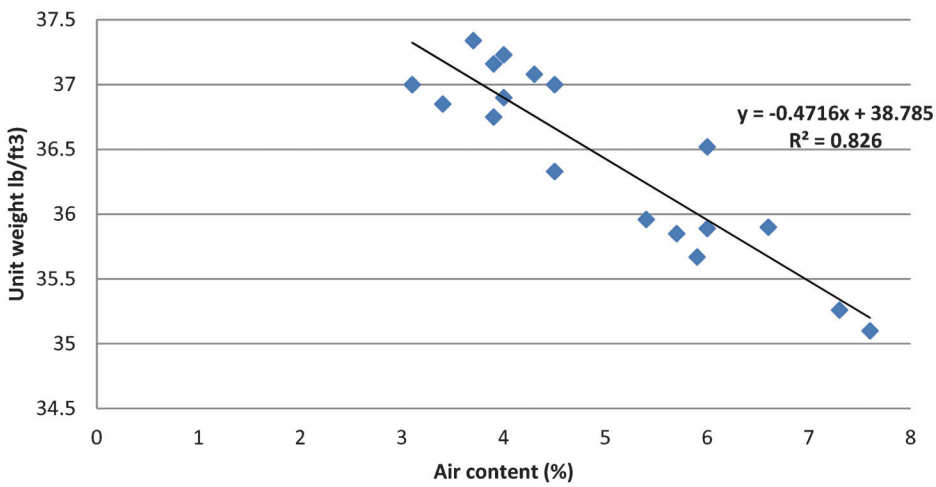

Figure D.8 Correlation between unit weight and total air content.

mixtures. Good linear correlation ($R^2 \sim 0.83$) was observed between the total air content and unit weight values.

D.2.2 7- and 56-Day Compressive Strength Measurements

Table D.6 and Figure D.9 summarize the results of 7 and 56 day compressive strengths of concrete mixtures. All the concrete samples for strength testing were stored in curing room maintained at 23°C. Six extra samples of high temperature C1A1T mixture were also stored in a 37°C curing tank to study the effect of curing temperature.

The three plain cementitious mixtures mixed at room temperature had 7 day strength values greater than 3,000 psi. Remaining three mixtures, C1F3$_{60}$W2A2, C1F3$_{60}$W1A1 and C1A1T mixtures had 7 day strength less than critical strength of 3000 psi. It is also notable that the 56 day compressive strength of C1F3$_{60}$W2A2 mixture was less than 3000 psi.

Figure D.10 summarizes the effect of curing temperature on the compressive strength of C1A1T concrete mixture. Samples cured at high temperature had lower strength values compared to the samples cured at 23°C. Difference in the strength values was highest at 56 days. The average 56 day compressive strength of concrete sample cured at 23°C was 1155 psi higher than those cured at 37°C.

TABLE D.6
Average 7 day and 56 day compressive strengths of concrete mixtures

	7 day results		56 day results	
Mix #	Avg peak load (lbs)	Avg peak stress (psi)	Avg peak load (lbs)	Avg peak stress (psi)
C1W1A2	57430	4475	89370	7420
C1W2A2	59335	4650	88630	7345
C1W2A1	49940	3915	79805	6510
C1F3$_{60}$W2A2	12970	1030	36740	2990
C1F3$_{60}$W1A1	15095	1180	41990	3450
C1A1 T (23°C curing)	37500	2980	61630	4990
C1A1 T (37°C curing)	36925	2935	42380	3835

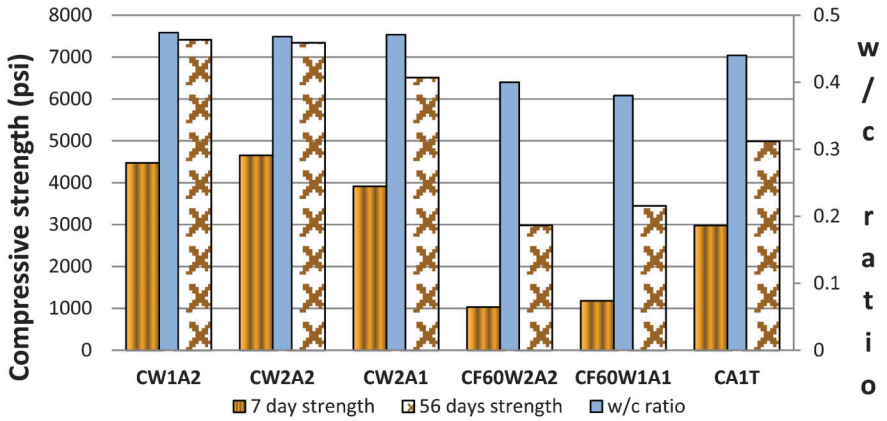

Figure D.9 Summary of w/b ratio and compressive strength results of concrete samples cured at 23°C.

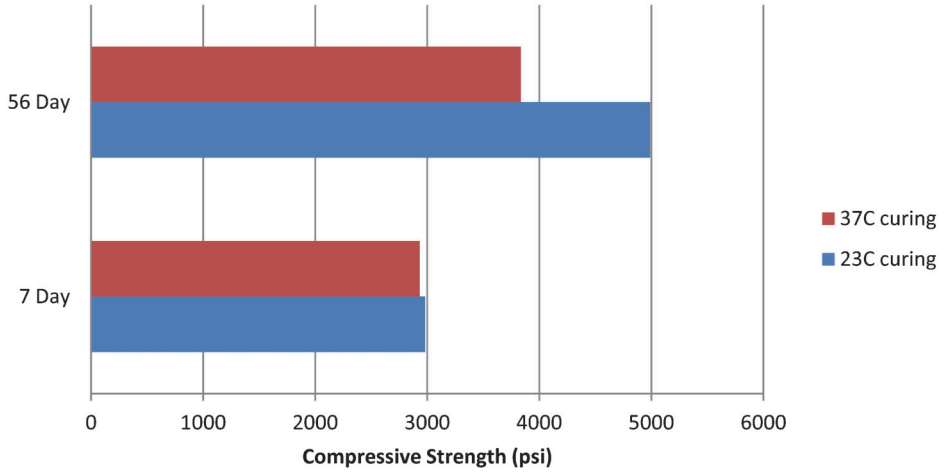

Figure D.10 Effect of curing temperature (23°C vs. 37°C) on the compressive strength of C1A1T concrete mixture.

APPENDIX E. STATISTICAL MODELING

This chapter summarizes the statistical modeling performed based on the results of mixtures tested in subtask I of Phase I. Section E.1 presents the results of regression modeling to predict the initial set time. Section E.2 summarizes the regression analysis performed to predict the results of mini slump experiments followed by set time predictions using calorimetry results in Section E.3.

Linear regression analysis was performed on 68 different combinations. Binder (plain and fly ash cementitious systems) component of various combinations is represented by the tricalcium aluminates content, sulfate content and the total alkali content in the mixture (Table E.1). While each of the water reducing agents and air entraining agents were represented separately by their corresponding dosage levels in the mixtures. Figure E.1 summarizes the input parameters and the corresponding representation of each of the materials.

Construction of the prediction models was done using the SPSS statistical package. Stepwise linear regression modeling was adopted wherein; insignificant decision (independent) variables were removed from the final model in a sequential process. For an independent variable to be significant, its corresponding p-value should be less than 0.05. Also the model with highest adjusted R^2 value was selected as the best fit model. Initial set time along with area of spread (pat) of paste slurries at 2, 5 and 30 minutes were estimated using the linear regression model. The pat areas at the respective times were obtained from mini slump testing performed on paste slurries (0.43 w/c ratio). Parameters estimated from the semi-adiabatic calorimetry curves were used to predict the initial set time in the final section of this chapter.

E.1 REGRESSION MODEL FOR PREDICTING INITIAL SET TIME

Stepwise linear regression modeling identified the chemical properties of the binder and the presence of PC type SP (W2) as the significant decision variables. R^2 value for the model was found to be 0.564 while the adjusted R^2 value was 0.535. The linear regression model to predict the initial set time (in minutes) is given by Equation E.1:

TABLE E.1
Chemical properties of fly ash cementitious systems tested in sub-phase I of Phase I

Fly ash cementitious systems (20% replacement by weight)	% C_3A	% SO_3	% Na_2O_{equ}
C1F1	7.2	2.78	0.67
C1F2	7.2	2.99	0.62
C2F1	8.08	2.14	0.68
C2F2	8.08	2.35	0.63
C3F1	8.00	3.10	1.27
C3F2	8.00	3.31	1.22
C4F1	6.16	3.10	1.21
C4F2	6.16	3.31	1.16

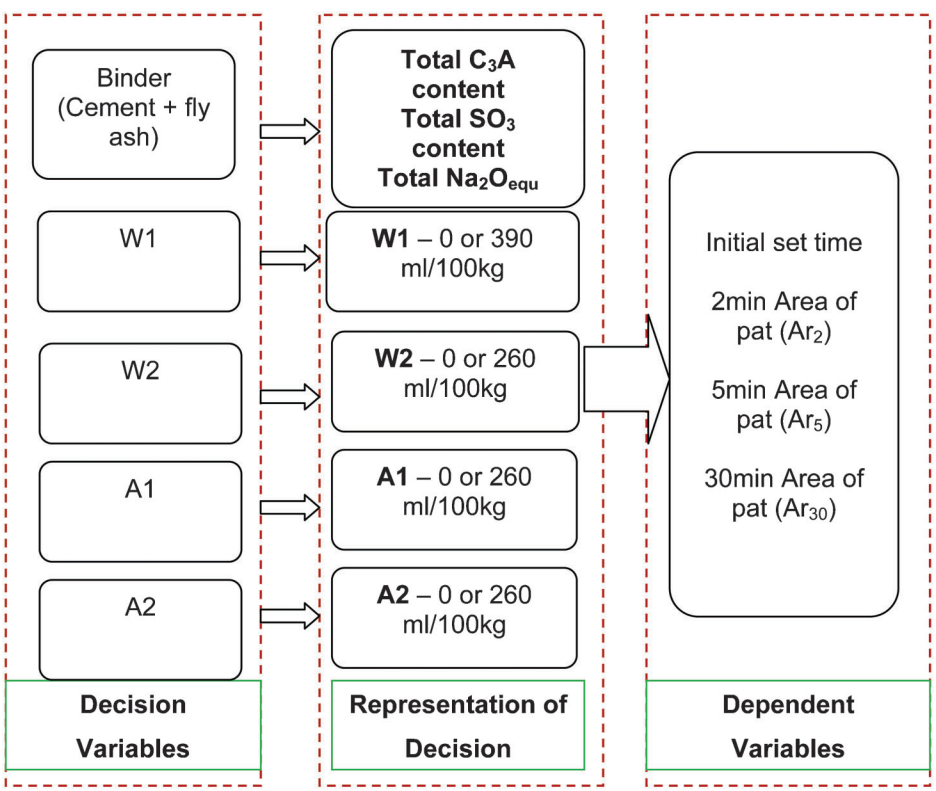

Figure E.1 Summary of inputs for regression modeling.

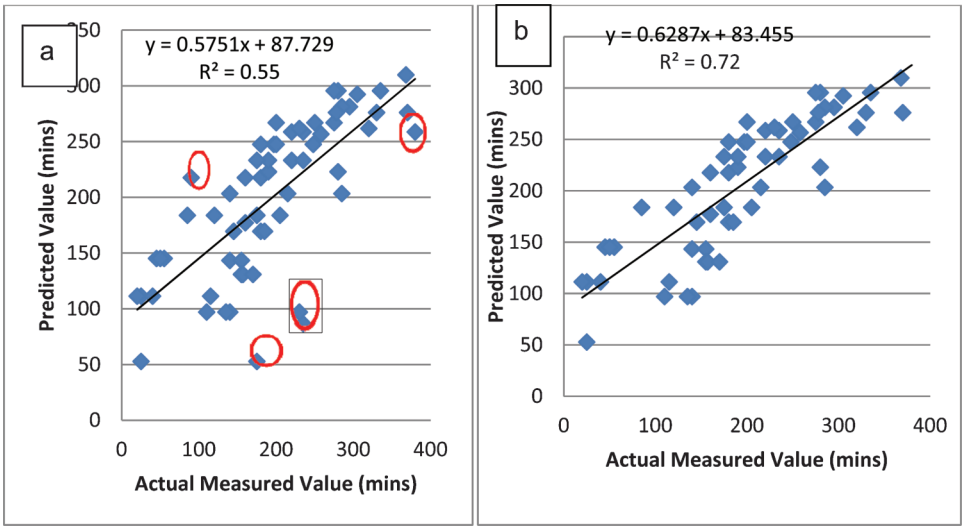

Figure E.2 Predicted values of initial set time vs. experimentally measured values by: (a) plot with all the data points; (b) plot with outliers eliminated.

$$\textbf{Initial set} = -4.65 - 18.03 * \mathbf{C_3A} + 89.51 * \mathbf{SO_3} + 82.38 * \mathbf{Na_2O_{equ}} + 0.13 * \mathbf{W2} \quad \text{(E.1)}$$

For mixtures prepared with chemical admixtures, a linear relation between parameters W1 and W2 exists (depicted by line passing through co-ordinates (0,390) and (260, 0)). Hence in the final model, only one of the two parameters was considered significant. Therefore it should be noted that the initial set time depends on the type of admixture present in the mixture rather than just the presence of W2 in the mixture.

Figure E.2 presents the relation between the predicted values and the values obtained from laboratory experiments. Reasonably (R^2 value of 0.55) good linear relation between the actual measured experimental values and the values predicted using the regression model. The R^2 value improved to 0.72 after removing the outliers that are highlighted by circles in Figure E.2(a). The five outliers were identified as C1F2W2, C2, C2W2, C2F1, and C4W1. It can be seen that four out of the five mixtures were prepared with low (<0.3%) alkali cements (C1 and C2).

One of the underlying assumptions in linear regression analysis is that the residuals (difference in the values of predicted and measured dependent variable) are normally distributed with average around zero. Average (avg.) and standard deviation (S.D) values of the distribution can be used to identify and eliminate outliers to improve the regression fit. In a normal distribution, 68% of the data points lie within the range of avg. $\pm$ S.D. The five extreme points that were eliminated in Figure E.2(b) were way outside the range of avg. $\pm$ S.D.

In order to determine its validity, the regression model developed in this study wad was used to predict the initial set time values measured by Taylor et al. (*10*). Material properties of

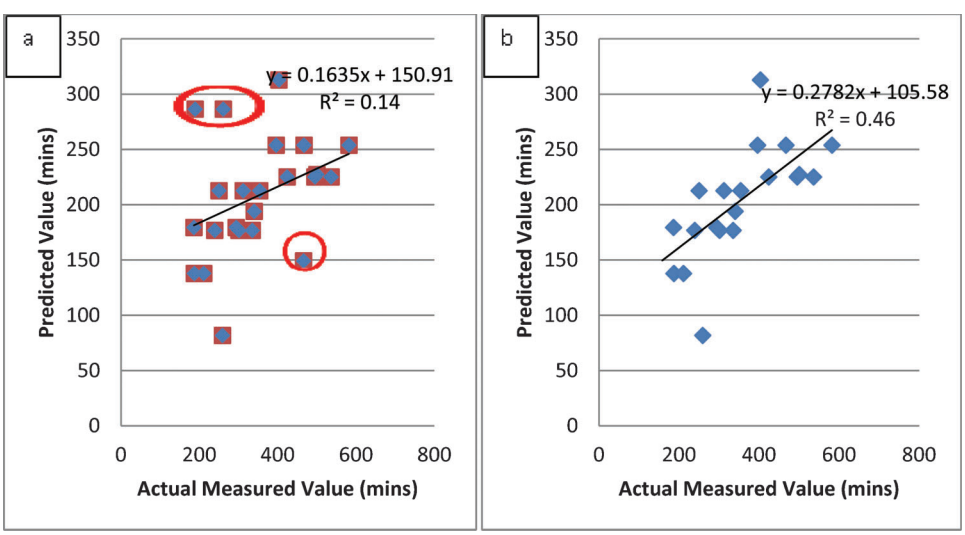

Figure E.3 Predicted values of initial set time vs. experimentally measured values by Taylor et al. (*10*): (a) plot with all the data points; (b) plot with outliers eliminated.

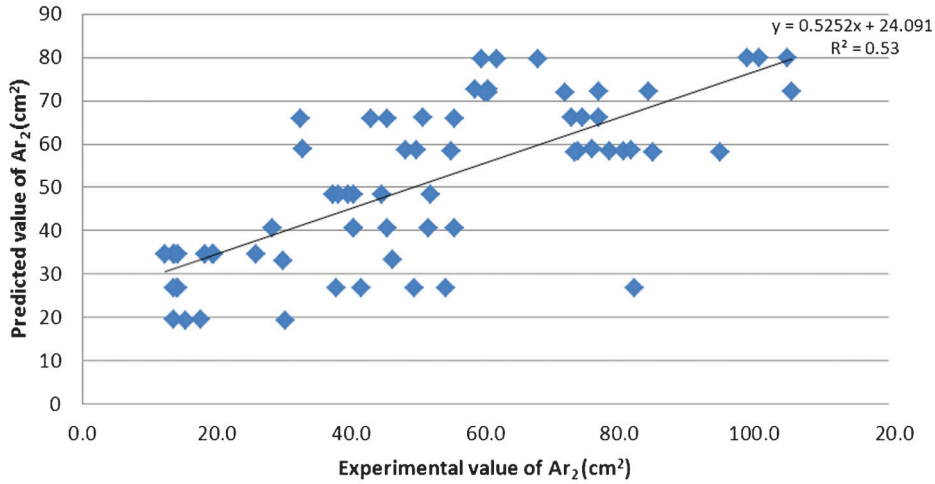

Figure E.4 Predicted vs. theoretical values of area of pat at 2 minutes.

various combinations and the corresponding results of initial set time experiments were used for the evaluation of the regression model. After eliminating the three outliers, there appeared to be reasonably good (R^2 value = 0.46) linear relationship between the values from experiments by Taylor et al. (*10*) and the values predicted using the regression model (Figure E.3). The three outliers (the residual values of which were beyond the range of avg. ± S.D) were identified as results of the mixtures 3CA, 5P and 5PA. All the three mixtures were prepared with high (10%) C_3A content cement but the alkali (0.38% and 2.26%) and sulfate content of cements 2 and 5 were different.

E.2 REGRESSION MODEL FOR PREDICTING MINI SLUMP PARAMETERS

Stepwise linear regression analysis was also used to predict the results of mini slump experiments. Models to predict the areas of the spread measured at 2, 5 and 30 minutes after the time of contact of water with binder were constructed. It was again observed that the chemical properties of the binder and the presence of PC type SP were identified to be the significant decision variables in predicting the above three variables. However, no significant model with adjusted R^2 value was found when predicting the false setting (F.S.I.) and stiffening (S.I.) indices.

R^2 value for the model to predict the area of spread at 2 minutes was found to be 0.526 while the adjusted R^2 value was 0.495. The linear regression model to predict the area of spread after 2 minutes (in cm^2) is given by Equation E.2:

$$\mathbf{Area}_{2mins} = 126.93 - 15.70 * \mathbf{C_3A} + 27.12 * \mathbf{SO_3} - 46.31 * \mathbf{Na_2O_{equ}} + 0.053 * \mathbf{W2} \quad \text{(E.2)}$$

Figure E.4 presents the relation between the predicted values and the values obtained from laboratory experiments. It was observed that there exists reasonably (R^2 value of 0.52) linear relation between the measured values and those predicted using the regression model.

R^2 value for the model to predict the area (cm^2) of spread at 5 minutes was found to be 0.568 while the adjusted R^2 value was 0.541. The linear regression model to predict the area of spread measured at 5 minutes (in cm^2) is given by Equation E.3:

$$\mathbf{Area}_{5mins} = 135.84 - 14.39 * \mathbf{C_3A} + 19.51 * \mathbf{SO_3} - 34.5 * \mathbf{Na_2O_{equ}} + 0.051 * \mathbf{W2} \quad \text{(E.3)}$$

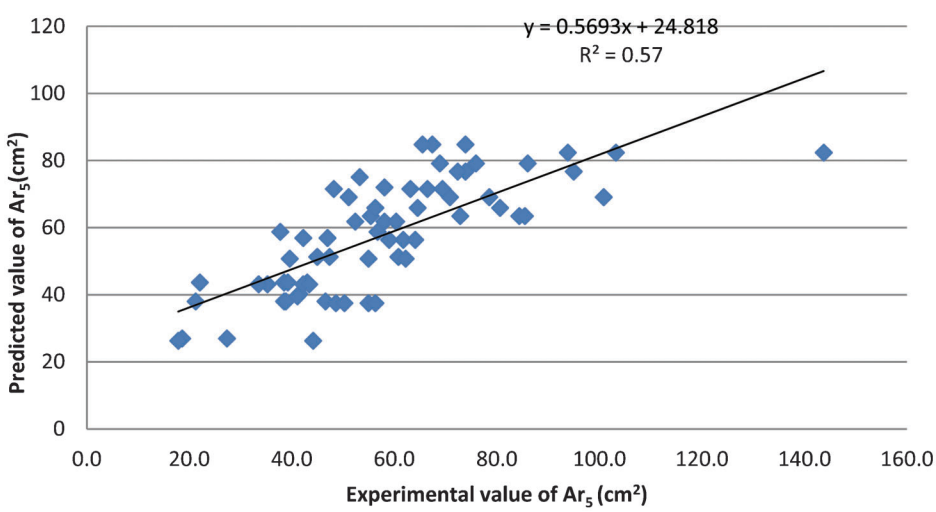

Figure E.5 Predicted vs. theoretical values of area of pat at 5 minutes.

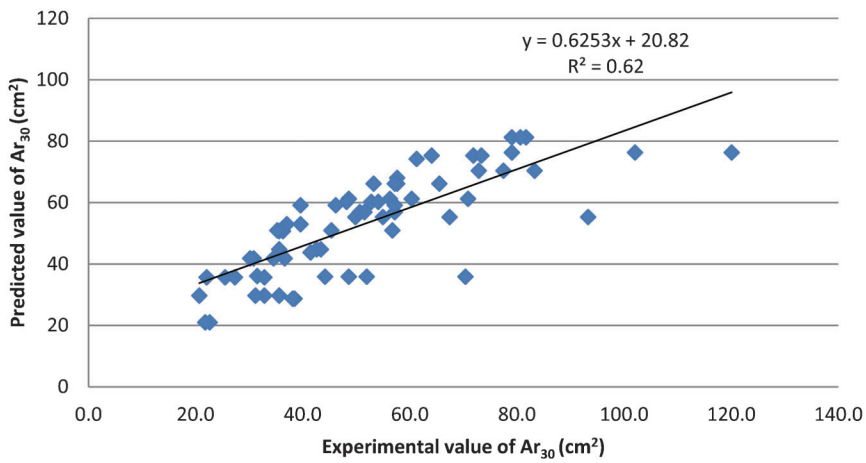

Figure E.6 Predicted vs. theoretical values of area of pat at 30 minutes.

Figure E.5 presents the relation between the predicted values and the values obtained from laboratory experiments. It was observed that there exists reasonably (R^2 value of 0.57) good linear relation between the actual measured experimental values and the values predicted using the regression model.

Similarly, R^2 value for the model to predict the area (cm^2) of spread at 30 minutes was found to be 0.622 while the adjusted R^2 value was 0.598. The linear regression model to predict the area of spread at 30 minutes (cm^2) is given by Equation E.4:

$$\mathbf{Area}_{30\text{mins}} = 100.31 - 12.39 * \mathbf{C_3A} + 22.58 * \mathbf{SO_3} - 27.87 * \mathbf{Na_2O_{equ}} + 0.058 * \mathbf{W2} \quad \text{(E.4)}$$

Figure E.6 presents the relation between the predicted values and the values obtained from laboratory experiments. It was observed that there exists reasonably (R^2 value of 0.62) good linear relation between the actual measured experimental values and the values predicted using the regression model.

An attempt was made to predict the false stiffening index (F.S.I., calculated as the ratio of area of spread of pats measured at 5 and 2 minutes) and stiffening index (S.I., calculated as the ratio of area of spread of pats measured at 30 and 5 minutes). However a significant model, that has adjusted R^2 value greater than 0.3, could not be developed to predict the parameters S.I. and F.S.I.

E.3 REGRESSION ANALYSIS USING THE RESULTS FROM SEMI-ADIABATIC CALORIMETER EXPERIMENTS

The results from semi-adiabatic calorimeter (SAC) were used to predict the initial set time. Various parameters of the SAC results that were used to predict the set time are listed in Table E.2 and graphically represented in Figure E.7. Maximum peak temperature and the corresponding time of occurrence were obtained from the calorimeter experiments. Start and end times.

Stepwise linear regression modeling (model #5) identified maximum peak temperature (TMPmax), time (Td) and area under the curve until the end of dormant region (Ae) as the significant decision variables. R^2 value for the model was found to be 0.55 while the adjusted R^2 value was 0.52. Equation of the linear regression model to predict the initial set time (in minutes) is given by Equation E.5:

$$\mathbf{Initial\ set\ (mins)} = -447.45 + 5.452 * \text{TMPmax} + 33.02 * \text{Td} - 2.67 * \text{Ae} \quad \text{(E.5)}$$

Figure E.8 presents the relation between the predicted values and the values obtained from laboratory experiments. It was observed that there exists reasonably (R^2 value of 0.40) good linear relation between the actual measured experimental values and the values predicted using the regression model. The R^2 value improved to 0.52 after removing the outliers that are highlighted by circles in Figure E.8(a). The five outliers were identified as C1F2W1A1 AND C1F2W1A2, C2F1W1A2, C2F2W2 and C4F2W2A1. Thus it can be seen that four out of the five mixtures were prepared with low (<0.3%) alkali cements (C1 and C2). The residual values of all the five mixtures were beyond the range of avg. $\pm$ S.D.

The initial set time values thus predicted by the above model were compared with those obtained from the model represented by Eq. E.1, which accepts material properties as the input. Figure E.9 represents the linear relation (R^2 value = 0.55) between the values predicted from both the models.

TABLE E.2
List of semi-adiabatic calorimetry parameters used for the analysis

Decision variables	Regression method	Predicted variable
• TMPmax, Maximum peak temperature • Tmax, Time for maximum peak • At, Total area under the curve • Ti, Time of initial peak (start of dormant region) • Td, Time of end of dormant region • ΔT, Length of dormant region • Ai, Area under the curve until the start of dormant region • Ae, Area under the curve until the end of dormant region	Stepwise linear regression modeling	Initial set time

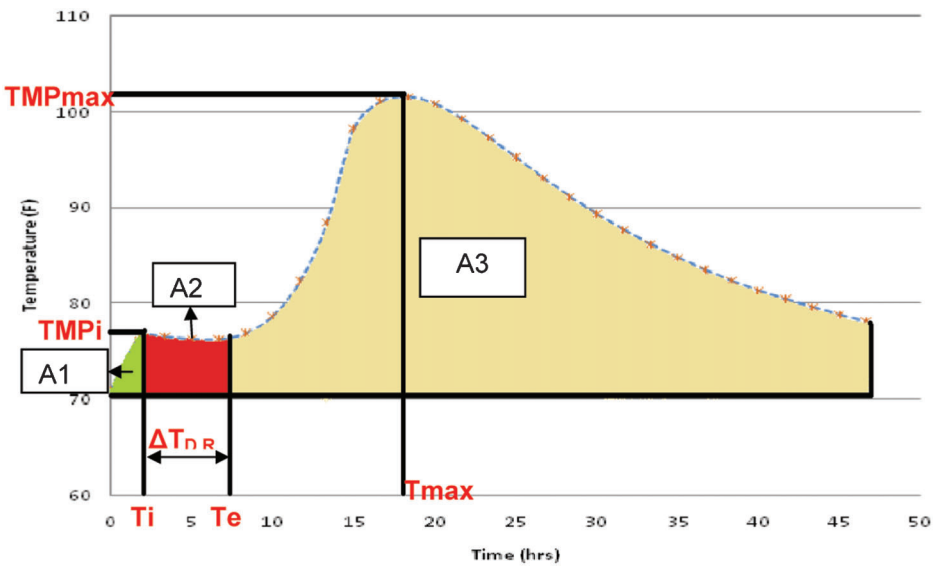

Figure E.7 Typical SAC curve. New parameters considered for analysis of the dormant region (D.R.) were approximately estimated from the SAC plots while the area under the curve was calculated using trapezoid rule.

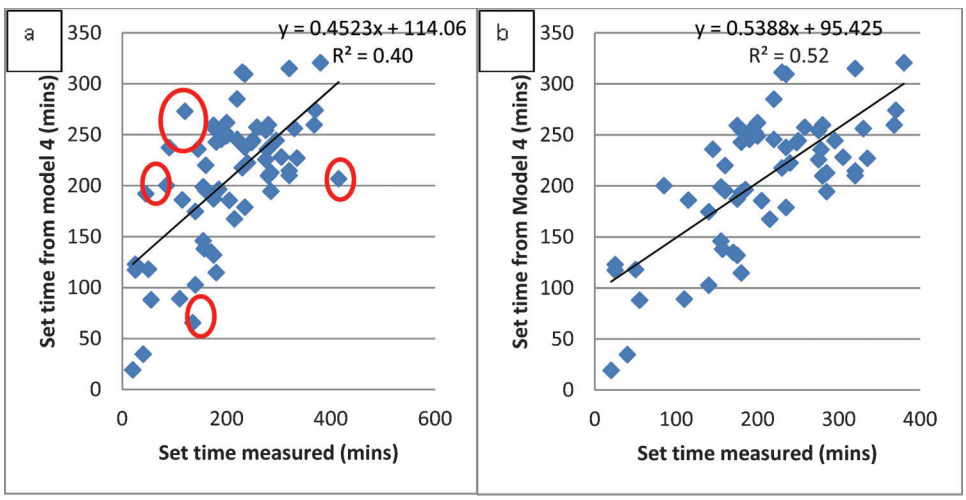

Figure E.8 Predicted values of initial set time vs. experimentally measured values: (a) plot with all the data points; (b) plot with outliers eliminated.

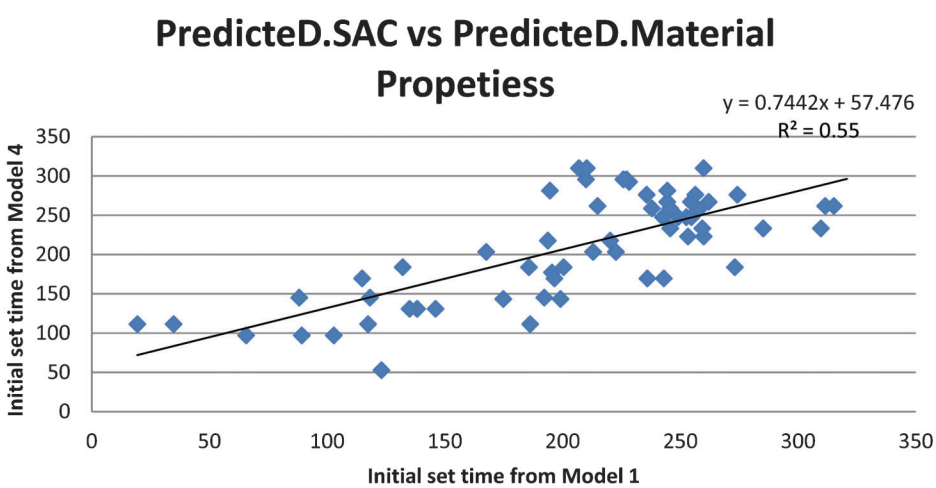

Figure E.9 Initial set time (in minutes) values predicted using the regression analysis of SAC data and material properties.

REFERENCES

1. Cost, V. T., and G. Knight. Use of Thermal Measurements to Detect Potential Incompatibilities of Common Concrete Materials. *ACI*, SP-241-4, 2007, pp. 39–58.
2. Tanikella, P. Incorporating Physical and Chemical Characteristics of Fly Ash in Statistical Modelling of Binder Properties. MS thesis. Department of Civil Engineering, Purdue University, West Lafayette, Indiana, 2009, p. 341.
3. Tang, F. J., and S. Bhattacharja. *Early Stiffening Test Development for Portland Cement*. R&D Serial No. 1999. Portland Cement Association, Skokie, Illinois, 1996.
4. Kosmatka, S. H., B. Kerkhoff, and W. C. Panarese. *Design and Control of Concrete Mixtures*, 14th ed. Portland Cement Association, Skokie, Illinois, 2002.
5. Neville, A. M. *Properties of Concrete*, 4th ed. Dorling Kindersley (India) Pvt Ltd, 1995, pp. 12–21, 184–200, 243–262, 546–547.
6. Sandberg, P. J., and L. R. Robert. Cement-Admixture Interactions Related to Aluminate Control. *Journal of ASTM International*, Vol. 2, 2005.
7. Jolicoeur, C., and M. C. Simard. Chemical Admixture-Cement Interactions: Phenomenology and Physico-Chemical Concepts. *Cement and Concrete Composites*, Vol. 20, Nos. 2–3 1998, 87–101. doi: 10.1016/S0958-9465(97)00062-0.
8. Zingg, A., F. Winnefeld, L. Holzer, J. Pakusch, S. Becker, R. Figi, and L. Gauckler. Interaction of Polycarboxylate-Based Superplasticizers with Cements Containing Different C3A Amounts. *Cement and Concrete Research*, 2009, pp. 153–162.
9. Lawrence, R. R., and P. C. Taylor. Understanding Cement-SCM-Admixture Interaction Issues. *Concrete International*, January 2007, pp. 33–41.
10. Taylor, P. C., L.A. Graf, J. Z. Zemajtis, V. C. Johansen, R. L. Kozikowski, and C. F. Ferraris. *Identifying Incompatible Combinations of Concrete Materials: Volume I-Final Report*. Publication FHWA-HRT-06-079. Federal Highway Administration (FHWA), Washington, D.C., 2006.
11. Andersen, P. J., A. Kumar, D.M. Roy, and D. Wolfe-Confer. The Effect of Calcium Sulphate Concentration on the Adsorption of a Superplasticizer on a Cement: Methods, Zeta Potential and Adsorption Studies. *Cement and Concrete Research*, 16, 2, 1986, pp. 255–259. doi: 10.1016/0008-8846(86)90142-0.
12. Ohno, A., and T. Yamamoto. Fluidity of Various Cement Pastes Added Polycarboxylic Acid Type Admixture. *JCA Proceedings of Cement & Concrete*, Vol. 51, 1997, 258–263.
13. Jiang, S., B.-G. Kim, and P.-C. Aitcin. Importance of Adequate Soluble Alkali Content to Ensure Cement/Superplasticizer Compatibility. *Cement and Concrete Research*, Vol. 29, No. 1, 1999, pp. 71–78. doi: 10.1016/S0008-8846(98)00179-3.
14. Prince, W., M. Espagne, and P.-C. Aitcin. Ettringite Formation: A Crucial Step in Cement Superplasticizer Compatibility, *Cement and Concrete Research*, Vol. 33, No. 5, 2003, pp. 635–641. doi: 10.1016/S0008-8846(02)01042-6.
15. Jennings, H., D. L. Johnson, G. M. Moss, and A. W. Saak. *Pooled Fund Study of Premature Rigid Deterioration*. Iowa Department of Transportation Research Project H-1063, Northwestern University Technological Institute, Evanston, Illinois, April 1997.
16. Kim, B.-G., S. Jiang, C. Jolicoeur, and P.-C. Aitcin. The Adsorption Behavior of PNS Super Plasticizer and its Relation to Fluidity of Cement Paste. *Cement and Concrete Research*, Vol. 30, No. 6, 2000, pp. 887–893. doi: 10.1016/S0008-8846(00)00256-8.
17. Flatt, R. J., and Y. F. Houst. A Simplified View on Chemical Effects Perturbing the Action of Superplasticizers. *Cement and Concrete Research*, Vol. 31, No. 8, 2001, pp. 1169–1176. doi: 10.1016/S0008-8846(01)00534-8.
18. Dubovoy, V. S., S. H. Gebler, and P. Kleiger. *Cement Alkali Level as it Affects Air Void Stability, Freeze Thaw Resistance and Deicer Scaling Resistance of Concrete*. RD128. Portland Cement Association, Skokie, Illiniois, 2002, p. 24.
19. Pigeon, M., P. Plante, R. Pleau, and N. Banthia. The Influence of Soluble Alkalies on the Production and Stability of the Air Void System in Superplasticized and Non-superplasticized Concrete. *ACI Materials Journal*, Vol. 89, 1992, pp. 24–31.
20. Plante, P., M. Pigeon, and C. Foy. The Influence of Water Reducers on the Production and Stability of the Air Void System in the Concrete. *Cement and Concrete Research*, Vol. 19, No. 4, 1989, pp. 621–633. doi: 10.1016/0008-8846(89)90014-8.
21. Cross, W., E. Duke, J. Kellar, and D. Johnson. *Investigation of Low Compressive Strengths of Concrete Paving, Precast and Structural Concrete*. SD98-03-F. South Dakota Department of Transportation, 2000.
22. Wang, H., C. Qi, H. Farzam, and J. Turici. Interaction of Materials Used in Concrete. *Concrete International*, April 2006, 47–52.
23. Ravina, D., and P. K. Mehta. Properties of Fresh Concrete Containing Large Amounts of Fly Ash. *Cement and Concrete Research*, Vol. 16, No. 2, 1986, pp. 227–248. doi: 10.1016/0008-8846(86)90139-0.
24. Gress, D. *Early Distress in Concrete Pavements*. SA-97-045. Federal Highway Administration. 1997, p. 53.
25. Gebler, S. H., and P. Klieger. *Effect of Fly Ash on Air Void Stability of Concrete*. RD085.01T. Portland Cement Association, Skokie, Illinois, 1983.
26. Zhang, D. S. Air Entrainment in Fresh Concrete with PFA. *Cement and Concrete Composites*, Vo. 18, No. 6, 1996, 409–416. doi: 10.1016/S0958-9465(96)00033-9.
27. Laots, I. K., R. H. Hurt, and E. M. Suuberg. Size Distribution of Unburned Carbon in Coal Fly Ash and its Implications. *Fuel*, Vol. 83, 2003, pp. 223–230.
28. Hill, R. L., S. L. Sarkar, R. F. Rathbone, and J. C. Hower. An Examination of Fly Ash Carbon and its Interacations with Air Entraining Agent. *Cement and Concrete Research*, Vol. 27, No. 2, 1997, pp. 193–204. doi: 10.1016/S0008-8846(97)00008-2.
29. Dodson, V. H., and T. D. Hayden. Another Look at the Portland Cement/Chemical Admixture Incompatibility Problem. *Journal of Cement, Concrete and Aggregates*, Vol. 11, No. 1, 1989, pp. 52–56. doi: 10.1520/CCA10102J.
30. Khalil, S. M., and M. A. Ward. Influence of SO_3 and C_3A on the Early Reaction Rates of Portland Cement in the Presence of Calcium Lignosulfonate. *American Ceramic Society Bulletin*, Vol. 57, No. 12, 1978, pp. 1116–1222.
31. Aitcin, P. C, C. Jolicoeur, and J. G. Macgregor. Superplasticizers: How They Work and Why They Occassionally Don't. *Concrete International*, Vol. 16, 1994, pp. 45–52.
32. Hanehara, S., and K. Yamada. Rheology and Early Age Properties of Cement Systems. *Cement and Concrete*

Research, Vol. 38, No. 2, 2008, pp. 175–195. doi: 10.1016/j.cemconres.2007.09.006.
33. Hanehara, S., and K. Yamada. Interaction between Cement and Chemical Admixture from the Point of Cement Hydration, Adsorption Behavior of Admixture, and Paste Rheology. *Cement and Concrete Research*, Vol. 29, No. 8, 1999, pp. 1159–1165. doi: 10.1016/S0008-8846(99)00004-6.
34. Nagi, M. A., P. A. Okamoto, R. L. Kozikowski, and K. Hover. *Evaluating Air- Entraining Admixtures for Highway Concrete*. NCHRP Report 578. National Cooperative Highway Research Program, Transportation Research Board of the National Academies, Washington, D.C., 2007.
35. Ansari, F., Z. Zhang, A. Maher, and P. Szary. *Effect of Synthetic Air Entraining Agents on Compressive Strength of Portland Cement Concrete Mechanism of Interaction and Remediation Strategy*. Final Report. Publication FHWA-NJ-2002-025. New Jersey Department of Transportation, 2002.
36. Wang, H., C. Qi, K. Parks, and J. M. Donovan. Complex Admixture Combinations-An Investigation of Abnormal Effects on Cement Hydration. *Concrete International*, January 2009, pp. 37–42.
37. Bedard, C., and P. N. Mailvaganam. The Use of Chemical Admixtures in Concrete. Part II: Admixture-Admixture Compatibility and Practical Problems. *J. Perform. Constr. Facil.*, Vol. 20, No. 1, 2006, pp. 2–5. doi: 10.1061/(ASCE)0887-3828(2006)20:1(2).
38. Hewlett, P. C. The Role of Admixtures in Concrete. *International Journal of Materials in Engineering Appilcations*, Vol. 1, No. 6, 1979, pp. 335–342. doi: 10.1016/0141-5530(79)90013-X.
39. Kozikowski, R. L., D. B. Vollmer, P. C. Taylor, and S. H. Gebler. *Factors Affecting the Origin of Air Void Clustering*. R&D Serial No. 2789. Portland Cement Association, Skokie, Illinois, 2005.
40. Masood, I., and S. K. Agarwal. Effect of Various Super Plasticizers on the Rheological Properties of Cement and Mortar. *Cement and Concrete Research*, Vol. 24, No. 2, 1994, pp. 291–302. doi: 10.1016/0008-8846(94)90055-8.
41. Uchikawa, H., D. Sawaki, and S. Hanehara. Influence of Kind and Added Timing Organic Admixture Type and Addition Time on Composistion, Structure and Property of Fresh Cement Paste. *Cement and Concrete Research*, Vol. 25, No. 2, 1995, pp. 353–364. doi: 10.1016/0008-8846(95)00021-6.
42. Chiocchio, G., and A. E. Paolini. Optimum Time for Adding Superplasticizers to Portland Cement Pastes. *Cement and Concrete Research*, Vol. 15, No. 5, 1985, pp. 901–908. doi: 10.1016/0008-8846(85)90157-7.
43. Dodson, V. H. *Concrete Admixtures*. Van Nostrand Reinhold, New York, 1990.
44. Wang, H., E. Dunstan, and H. Chen. False Set and Flash Set-Can ASTM C 359 Be Used to Diagnose the Causes? *Cement, Concrete and Aggregates*, Vol. 24, 2002.
45. Kantro, D. L. Influence of Water-Reducing Admixtures on the Properties of Cement Paste-A Miniature Slump Test. *PCA R & D Bulletin*, RD079.01T, Portland Cement Association, Skokie, Illinois, 1980, pp. 95–102.
46. Nkinambanzi, P. C., and B. Fournier. Evaluation of the Potential Use of the Superplasticizer Alphalith FT30LV with Canadian Cements. *Materials Technology Laboratory*, Vol. 44, 2003.
47. Lashley, L. The Compatibility and Performance of Cementitious Materials and Chemical Admixtures. Portland Cement Association Thesis, Master of Applied Science, SN 3106. Department of Civil Engineering, University of Toronto, 2009.
48. Helmuth, R., L. M. Hills, D. A. Whiting, and S. Bhattacharja. *Abnormal Concrete Performance in the Presence of Admixtures*. Portland Cement Association, Skokie, Illinois, 2006.
49. Park, C. K., M. H. Noh, and T. H. Park. Rheological Properties of Cementitious Materials Containing Mineral Admixtures. *Cement and Concrete Research*, Vol. 35, No. 5, 2005, pp. 842–849. doi: 10.1016/j.cemconres.2004.11.002.
50. Poole, T. *Revision of Test Methods and Specifications for Controlling Heat of Hydration in Hydraulic Cement*. Portland Cement Association, Skokie, Illinois, 2007.
51. Flick, G. J. *Testing Guide for Implementing Concrete Paving Quality Control Procedures*. National Concrete Pavemant Technology Center, Iowa State University, Ames, Iowa, 2008.
52. Taylor, P. C., L. A. Graf, J. Z. Zemaitis, V. C. Johansen, R. L. Kozikowski, C. F. Ferraris. *Identifying Incompatible Combinations of Concrete Materials: Volume II-Test Protocol*. FHWA HRT-06-080. Federal Highway Administration, Turner-Fairbank Highway Research Center, MacLean, Virginia, 2006.
53. Schindler, A. K., and K. J. Folliard. Influence of Supplementary Cementing Materials on the Heat of Hydration of Concrete. Presented at Advances in Cement and Concrete IX Conference, Copper Mountain, Colorado, August 10–14, 2003.
54. Bentz, D. P., M. A. Peltz, and J. Winpigler. Early-Age Properties of Cement-Based Materials. II: Influence of Water-to-Cement Ratio. *Journal of Materials in Civil Engineering*, Vol. 21, No. 9, 2009, pp. 512–517. doi: 10.1061/(ASCE)0899-1561(2009)21:9(512).
55. Gutmann, P. F. Bubble Characteristics as They Pertain to Compressive Strength and Freeze-Thaw Durability. *ACI Materials Journal*, No. 85-M40, 1989.
56. Cross, W., E. Duke, J. Kellar, and D. Johnson. *Investigation of Low Compressive Strengths of Concrete Paving, Precast and Structural Concrete*. SD98-03-F. South Dakota Department of Transportation, 2000.
57. Walker, H. N., D. S. Lane, and P. E. Stutzman. *Petrographic Methods of Examining Hardened Concrete: A Petrographic Manual*. Publication FHWA-HRT-04-150. Federal Highway Administration, Washington, D.C., 2006.
58. Schlorholtz, S. *Determine Initial Cause for Current Premature Portland Cement Concrete Pavement Deterioration*. TR-406. Iowa Highway Research Board, Iowa Department of Transportation, 2000.
59. Magura, D. D. *Air Void Analyzer Evaluation*. Publication FHWA-SA-96-02, Federal Highway Administration, Washington, D.C., 1996.
60. Wojakowski, J. *Air in Portland Cement Concrete Pavements*. Kansas Department of Transportation, 2002.
61. Taylor, P. C. L. A. Graf, J. Z. Zemaitis, V. C. Johansen, R. L. Kozikowski, and C. F. Ferraris. *Protocol to Identify Incompatible Combinations of Concrete Materials*. Publication FHWA-HRT-06-082. Federal Highway Administration, Washington, D.C., 2006.
62. Lawler, J. S., J. D. Connolly, P. D. Krauss, S. L. Tracy, and B. E. Ankenman. *Guidelines for Concrete Mixtures Containing Supplementary Cementitious Materials to Enhance Durability of Bridge Decks*. NCHRP Report No. 566. Transportation Research Board, Washington, D.C., 2007.
63. Grove, J., G. Fick, T. Runow, and F. Bektas. *Material and Construction Optimization for Premature Pavement Distress in PCC Pavements: Final Report*. TPF-5(066). National Concrete Pavement Technology Center, Iowa State University, Ames, Iowa. 2008.