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Effects of high volumes of fly ash on cement paste

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EFFECTS OF HIGH VOLUMES OF FLY ASH ON CEMENT PASTE

by

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Approved by

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ABSTRACT

The study of high-volume fly ash (HVFA) concrete mixtures has become popular due to the significant environmental and economic benefits which the material may provide. By including fly ash at 50 percent or greater replacement levels, substantial benefits could be obtained. However, the inclusion of fly ash can have negative effects, including incompatibilities between constituents of a mixture. As the fly ash replacement level increases, the degree and likelihood of these problems increases.

In this study, paste mixtures were made, as part of a larger HVFA concrete study, in order to determine the degree to which varying levels of fly ash would affect the paste mixtures and to determine potential methods of mitigating the negative effects of high volumes of fly ash on concrete mixtures. Five Type I or I/II portland cements were tested in combination with five Class C fly ashes at 0, 25, 50, and 70 percent replacement levels. The effects of gypsum, calcium hydroxide, and rapid set cement additions were evaluated at fly ash replacement levels of 50 and 70 percent, and the effects of a Type A/F water-reducing admixture were examined for all fly ash replacement levels. The paste properties that were evaluated included compressive strength, heat of hydration, consistency, and setting time.

Analysis of the results showed general trends for increasing fly ash replacement levels, such as slower strength gain, decreased heat of hydration, delayed setting times, and increased fluidity of the paste at very early ages. However, there were also many inconsistencies in the results, which were attributable to sulfate imbalances and increased aluminate hydration at early ages. It was found that, in many cases, these sulfate imbalances were lessened by the addition of gypsum. The additions of calcium hydroxide and rapid set cement also showed improvements, such as increased rates of strength gain and accelerated setting times.

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TABLE OF CONTENTS

Page

ABSTRACT iii

ACKNOWLEDGMENTS iv

LIST OF ILLUSTRATIONS ix

LIST OF TABLES xii

SECTION

- 1. INTRODUCTION 1
  - 1.1 STATEMENT OF PROBLEM 1
  - 1.2 OBJECTIVES 2
  - 1.3 SCOPE OF INVESTIGATION 2
- 2. REVIEW OF LITERATURE 4
  - 2.1 PORTLAND CEMENT HYDRATION 4
  - 2.2 FLY ASH PRODUCTION AND CLASSIFICATION 6
  - 2.3 EFFECTS OF FLY ASH ON HYDRATION 7
  - 2.4 INCOMPATIBILITIES IN HVFA MIXTURES 10
  - 2.5 POWDER ADDITIONS FOR HVFA MIXTURES 12
  - 2.6 METHODS OF EVALUATING HEAT EVOLUTION 16
    - 2.6.1. Isothermal Calorimetry 16
    - 2.6.2. Semi-Adiabatic Calorimetry 17
    - 2.6.3. Adiabatic Calorimetry 18
    - 2.6.4. Solution Calorimetry 19
  - 2.7 DEVELOPMENT OF THE MINIATURE SLUMP TEST 19

2.8 EFFECTS OF HIGH VOLUMES OF FLY ASH ON PASTE PROPERTIES 20

2.8.1. Compressive Strength 20

2.8.2. Heat Evolution 21

2.8.3. Consistency 22

2.8.4. Setting Time 22

3. LABORATORY INVESTIGATION 23

3.1 EXPERIMENTAL DESIGN 23

3.1.1. Screening Study 23

3.1.2. Main Study 24

3.2 EQUIPMENT 27

3.2.1. Mixing Equipment 27

3.2.2. Cube Molding Equipment 29

3.2.3. Curing Equipment 31

3.2.4. Compressive Strength Testing Equipment 31

3.2.5. Semi-Adiabatic Calorimetry Equipment 32

3.2.6. Miniature Slump Equipment 33

3.2.7. Vicat Setting Time and Normal Consistency Equipment 34

3.3 MATERIALS 37

3.3.1. Portland Cements 37

3.3.2. Fly Ashes 38

3.3.3. Powder Additions 38

3.3.4. Water Reducer 40

3.3.5. Water 40

3.4 TEST PROCEDURES 41
3.4.1. Pre-blending Dry Constituents 41
3.4.2. Determination of Rotational Speeds for Handheld Mixer 41
3.4.3. Combined Mixing Procedure 41
3.4.4. Cube Compressive Strength 42
3.4.5. Semi-adiabatic Calorimetry 44
3.4.6. Miniature Slump 49
3.4.7. Normal Consistency and Vicat Time of Setting 50
4. RESULTS AND DISCUSSION 52
4.1 SCREENING STUDY RESULTS 52
4.1.1. Cube Compressive Strength 52
4.1.2. Semi-adiabatic Calorimetry 74
4.1.3. Miniature Slump 88
4.1.4. Vicat Setting Time 94
4.2 MAIN STUDY RESULTS 99
4.2.1. Outlier Analysis 99
4.2.2. Effects of Water Reducer Addition 110
4.2.3. Effects of Gypsum Addition 118
4.2.4. Effects of Calcium Hydroxide-Gypsum Addition 126
4.2.5. Effects of Rapid Set Cement-Gypsum Addition 133
4.3 CORRELATIONS 140
5. SUMMARY AND CONCLUSIONS 143
5.1 SUMMARY 143

5.2 CONCLUSIONS... 144
5.3 FUTURE RESEARCH 146

APPENDICES

A. TESTING PROCEDURES 148
B. OUTLIER ANALYSIS FOR CALORIMETRY DATA 174
C. SCREENING STUDY THERMAL CURVES 182
D. MAIN STUDY THERMAL CURVES 196
E. SCREENING STUDY MINIATURE SLUMP PLOTS 207
F. MAIN STUDY MINIATURE SLUMP PLOTS 221
REFERENCES 232
VITA 235

LIST OF ILLUSTRATIONS

Page

Figure 3.1. Black and Decker Hand Mixer 27

Figure 3.2. Equipment used in the Combined Mixing Procedure 29

Figure 3.3. Cube Molding Equipment 30

Figure 3.4. Tinius-Olsen Load Frame and Computer 32

Figure 3.5. F-Cal 4000, Computer, and Cylinder Molds 33

Figure 3.6. Miniature Slump Cones and Equipment 34

Figure 3.7. Vicat Apparatus with Ring and Glass Plate 35

Figure 3.8. Hobart Mixer and Bowl Scraper 36

Figure 3.9. Examples of Signal and Noise Quantities 46

Figure 3.10. Representation of the ΔT Quantity 47

Figure 3.11. Example of Setting Time Prediction by the Fractions Method 48

Figure 4.1. One-day Compressive Strengths for Cement 1 Combinations 56

Figure 4.2. 28-day Compressive Strengths for Cement 1 Combinations 57

Figure 4.3. One-day Compressive Strengths for Cement 2 Combinations 60

Figure 4.4. 28-day Compressive Strengths for Cement 2 Combinations 61

Figure 4.5. One-day Compressive Strengths for Cement 3 Combinations 64

Figure 4.6. 28-day Compressive Strengths for Cement 3 Combinations 65

Figure 4.7. One-day Compressive Strengths for Cement 4 Combinations 68

Figure 4.8. 28-day Compressive Strengths for Cement 4 Combinations 69

Figure 4.9. One-day Compressive Strengths for Cement 5 Combinations 72

Figure 4.10. 28-day Compressive Strengths for Cement 5 Combinations 73

Figure 4.11. Typical Series of Thermal Curves Showing Delayed Silicate Hydration and Decreased Main Hydration Peaks 76

Figure 4.12. Series of Thermal Curves Showing Accelerated Hydration at 70% Fly Ash Replacement 77

Figure 4.13. Example of Type A Thermal Curve Shape 82

Figure 4.14. Example of Type B Thermal Curve Shape 82

Figure 4.15. Example of Type C Thermal Curve Shape 83

Figure 4.16. Example of Type D Thermal Curve Shape 83

Figure 4.17. Example of Type E Thermal Curve Shape 84

Figure 4.18. Example of Type F Thermal Curve Shape 84

Figure 4.19. Example of Type G Thermal Curve Shape 85

Figure 4.20. Comparison of Curve Types 89

Figure 4.21. Example of Miniature Slump Results for Increasing Fly Ash Contents 90

Figure 4.22. Effect of Water Reducer on One-Day Cube Strengths for Combination 4-1 111

Figure 4.23. Effect of Water Reducer on One-Day Cube Strengths for Combination 1-3 111

Figure 4.24. Effect of Water Reducer on 56-Day Cube Strengths for Combination 4-1 112

Figure 4.25. Effect of Water Reducer on 56-Day Cube Strengths for Combination 1-3 112

Figure 4.26. Thermal Curves Showing the Retarding Effect of Water Reducer 114

Figure 4.27. Effect of Gypsum Addition on Strength Gain for Combination 4-1 120

Figure 4.28. Effect of Gypsum Addition on Strength Gain for Combination 1-3 121

Figure 4.29. Series of Thermal Curves Showing the Effect of Gypsum Addition 122

Figure 4.30. Effect of Lime on Combination 4-1 Mixtures with Four Percent Gypsum 127

Figure 4.31. Effect of Lime on Combination 1-3 Mixtures with Four Percent Gypsum 127

Figure 4.32. Series of Thermal Curves Showing the Effect of Calcium Hydroxide Addition 129

Figure 4.33. Effect of RSC on Combination 4-1 Mixtures with Four Percent Gypsum 134

Figure 4.34. Effect of RSC on Combination 1-3 Mixtures with Four Percent Gypsum 134

Figure 4.35. Series of Thermal Curves Showing the Effect of RSC Addition 136

Figure 4.36. Correlation of Percentage Method Final Set Times for All Mixtures 141

Figure 4.37. Correlation of Percentage Method Final Set Times for Type A Mixtures 142

LIST OF TABLES

Page

Table 3.1. Main Study Combinations 26

Table 3.2. Hand Mixer Rotational Speeds 28

Table 3.3. Cement Oxide Analyses (Screening Study) 37

Table 3.4. Cement Oxide Analyses (Main Effects Study) 37

Table 3.5. Fly Ash Oxide Analyses 38

Table 3.6. Oxide Analysis of RSC 39

Table 3.7. CTS Rapid Set Cement Compressive Strength Results 40

Table 3.8. Combined Mixing Procedure Sequence 43

Table 4.1. 1-Day Cube Strength Outlier Analysis for Cement 1 Combinations 54

Table 4.2. 28-Day Cube Strength Outlier Analysis for Cement 1 Combinations 55

Table 4.3. 1-Day Cube Strength Outlier Analysis for Cement 2 Combinations 58

Table 4.4. 28-Day Cube Strength Outlier Analysis for Cement 2 Combinations 59

Table 4.5. 1-Day Cube Strength Outlier Analysis for Cement 3 Combinations 62

Table 4.6. 28-Day Cube Strength Outlier Analysis for Cement 3 Combinations 63

Table 4.7. 1-Day Cube Strength Outlier Analysis for Cement 4 Combinations 66

Table 4.8. 28-Day Cube Strength Outlier Analysis for Cement 4 Combinations 67

Table 4.9. 1-Day Cube Strength Outlier Analysis for Cement 5 Combinations 70

Table 4.10. 28-Day Cube Strength Outlier Analysis for Cement 5 Combinations 71

Table 4.11. Thermal Curve Data for Cement 1 Combinations 78

Table 4.12. Thermal Curve Data for Cement 2 Combinations 78

Table 4.13. Thermal Curve Data for Cement 3 Combinations 79

Table 4.14. Thermal Curve Data for Cement 4 Combinations 79

Table 4.15. Thermal Curve Data for Cement 5 Combinations 80

Table 4.16. Miniature Slump Results for Cement 1 91

Table 4.17. Miniature Slump Results for Cement 2 91

Table 4.18. Miniature Slump Results for Cement 3 92

Table 4.19. Miniature Slump Results for Cement 4 92

Table 4.20. Miniature Slump Results for Cement 5 93

Table 4.21. Vicat Setting Time Results for Cement 1 95

Table 4.22. Vicat Setting Time Results for Cement 2 95

Table 4.23. Vicat Setting Time Results for Cement 3 96

Table 4.24. Vicat Setting Time Results for Cement 4 96

Table 4.25. Vicat Setting Time Results for Cement 5 97

Table 4.26. Outlier Analysis of 1-Day Cube Strengths for Combination 4-1 Mixtures 100

Table 4.27. Outlier Analysis of 3-Day Cube Strengths for Combination 4-1 Mixtures 101

Table 4.28. Outlier Analysis of 7-Day Cube Strengths for Combination 4-1 Mixtures 102

Table 4.29. Outlier Analysis of 28-Day Cube Strengths for Combination 4-1 Mixtures 103

Table 4.30. Outlier Analysis of 56-Day Cube Strengths for Combination 4-1 Mixtures 104

Table 4.31. Outlier Analysis of 1-Day Cube Strengths for Combination 1-3 Mixtures 105

Table 4.32. Outlier Analysis of 3-Day Cube Strengths for Combination 1-3 Mixtures 106

Table 4.33. Outlier Analysis of 7-Day Cube Strengths for Combination 1-3 Mixtures 107

Table 4.34. Outlier Analysis of 28-Day Cube Strengths for Combination 1-3 Mixtures 108

Table 4.35. Outlier Analysis of 56-Day Cube Strengths for Combination 1-3 Mixtures 109

Table 4.36. Calorimetry Results for Mixtures with Increasing Water Reducer Dosages 115

Table 4.37. Miniature Slump Results for Mixtures with Increasing Water Reducer Dosages 117

Table 4.38. Vicat Results for Mixtures with Increasing Water Reducer Dosages 119

Table 4.39. Calorimetry Results for Mixtures with Increasing Gypsum Additions 123

Table 4.40. Miniature Slump Results for Mixtures with Increasing Gypsum Additions 125

Table 4.41. Vicat Results for Mixtures with Increasing Gypsum Additions 126

Table 4.42. Calorimetry Results for Mixtures with Increasing Calcium Hydroxide Additions and Four Percent Gypsum 130

Table 4.43. Miniature Slump Results for Mixtures with Increasing Lime Addition and Four Percent Gypsum 131

Table 4.44. Vicat Results for Mixtures with Increasing Lime Additions 132

Table 4.45. Calorimetry Results for Mixtures with Increasing RSC Additions and Four Percent Gypsum 137

Table 4.46. Miniature Slump Results for Mixtures with Increasing RSC Addition and Four Percent Gypsum 138

Table 4.47. Vicat Results for Mixtures with Increasing RSC Additions 139

1. INTRODUCTION

The study of high-volume fly ash concrete mixtures has become popular due to the potential of the material to provide significant environmental and economic benefits. By increasing the amount of fly ash introduced into concrete mixtures, less cement would be produced, which would decrease CO_2 emissions, and less fly ash would be placed in landfills. The use of less cement, along with the sustainability benefits of HVFA concrete, would also decrease the amount of raw materials which would need to be extracted to produce portland cement concrete. Immediate economic benefits occur because portland cement is replaced with a less expensive by-product material. For properly designed HVFA mixtures, increased durability and long-term strengths would provide long-term economic benefits, because infrastructure components would have to be replaced less often. By being able to increase the incorporation of fly ash into concrete at 50 percent or greater replacements, substantial benefits could be obtained.

1.1 STATEMENT OF PROBLEM

Incorporating fly ash in a concrete mixture provides benefits to both fresh and hardened properties of the concrete. Improvements in fresh properties include increased workability, increased pumpability, and reduced bleeding. Hardened concrete benefits could include greater long-term strength, decreased early-age temperature rise, and increased durability. The use of fly ash can also have negative effects on concrete mixtures. These commonly include decreased strengths at early ages, delayed setting times, loss of certain forms of durability, and lower later strengths. Also, incompatibilities between constituents of the mixture can lead to detrimental effects on the properties of the concrete.

As the amount of fly ash used in a mixture increases, the degree and likelihood of the above-mentioned problems increases. Therefore, in high volume fly ash concrete, it is necessary to assess the degree to which these problems may occur and determine methods of mitigating these problems in order for HVFA concrete to be a viable construction material.

1.2 OBJECTIVES

The objectives of this study were to determine the degree to which paste mixtures are affected by varying levels of Class C fly ash and determine strategies to mitigate the negative effects of increasing the proportion of fly ash in a paste mixture. The properties that were evaluated included compressive strength, heat of hydration, consistency, and setting time.

As part of a larger HVFA concrete project, the paste testing was done to gain knowledge of the cementitious materials without the effect of coarse and fine aggregates. Also, the nature of paste testing allowed a greater volume of cementitious combinations to be evaluated in a given period of time than would have been possible with concrete testing.

1.3 SCOPE OF INVESTIGATION

To evaluate a variety of cement and fly ash combinations, five Type I portland cements and five Class C fly ashes were chosen to be representative of those commonly available in the State of Missouri. The levels of fly ash replacement were 0, 25, 50, and 70 percent by mass. The use of gypsum, calcium hydroxide, and rapid set cement were each evaluated, at two dosage levels, as powder additions to improve properties of the HVFA combinations. All mixtures were evaluated at a constant water-cementitious materials ratio (w/cm) of 0.40. Also, a water reducing admixture was added to some of the mixtures to evaluate its influence on properties of the paste.

The paste mixtures were tested for compressive strength, heat of hydration, consistency, and setting time. Compressive strength testing was performed using two-inch cubes at testing ages of 1, 3, 7, 28, and 56 days. The paste setting time was evaluated for each combination using the Vicat time of set method, in accordance with ASTM C 191. Heat evolution of the paste mixtures was evaluated using a semi-adiabatic field calorimeter, which collected temperature data on three replicates for each mixture simultaneously over a 48-hour period. The consistency of the paste mixtures was evaluated at 2, 5, 15, 30, and 45 minutes after initial mixing using miniature slump cones.

2. REVIEW OF LITERATURE

2.1 PORTLAND CEMENT HYDRATION

Four primary compounds make up approximately 90 percent of portland cement by mass. These compounds are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). C_3S is also known as alite and C_2S is also known as belite. The remaining portion of the cement consists of a calcium sulfate source and grinding aids, both of which are added during the grinding process. The calcium sulfate source, which constitutes four to six percent of the cement, may be in the form of anhydrous calcium sulfate, calcium sulfate dihydrate, calcium sulfate hemihydrate, or a combination of these forms. Calcium sulfate dihydrate, also known as gypsum, is the most common source of sulfate in portland cement. Hemihydrate is formed during the finish grinding of the cement (Kosmatka, Kerkhoff, & Panarese, 2003).

The hydration of cement begins immediately with the addition of water to cement. It is thought that cement hydration takes place by two mechanisms, through-solution hydration and topochemical hydration, also known as solid-state hydration. Through-solution hydration is thought to occur during early ages. With this mechanism, the compounds go in to solution and form hydrates. The solution then becomes supersaturated and the hydrates precipitate from the solution. The other hydration mechanism, solid-state hydration, is thought to occur at later ages. With this mechanism, the compounds do not go into solution and the hydration reactions occur at the surface of the compounds (Mehta & Monteiro, 1993).

The hydration reactions of the aluminates, C_3A and C_4AF, are immediate upon contact with water and are both similar. Their rapid reaction is slowed by the inclusion of a calcium sulfate source. The calcium sulfates go into solution quickly and decrease the solubility of the aluminates, which retards their hydration. During early hydration, the sulfate-aluminate ratio in solution is high and ettringite, or high-sulfate, is formed. The formation of ettringite is primarily responsible for early stiffening, setting, and strength gain. At later ages, when the sulfate supply is depleted, the aluminate reactions are no longer suppressed and they begin reacting more rapidly. This causes the already formed ettringite to become unstable and convert to monosulfate, also known as low-sulfate. It should be noted that the sulfate-aluminate balance highly influences setting behavior. In an under-sulfated system, the rapid aluminate reactions will result in flash set, which involves immediate setting, large amounts of released heat, and low ultimate strengths. In an extremely over-sulfated system, the high concentration of calcium and sulfate in solution will result in the quick formation of gypsum. This does not cause large amounts of heat to be released and can be undone by remixing. However, over-sulfating can lead to other problems, such as lower strengths and higher amounts of shrinkage (Mehta & Monteiro, 1993).

The hydration of the silicates, C_3S and C_2S, results in the formation of calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). C-S-H has a variable chemical composition and is primarily responsible for the strength of the paste. CH has a definite chemical composition and, when compared to C-S-H, has a much lower contribution to strength. Also, high amounts of CH in a system can lead to durability issues because it has a much higher solubility in acidic solutions, when compared to C-S-H, and is a necessary component of the delayed, expansive ettringite formation known as sulfate attack. Therefore, cement pastes with greater amounts of C-S-H and lower amounts of CH will be stronger and more durable. When compared to C_2S, the hydration of C_3S occurs more rapidly, produces less C-S-H, and produces more CH. It contributes to setting and early strength gain. C_2S, which reacts slowly and produces more C-S-H, contributes to the ultimate strength of the paste. It should also be noted that the presence of sulfate in solution increases the solubility of the silicate compounds, which increases the hydration rates of the silicates (Mehta & Monteiro, 1993).

2.2 FLY ASH PRODUCTION AND CLASSIFICATION

Fly ash is a by-product of power production from coal-fired power plants. As the finely ground coal passes through the furnace, most of the volatile matter and carbon are burnt off. The mineral impurities remain in the flue gas and fuse together. As the flue gas leaves the furnace, the ash is cooled rapidly and either agglomerates to form bottom ash or remains in the gas stream as fly ash. Before leaving the plant, fly ash is removed from the gasses by electrostatic precipitators or bag filters. The material consists of spherical, glassy particles that generally require no processing before use in concrete applications (Malhotra & Mehta, 1996).

Fly ashes are generally categorized as high-calcium or low-calcium, which corresponds to the ASTM classifications of Class C and Class F, respectively. The four principle constituents of fly ash are silica (SiO_2), alumina (Al_2O_3), iron (Fe_2O_3), and calcium (CaO). The proportions of these constituents vary widely and are dependent on the source of coal used in production. Generally, Class C fly ashes are produced from sub-bituminous and lignite coal sources, while Class F fly ashes are produced from bituminous and anthracite coal sources. Carbon may also be present in the fly ash due to incomplete combustion of the coal. Typical Class C fly ashes have less than 1% carbon, while some Class F fly ashes may contain up to 20%, based on Loss on Ignition (LOI) tests (ACI Committee 232, 2003).

To be classified as ASTM Class C, the sum of the SiO_2, Al_2O_3, and Fe_2O_3 constituents of the fly ash must be greater than 50%. This is lower than the requirements for Class F, because most Class C fly ashes have CaO contents exceeding 20% (ACI Committee 232, 2003). In general, these fly ashes possess cementitious as well as pozzolanic properties.

ASTM requirements state that the sum of the SiO_2, Al_2O_3, and Fe_2O_3 constituents of a fly ash must be greater than 70% to be classified as Class F (ACI Committee 232, 2003). This allows for much lower CaO concentrations than in Class C fly ash. Because of this, Class F fly ashes typically have very little or no cementitious properties of their own and are primarily pozzolanic.

2.3 EFFECTS OF FLY ASH ON HYDRATION

As mentioned previously, the hydration of the silicates in portland cement produces C-S-H and CH. With the addition of a pozzolan such as fly ash, silica is added to the system which reacts with CH in the presence of water to form C-S-H. This is known as the pozzolanic reaction. The pozzolanic reaction is comparatively slow and results in slower rates of heat evolution and strength gain. However, the consumption of

CH and filling of pores in the paste results in higher ultimate strengths and improved durability (Mindess, et al., 2003; Mehta & Monteiro, 1993).

Wang, et al. (2006) studied the effect of fly ash and chemical admixtures on the heat release of paste mixtures. Type I and Type II cements were used in combination with Class F and Class C fly ashes at 20 percent replacement. Type A, water-reducing, and Type B, retarding admixtures were also evaluated. It was found that the Class F fly ash had little effect on the timing of the main hydration peak, but did significantly reduce the total heat released in the first 24 hours. This reduction in the rate of heat release was attributed to the dilution of the more reactive cement with less reactive fly ash. The sulfate depletion peak, usually observed as a shoulder that occurs after the peak on the main hydration curve, was also not significantly affected, which indicates that the rate of sulfate consumption was not affected by the fly ash. The use of Class C fly ash resulted in a severely delayed main hydration curve. As with the Class F fly ash, it also reduced the total heat released and did not appear to affect the rate of sulfate consumption. However, since the main hydration curve was delayed, the shoulders, indicating sulfate depletion, occur before the peak of the main curve. The addition of the chemical admixtures resulted in significantly delayed main hydration curves for all of the mixtures. The effect was more pronounced for the Class C fly ash mixtures, which also showed a greater reduction in the total heat released. For the Type II cement in combination with either fly ash, the higher admixture dosage caused hydration to almost completely stop.

Jiang, et al.(1999) studied the hydration of paste mixtures made with portland cement and Class F fly ash at 40, 55, and 70 percent replacement levels. They also varied the w/cm and included water-reducing and activating admixtures in some of the pastes. It was found that the fly ash mixtures had lower early strengths, but showed greater rates of strength gain at later ages, when compared to the control mixture. The CH content of the mixtures at 28 days generally decreased with increasing fly ash contents, though it was found that the 70 percent fly ash mixture had a higher CH content than both the 40 and 55 percent fly ash mixtures. From pore structure analysis, it was determined that the total porosity at 28 days increased with increasing fly ash contents. However, the pore size distributions showed that the pore sizes were decreased with the inclusion of fly ash. Scanning electron microscopy of the paste microstructure at early and later ages showed that increasing fly ash contents led to a less dense microstructure and also revealed that, even at 90 days, unreacted fly ash particles remained in the paste structure. It was also found in this study that the addition of an activator admixture would increase the activity of the fly ash.

In a study by Hubert, et al. (2001), the hydration products of high volume fly ash binders were investigated. Paste mixtures were prepared with portland cement and one of two fly ashes. Mixtures were made with 0, 60, 70, and 85 percent by weight of each fly ash. Hydration was stopped after 3, 7, 28, and 90 days to study the hydration products and pore solution of the hardened paste. It was found that increasing amounts of fly ash decreased the CH content of the paste. A similar effect was seen with the ettringite content except that, for one of the fly ashes, the ettringite content was still high compared to the control, which means it was a hydration product of the fly ash. The other fly ash had a lower sulfate content and resulted in lower ettringite levels. By observing the amount of active silica in the pastes, it was determined that the inclusion of fly ash led to increased C-S-H contents in the paste. The greatest improvement in C-S-H formation for

Fly Ash 1 was seen at 85 percent replacement, while the greatest improvement for Fly Ash 2 was found at 60 percent replacement. However, Fly Ash 2 had a lower silica content at 85 percent replacement than Fly Ash 1. This was attributed to the higher reactivity of Fly Ash 2, which would have led to quicker consumption of the CH and an earlier end to the pozzolanic reaction. From this it was observed that the reactivity of the fly ash and the amount of available CH should be balanced for optimum C-S-H formation.

2.4 INCOMPATIBILITIES IN HVFA MIXTURES

The composition of mineral admixtures varies considerably, even between those that fall under the same classification, such as Class C fly ash. This leads to complexity in cementitious systems, as the use of mineral admixtures in concrete mixtures is commonplace. Due to this complexity, problems such as slump loss, delayed setting, and slow rates of strength gain, are more likely to occur as a result of incompatibilities between the materials. The most common cause of incompatibility is related to the sulfate concentration in a system. If there is not a sufficient amount of sulfate, the aluminates (C_3A and C_4AF) will react rapidly and consume a large portion of the available calcium in the system. This will cause the hydration of the silicates (C_3S and C_2S) to slow down and possibly stop completely (Roberts & Taylor, 2007).

Using isothermal calorimetry, Lerch (1946) illustrated the effect of insufficient sulfate levels on portland cement. In the study, cements with differing C_3A and alkali contents were tested with varying amounts of gypsum added. It was found that as the sulfate levels decreased, the initial (aluminate) peak occurred more rapidly. This occurred because sulfate was not available to decrease the solubility of the aluminates or form a protective film of hydration products on the surfaces of the particles. The second (silicate) peak was delayed and suppressed with decreasing sulfate levels. This was attributed to a depletion of available calcium, by the aluminates, for hydration of the silicates and a lack of sulfate, which acts to increase the solubility of the silicates. Also, some mixtures showed an additional peak, which was caused by renewed aluminate hydration. It was found that this third peak was delayed and suppressed by increasing gypsum additions.

Roberts and Taylor (2007) discussed incompatibilities related to changing sulfate requirements with the additions of supplementary cement materials, admixtures, or both. It was pointed out that while increasing water reducer dosages typically result in delayed silicate hydration and slightly delayed sulfate depletion, extremely high dosages can increase initial aluminate hydration, severely delay silicate hydration, and cause sulfate depletion to occur at earlier times. The effects of Class C fly ash were attributed to the increased level of calcium aluminates in the system, which can cause the system to become under-sulfated. This leads to increased aluminate hydration, which consumes more calcium during the early stages of hydration. Due to a lack of available calcium, silicate hydration can become depressed and delayed or may stop completely. Also, the lack of sulfate decreases the solubility of the silicates which will result in slower silicate hydration.

Cost and Knight (2007) also discussed the use of Class C fly ash as a common cause of abnormal behavior in concrete, due to increased aluminate levels, along with high temperatures, sulfate levels, chemical admixtures, and hot-weather concreting practices. It was noted that the potential for erratic behavior may increase in hot-weather concrete operations if the dosage of Class C fly ash is increased to utilize the retarding effect of the material. As part of the study, the heat generation of several paste mixtures was evaluated, using semi-adiabatic calorimetry, to detect incompatibilities. The paste was made with a Type II cement at varying sulfate levels and a Class C fly ash at varying replacement levels. The results showed that the only combination to generate a typical silicate peak was the 3.3% sulfate cement with 10% fly ash. The combinations of this cement with 25% and 35% fly ash both showed extremely depressed silicate hydration peaks. The 3.7% sulfate cement with 25% fly ash showed improvement in the silicate peak, but at 35% fly ash only a small peak was developed. To investigate an additional increase in sulfate, the sulfate content of the cement was increased to 4.1% in combination with the 35% replacement level of Class C fly ash. This seemed to somewhat restore the silicate peak, but it was delayed significantly.

As can be seen, the use of Class C fly ash can cause significant problems in concrete when the proper sulfate balance has been compromised. High temperatures and the use of chemical admixtures, such as water reducers, can increase the magnitude of incompatibility related problems as these can affect the solubility and reaction rate of compounds in the system (Cost & Knight, 2007).

2.5 POWDER ADDITIONS FOR HVFA MIXTURES

Bentz (2010) noted that for HVFA mixtures to be commonly used in construction, it would be necessary to ensure improved and consistent early age performance from these mixtures. In his study, isothermal calorimetry was used to evaluate the effectiveness of various powder additions in correcting the severe retardation illustrated by many calorimetric studies of HVFA mixtures. A Type II/V portland cement in combination with a Class C fly ash and a Class F fly ash were evaluated at 50 percent replacements. The powder additions included aluminum trihydroxide, calcium hydroxide, cement kiln dust, condensed silica fume, limestone, and rapid-set cement. A polycarboxylate type high-range water reducer (HRWR) was also included in some of the paste mixtures.

To separate the retarding effects of dilution of the cement, sulfate imbalance, and HRWR from those of the fly ash alone, these were studied separately. Paste mixtures were made with the Type II/V cement at 0.3 and 0.6 water-cement ratios. It was found that while this increase in w/cm retarded the silicate peak by approximately one hour, it did not explain the almost four hour retardation seen in the 50 percent fly ash mixtures. To achieve a proper sulfate balance in the mixtures with 50 percent Class C fly ash, which is known to disturb the sulfate balance, mixtures with 50 percent Class C fly ash, varying gypsum additions, and no HRWR were tested. From the results, a gypsum addition of two percent was chosen for the remaining mixtures to be tested. It was noted that while the addition of gypsum eventually produced normal hydration characteristics, it did not resolve the severe retardation of the system. The effect of the HRWR was evaluated for both Class C and Class F fly ash mixtures. For the Class C mixtures, it was found that the retardation seen with the mixture containing both Class C fly ash and HRWR was more severe than that caused by either component when added individually to the mixture. For Class F fly ash, no retardation was observed with the addition of the fly ash alone, but the addition of the HRWR did cause retardation of the system (Bentz, 2010).

The effects of the powder additions were evaluated for the Class C fly ash mixtures with the two percent gypsum addition. A five percent addition of limestone powder had little effect on hydration. A 10 percent addition of aluminum trihydroxide did little to accelerate hydration but did increase the height of the peaks slightly. The 10 percent addition of cement kiln dust caused slight acceleration but more significantly increased the area under the curve, indicating increased early-age hydration. The five percent addition of condensed silica fume accelerated hydration by more than one hour, but this was not enough to restore the timing of the hydration to that seen with the 100 percent cement control mixture. The two other powder additions, calcium hydroxide and rapid set cement, showed more promise in mitigating retardation of the Class C fly ash systems (Bentz, 2010).

Calcium hydroxide was added because it has been established that if early aluminate hydration consumes enough of the available calcium, silicate hydration can be severely retarded or fail to occur completely. While the addition of gypsum does supply additional calcium it is likely that this is consumed by aluminate hydration, so the addition of calcium hydroxide was used to provide additional calcium to the system to aid in hydration of the silicates. The effect of the five percent, by mass of total cementitious materials, calcium hydroxide addition was evaluated for mixtures containing no fly ash, with and without the HRWR. For the mixture without HRWR, an acceleration of approximately 1.5 hours was observed, along with an increase in the area under the curve. For the mixture with HRWR, an acceleration of approximately 2.5 hours was observed. Next, the calcium hydroxide addition was evaluated for the 50 percent fly ash mixtures with their required HRWR dosages. For the Class C fly ash, an acceleration of approximately 5.5 hours was observed, which almost restored the timing of the hydration curve to that of the 100 percent cement control mixture. For the Class F fly ash, an acceleration of approximately 5 hours was observed. These accelerations were verified by similar accelerations in setting times, which were tested by needle penetration. It was noted, however, that the calcium hydroxide additions resulted in significantly lower cube compressive strengths at 28 days for the Class F fly ash mixtures (Bentz, 2010).

Because it was thought that rapid set cement may not be significantly affected by the retarding effect of the fly ash, it was added in an effort to improve the early hydration reactions and strength development of the system. Accelerations were observed for 10 and 20 percent additions of rapid set cement to the Class C fly ash mixtures. The 10 percent addition was chosen for further study to avoid the possibility of setting occurring too quickly with the 20 percent addition. To evaluate the effect of the fly ashes and HRWR on the rapid set cement alone, mixtures were made with the rapid set cement alone, rapid set cement with 50 percent fly ash replacements, and rapid set cement with 50 percent fly ash replacements and HRWR addition. It was found that the Class C fly and HRWR both contributed to retardation in the mixtures. However, the Class F fly ash accelerated the hydration. In all cases, the mixtures produced peaks which were within one hour of that of the 100 percent rapid set cement mixture. This indicates that the rapid set cement is not as sensitive to the effect of fly ash, when compared to the Type II/V cement. Following the study of the effect of fly ash and HRWR on the rapid set cement, the rapid set cement was evaluated at a 10 percent addition in the Type II/V cement mixtures with 50 percent fly replacements and required HRWR dosages. It was found that the rapid set cement provided two contributions to the system. These were the hydration of the rapid set cement alone and an acceleration of the portland cement-fly ash combination. For the Class C fly ash mixture, it was observed that the rapid set cement reacted immediately and provided an acceleration of approximately four hours. For the Class F fly ash mixture, it was observed that the rapid set cement reactions peaked after two hours, while the retardation of the system was increased by approximately eight hours. It was noted that mortar cube compressive strengths at 28 days for the Class C fly ash with a 10 percent addition of rapid set cement were 105 percent of those obtained without rapid set cement. For the Class F fly ash with a five percent addition of rapid set cement, cube compressive strengths at 28 days were 92 percent of those obtained without the rapid set cement, while the strengths with and without rapid set cement were similar at 56 days (Bentz, 2010).

2.6 METHODS OF EVALUATING HEAT EVOLUTION

There are many calorimetry methods and tools used to evaluate the heat evolution of cementitious mixtures. Some of the more widely used calorimeters include isothermal, semi-adiabatic, adiabatic, and solution calorimeters. The type of calorimetry device, mixing method, temperature of mixing environment, and sample size can all affect the results for a given mixture. Also, calorimetry results are reported in different ways, depending on the type of calorimeter being used. Therefore, it is necessary to have an understanding of the method behind varying calorimetry techniques when interpreting the results of heat of hydration experiments (Wang, 2006).

2.6.1. Isothermal Calorimetry. Isothermal calorimetry is used to measure the rate of heat production of a specimen kept at near isothermal conditions. This means that the temperature of the specimen is kept at a near constant temperature during hydration. A typical isothermal calorimeter employs two heat flow sensors, each with an attached specimen vial holder, and a heat sink with a thermostat. A prepared sample is placed in one of the vials and an inert specimen is placed in the other vial. Each vial is then placed into one of the vial holders. The heat released during hydration then passes to the heat flow sensors. The output of the inert specimen sensor is subtracted from the output of the test specimen sensor to result in the calorimeter output. The heat production is measured in watts (W) or joules per second (J/s). The results are usually reported in relation to the specimen mass as mW/g or J/s/g (ASTM C 1679, 2009). Isothermal calorimetry is used as a precise means of determining the heat produced solely by the cementitious materials at a given temperature. The results are generally used quantitatively.

2.6.2. Semi-Adiabatic Calorimetry. Semi-adiabatic calorimetry measures the temperature of a partially insulated specimen over time. There are a variety of semi-adiabatic systems available that differ in the size of sample used and the degree of insulation. The objective for a given system is to insulate the sample in a way that minimizes the influence of the ambient temperature, but also does not retain excessive heat that would accelerate the hydration of the specimen and distort the thermal profile. One common system uses plastic cylinder molds as the specimen container. The container is placed in a cylindrical receptacle in the device, which consists of an insulated box with a thermistor at the bottom, so that the thermal readings are taken from the bottom of the specimen. Another common method uses thermocouples or thermistors, which are inserted into the center of the specimen. With this method, the specimen container is anything that can hold a sufficient sample, such as plastic cylinders or even coffee cups (Cost, 2009).

Semi-adiabatic calorimetry is generally used as an economical alternative to isothermal calorimetry that can also be used in field conditions. The results are generally used for comparative and qualitative evaluation. However, some researchers have used more elaborate semi-adiabatic methods to achieve quantitative results, such as the adiabatic temperature rise or predicted setting times. Also, semi-adiabatic conditions may provide a better model for the thermal conditions inside a non-massive concrete structure, where gradual heat loss occurs.

2.6.3. Adiabatic Calorimetry. In adiabatic calorimetry, there is no heat loss or gain experienced by the specimen and the temperature of the specimen is measured during hydration. An economical adiabatic calorimeter used by Gibbon, Ballim, and Grieve consisted of a large tank with heater elements, a temperature probe, and stirrers. Inside of the tank, the specimen container was placed with a temperature probe inserted in the center of the specimen. The water temperature was controlled to be maintained at the same temperature as the hydrating sample. After completion of a test, the temperature readings were used to determine the specific heat and heat of hydration. The heat of hydration curve was then integrated to give a plot of total heat produced over time (Gibbon, et al., 1997).

This type of calorimetry is often used to determine the cumulative temperature rise of the concrete over time. It provides a model of the heat conditions in massive concrete structures, where there is little or no dissipation of heat.

2.6.4. Solution Calorimetry. Solution calorimetry is most often used to determine the adherence of a hydraulic cement to ASTM specifications on heat of hydration requirements at 7 and 28 days. However, it may also be used for research purposes to determine the heat of hydration at any age. The method involves dissolving two samples in a solution of nitric acid and hydrofluoric acid. One of the samples consists of the dry cementitious materials, while the other is a corresponding, partially hydrated paste specimen. The paste specimen is prepared ahead of time and stored in a sealed vile and placed in a water bath. At the time of testing, the paste specimen is removed from the vile and crushed with a mortar and pestle until all of the material passes through a No. 20 sieve. The heat of solution of the dissolving specimens is measured and the difference between the dry and partially hydrated specimens is taken as the heat of hydration (ASTM C 186, 2005).

2.7 DEVELOPMENT OF THE MINIATURE SLUMP TEST

Kantro (1980) developed the miniature slump test as a rapid means of determining the effects of admixtures on the rheological properties of cement pastes. In this study, a miniature slump cone was made of Lucite with a height of 2.25 inches, top diameter of 0.75 inches, and bottom diameter of 1.50 inches. These dimensions were chosen to be in proportion to the dimensions of the traditional slump cone used for ASTM C 143. After performing the test, the area of the paste pat was determined. The miniature slump test was used on paste mixtures with varying water-cement ratios and various admixtures. It was found that the method was suitable for comparative testing and evaluating loss in workability. Also, though it was determined that the miniature slump test was more sensitive, it was found that the overall effects observed with the paste testing correlated with the results of corresponding concrete testing.

Other researchers have utilized the miniature slump cone to evaluate the early stiffening behavior of pastes (Bhattacharja & Tang, 2001; Roberts & Taylor, 2007). In these studies, the paste was mixed following a standard procedure and the miniature slump test was performed at 2, 5, 15, and 30 minutes after the start of mixing. It was noted that later times, such as 45 minutes, may also be used. The use of an early stiffening index, which was calculated by dividing the pat area at 30 minutes by the pat area at 5 minutes, was discussed by Roberts and Taylor (2007). They stated that calculated indices less than 0.85 are generally considered to indicate rapid stiffening behavior. It was also noted by these researchers that because pastes are more sensitive to incompatibilities, paste systems that indicated potential problems may behave normally in concrete mixtures.

2.8 EFFECTS OF HIGH VOLUMES OF FLY ASH ON PASTE PROPERTIES

2.8.1. Compressive Strength. The rate of strength gain in mixtures containing high volumes of Class C fly ash will be slower due to the slow rate of the pozzolanic reaction. This results in lower early strengths. However, the pozzolanic reaction will also generally produce greater strengths at later ages. This is due to the replacement of the weak CH products with C-S-H, which is stronger, and the filling of pores with pozzolanic reaction products, which reduces the overall porosity of the paste and leads to an increase in strength (Detwiler, et al., 1996).

In a study by Jiang, et al. (1999), the strength development of paste mixtures with varying Class F fly ash contents, water-cementitious materials ratios, and admixture dosages were evaluated. Fly ash replacements of 40, 55, and 70 percent were used and the w/cm of these mixtures were between 0.24 and 0.38. It was found that early strengths decreased with increasing fly ash contents. Also, the fly ash mixtures showed greater increases in strength gain at later ages, though their strengths at 90 days were still less than that obtained by the 100 percent cement control mixture.

Bentz, et al. (2010) evaluated the strength gain characteristics of mortars containing 50 percent of either Class C or Class F fly ash. The strengths were evaluated at 1, 7, 28, 56, 182, and 365 days. It was found that one day strengths of the fly ash mixtures were only approximately 30 percent of those achieved with the 100 percent cement mortar. At later ages, the strengths of these mixtures approached that of the control. At 365 days, all of the mixtures with 50 percent fly ash had compressive strengths that were greater than 85 percent of the strength of the control mixture. Also, while both fly ash mixtures had similar strengths at 1 day, it was found that between 1 and 7 days, the Class C fly ash mixture showed greater strength gains, indicating that the Class C fly ash contributed more to early hydration reactions.

2.8.2. Heat Evolution. Schindler and Folliard (2003) performed semi-adiabatic calorimetry on combinations of Type I cement with 15, 25, 35, and 45 percent Class C or Class F fly ash replacements by volume. The results were then used to back-calculate the adiabatic temperature rise. It was found that with increasing Class C fly ash replacement, the total heat of hydration was not significantly affected, but the rate of hydration was slowed. It is also apparent from these results that the peak temperature decreased with increasing levels of Class C fly ash. With increasing levels of Class F fly ash, the total heat of hydration and the rate of heat evolution were reduced, which would result in little heat development at early ages.

Bentz (2010) evaluated the effects of 50 percent Class C and Class F fly ash replacement on Type II/V cement paste mixtures using isothermal calorimetry. It was found that the mixtures with Class C fly ash experienced retarded silicate hydration peaks. Even with the addition of gypsum to correct the sulfate imbalance, the silicate peak was significantly delayed. For the Class F fly ash mixtures, the silicate peak was not delayed.

2.8.3. Consistency. Due to their spherical particle shapes, fly ashes are known to increase the flowability of cementitious mixtures. This occurs because the spherical shape reduces friction between particles in the mixture (Mindess, et al., 2003).

2.8.4. Setting Time. It has been found by several researchers that the use of fly ash can significantly delay setting times (ACI Committee 232, 2003). Bentz et al. (2010) evaluated the effects of 50 percent Class C or Class F fly ash replacement on Type II/V cement pastes. It was found that initial set was delayed by at least three hours for both mixtures containing fly ash, when compared to the 100 percent cement control mixture. For the Class C fly ash mixture, final set was delayed by almost three hours, while a delay of over four hours was observed for the Class F fly ash mixture. It should be noted that the Class C fly ash mixture included a two percent addition of gypsum, by mass of total cementitious materials, to correct the sulfate imbalance caused by the fly ash.

3. LABORATORY INVESTIGATION

3.1 EXPERIMENTAL DESIGN

Five Type I portland cements and five Class C fly ashes, which are representative of those common to the eastern and western portions of the State of Missouri, were investigated in this study. Each cement was tested in combination with each Class C fly ash at replacement levels of 0, 25, 50, and 70 percent by mass of cement. The zero percent replacement level was used as a baseline. The 25 percent replacement level was chosen since it is typically the highest replacement level used in concrete mixtures containing fly ash. The 50 and 70 percent replacements levels were chosen based on previous research at the Missouri University of Science and Technology. Gypsum, hydrated lime, and rapid set cement were investigated as powder additions. Also, the addition of a water reducer was examined. In regard to w/cm, a survey of typical Missouri Department of Transportation (MoDOT) structural and paving revealed that a w/cm of 0.45 and 0.40 has been used. Because of concerns about low strength for high volume flyash mixtures, all of the paste mixtures were prepared with a constant water-cementitious materials ratio (w/cm) of 0.40.

3.1.1. Screening Study. The Screening Study included testing each combination of Type I cement and Class C fly ash at the four replacement levels, resulting in 80 combinations. These mixtures contained only cement, fly ash, and water. Testing for the Screening Study included semi-adiabatic calorimetry, cube compressive strength, miniature slump, and Vicat setting time. Compressive strength tests were performed at specimen ages of 1 day and 28 days.

3.1.2. Main Study. The Main Study investigated the effects of gypsum, hydrated lime, rapid set cement, and a water reducer on two combinations of cement and fly ash. The two cement-fly ash combinations were chosen for further study from the Screening Study based on having the highest and lowest reactivity of the cement-fly ash combinations. The levels of reactivity of the combinations were based on 1 -day cube strengths. A low dose, 2.75 fl. oz./cwt., and high dose, 5.00 fl. oz./cwt., of water reducer were investigated at each level of fly ash replacement. The gypsum, hydrated lime, and rapid set cement were investigated at the 50 and 70 percent levels of fly ash replacement with the low dose of water reducer. The gypsum levels were two and four percent of the actual percentage of fly ash. The hydrated lime and rapid set cement were evaluated at two levels with a gypsum level of four percent. The hydrated lime levels were five and ten percent of the actual percentage of fly ash, while the rapid set cement levels were 10 and 20 percent of the actual percentage of fly ash. This resulted in 48 paste mixtures for the Main Study. Equations 1 through 4, below, show the equations used in calculating the proportions of the cementitious materials. *Nominal % Activator* refers to the nominal percentage of either hydrated lime or rapid set cement used in the mixture, which are percentages by weight of flyash, as opposed to a total cementitious basis.

$$Actual\ \%\ Fly\ Ash = \frac{100}{1 + R + \dfrac{Nominal\ \%\ Gypsum}{100} + \dfrac{Nominal\ \%\ Activator}{100}} \tag{1}$$

$$Actual\ \%\ Portland\ Cement = R(Actual\ \%\ Fly\ Ash) \tag{2}$$

$$Actual\ \%\ Gypsum = \frac{Nominal\ \%\ Gypsum}{100}(Actual\ \%\ Fly\ Ash) \tag{3}$$

$$Actual\ \%\ Activator = \frac{Nominal\ \%\ Activator}{100}(Actual\ \%\ Fly\ Ash) \tag{4}$$

$$R = \frac{Nominal\ \%\ Portland\ Cement}{Nominal\ \%\ Fly\ Ash} \tag{5}$$

Table 3.1, on the following page, shows the combinations used in the Main Study. The percentages shown are nominal percentages. Cements are designated “1”, “2”, “3” ,”4”, or “5”, as are the fly ashes. Thus, a combination of Cement 4 and Fly ash 1 would be “4-1”.Testing for mixtures in the Main Study included semi-adiabatic calorimetry, cube compressive strength, miniature slump, and Vicat setting time. Compressive strength testing was performed at specimen ages of 1, 3, 7, 28, and 56 days.

Table 3.1. Main Study Combinations

Portland Cement	Fly Ash	Cement (%)	Fly Ash (%)	Gypsum (%)	Calcium Hydroxide (%)	Rapid Set Cement (%)	Water Reducer (fl. oz./cwt.)
4	1	100	-----	-----	-----	-----	-----
4	1	100	-----	-----	-----	-----	2.75
4	1	100	-----	-----	-----	-----	5.00
4	1	75	25	-----	-----	-----	-----
4	1	75	25	-----	-----	-----	2.75
4	1	75	25	-----	-----	-----	5.00
4	1	50	50	-----	-----	-----	-----
4	1	50	50	-----	-----	-----	2.75
4	1	50	50	-----	-----	-----	5.00
4	1	50	50	2	-----	-----	2.75
4	1	50	50	4	-----	-----	2.75
4	1	50	50	4	5	-----	2.75
4	1	50	50	4	10	-----	2.75
4	1	50	50	4	-----	10	2.75
4	1	50	50	4	-----	20	2.75
4	1	30	70	-----	-----	-----	-----
4	1	30	70	-----	-----	-----	2.75
4	1	30	70	-----	-----	-----	5.00
4	1	30	70	2	-----	-----	2.75
4	1	30	70	4	-----	-----	2.75
4	1	30	70	4	5	-----	2.75
4	1	30	70	4	10	-----	2.75
4	1	30	70	4	-----	10	2.75
4	1	30	70	4	-----	20	2.75
1	3		-----	-----	-----	-----	-----
1	3		-----	-----	-----	-----	2.75
1	3		-----	-----	-----	-----	5.00
1	3		25	-----	-----	-----	-----
1	3		25	-----	-----	-----	2.75
1	3		25	-----	-----	-----	5.00
1	3		50	-----	-----	-----	-----
1	3		50	-----	-----	-----	2.75
1	3		50	-----	-----	-----	5.00
1	3		50	2	-----	-----	2.75
1	3		50	4	-----	-----	2.75
1	3		50	4	5	-----	2.75
1	3		50	4	10	-----	2.75
1	3		50	4	-----	10	2.75
1	3		50	4	-----	20	2.75
1	3		70	-----	-----	-----	-----
1	3		70	-----	-----	-----	2.75
1	3		70	-----	-----	-----	5.00
1	3		70	2	-----	-----	2.75
1	3		70	4	-----	-----	2.75
1	3		70	4	5	-----	2.75
1	3		70	4	10	-----	2.75
1	3		70	4	-----	10	2.75
1	3		70	4	-----	20	2.75

3.2 EQUIPMENT

This section covers the equipment used for the mixing and testing procedures performed in this study. The section below on mixing equipment describes the equipment used to mix paste batches for the calorimetry, compressive strength, and miniature slump tests. The equipment used to mix paste batches for the Vicat setting time procedure is described later under Vicat Setting Time Equipment.

3.2.1. Mixing Equipment. The paste batches for semi-adiabatic calorimetry, compressive strength, and miniature slump testing were mixed using the same procedure and equipment. The batches were mixed using a 250-watt Black and Decker Model MX217 hand mixer with egg beater-style paddles, shown in Figure 3.1, below.

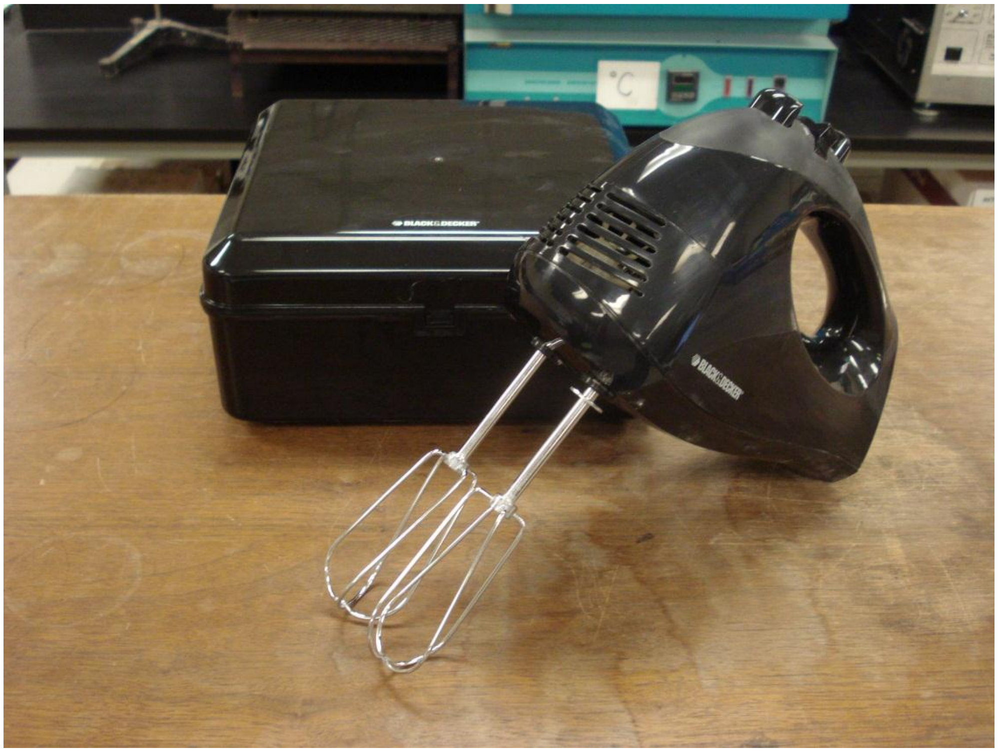

Figure 3.1. Black and Decker Hand Mixer

The mixer had six speed settings along with a “Power Boost” option that would increase the mixing speed when pushed. The rotational speeds for the various settings are given below in Table 3.2.

Table 3.2. Hand Mixer Rotational Speeds

Speed Setting	Rotational Speed (RPM)
1	390
2	440
3	490
4	540
5	600
6	670
Power Boost	700

The paste was mixed in a stainless steel mixing bowl from a Hobart Model A-200 mixer, which had a capacity of 20 quarts. Temperature measurements of the paste, after mixing, were made using an analog thermometer with a probe length of five inches. Other equipment included a stopwatch for timing of the mixing procedure and a ladle to transport the paste mixture from the mixing bowl. Figure 3.2, below, shows the mixing bowl, thermometer, and other equipment used during mixing.

Figure 3.2. Equipment used in the Combined Mixing Procedure

3.2.2. Cube Molding Equipment. Steel and plastic molds were used to mold the two-inch paste cubes. The steel molds contained three compartments and consisted of two sides with a thickness of one half of an inch, four slats with a thickness of two tenths of an inch, and a base plate with screws for holding the components together. The two thicker sides each had four grooves to hold the slats in place and the four slats were inserted between the thicker sides so that they were parallel to each other. This assembly was held in place on the base plate by two screws on one of the thicker sides and one screw on the other side, which was also used for tightening the assembly together. The plastic molds consisted of two side pieces, a base plate, and six thumb screws. The two side pieces were held together by two of the longer thumb screws to form the cubes diagonal to the length of the mold. The other four screws were used to hold the assembled side components to the base plate.

Other equipment used to mold the paste cubes included a tamper, trowel, and vacuum grease. The tamper was made of Plexiglas and had a width of about one inch, thickness of about one half of an inch, and a length of about four inches. The trowel was made of steel and had a rectangular blade 4.25 inches long and two inches wide. The vacuum grease was Dow Corning High-Vacuum Grease and was used to seal together the components of the cube molds. Figure 3.3, below, shows the cube molding equipment.

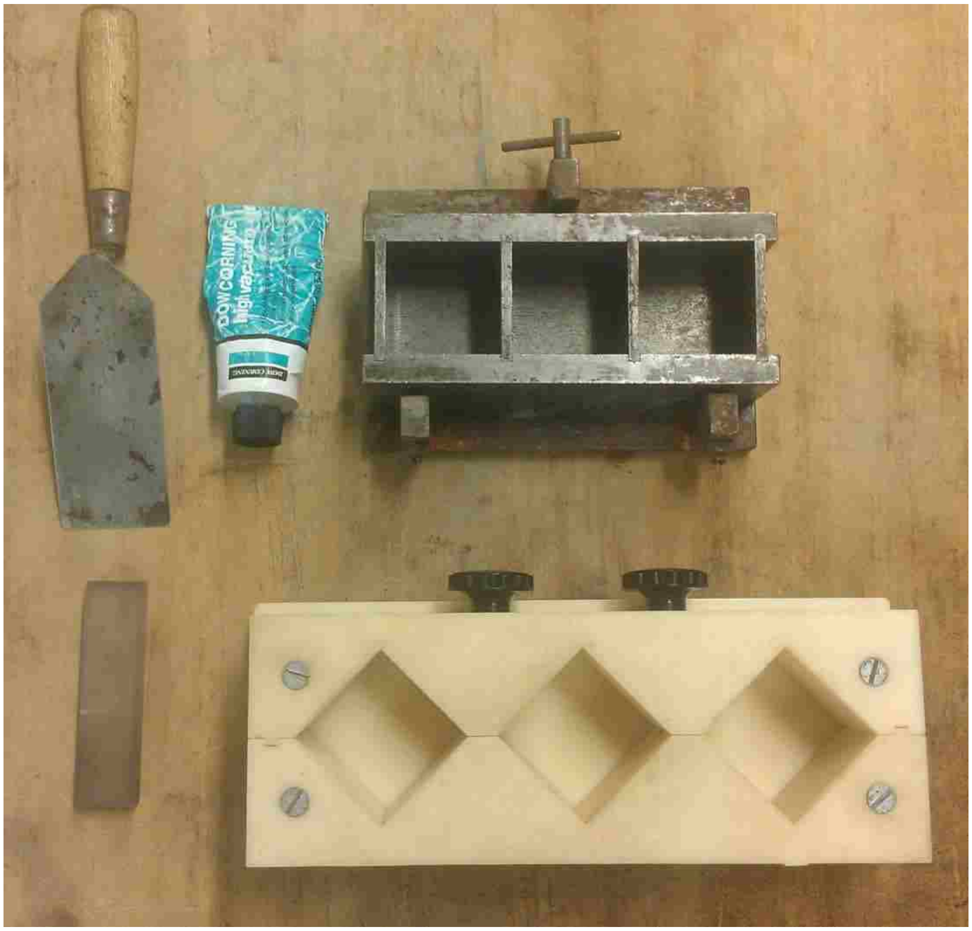

Figure 3.3. Cube Molding Equipment

3.2.3. Curing Equipment. After three days of curing, the paste cubes were removed from the molds and placed in buckets of water saturated with hydrated lime. The buckets had a capacity of five gallons and were stored in a moist room, which had a relative humidity maintained at 95% or greater. The moist room itself was not explicitly controlled for temperature, but the temperature was maintained at the same temperature as the surrounding building and was relatively constant.

3.2.4. Compressive Strength Testing Equipment. The two-inch cube specimens were tested for compressive strength on a hydraulic, Tinius-Olsen tension/compression machine with a capacity of 200,000 pounds. The Tinius-Olsen is controlled using a desktop computer with MTestW software. Two loading platens were used to apply the load to the two loading faces of the cube specimens. The lower, square loading platen was about twelve inches tall and had a diagonal dimension of 3.5 inches. It was attached to a larger, circular loading platen, typically used for cylinder testing, which rested on the lower table of the Tinius-Olsen machine. The upper, circular loading platen was about six inches tall and was attached to the upper crosshead of the Tinius-Olsen machine. The loading block of the upper platen was spherically seated and had a diameter of 3.5 inches. Figure 3.4 shows the Tinius-Olsen machine with the loading platens and the computer used to control the machine.

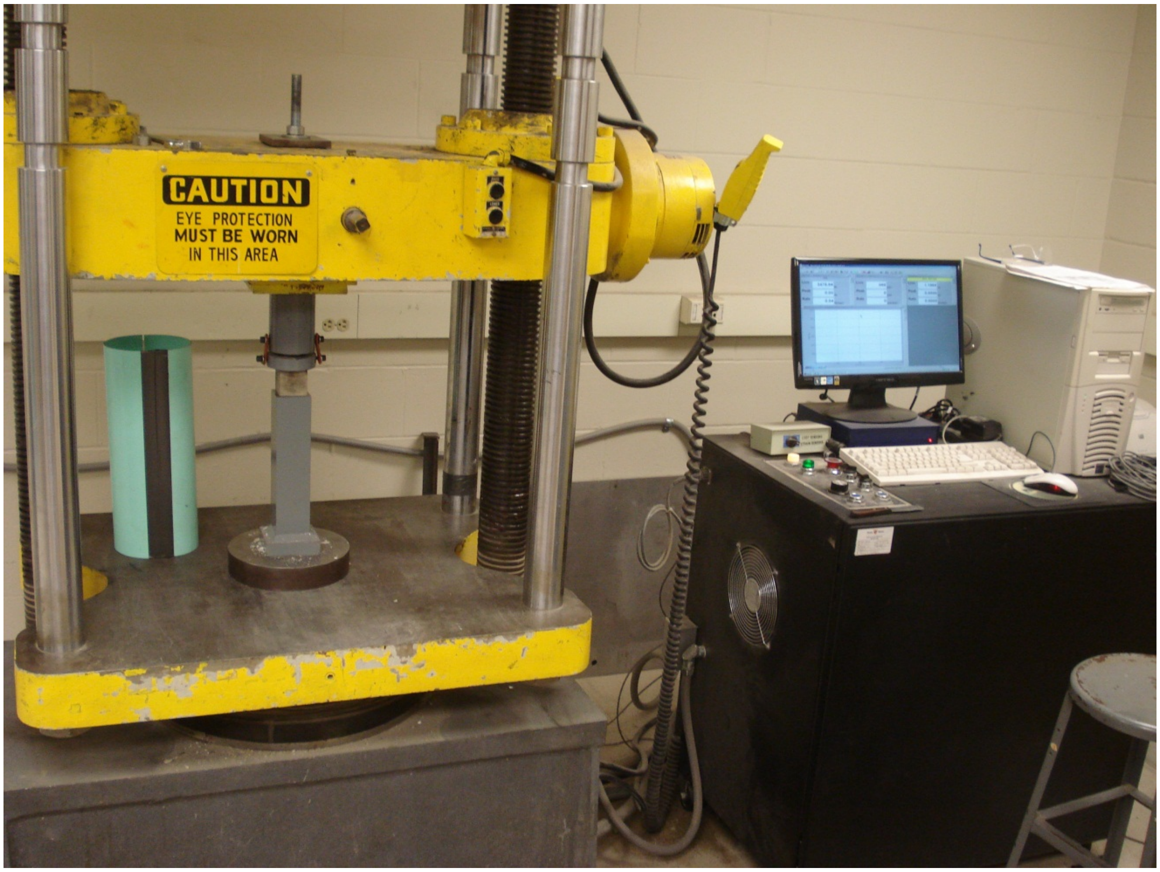

Figure 3.4. Tinius-Olsen Load Frame and Computer

Other equipment included digital calipers for measuring the dimensions of the specimen and sand paper to smooth the loading faces of the specimen. The sand paper had a grit size of 60. The complete testing method is detailed in Appendix A.

3.2.5. Semi-Adiabatic Calorimetry Equipment. Temperature measurements were taken on hydrating paste specimens over time using an F-Cal 4000 Field Calorimeter from Calmetrix, Inc., which is shown in Figure 3.5. The F-Cal 4000 consists of four receptacles in an insulated box with thermistors at the bottom of each receptacle. The thermistors, along with a USB port, are connected to a single data logger. The receptacles are sized to hold standard 4”x8” cylinder molds. Plastic 4”x8” cylinder molds were used in this study.

Figure 3.5. F-Cal 4000, Computer, and Cylinder Molds

Data was collected from the F-Cal 4000 data logger using the CalCommander v1.3 Software Suite from Calmetrix, Inc. This required the calorimeter to be connected to a desktop computer with a USB cable. Once data was collected by and exported from the CalCommander software, data reduction was performed using Microsoft Excel 2010 and TableCurve 2D software.

3.2.6. Miniature Slump Equipment. Two miniature slump cones were fabricated from Plexiglas with the dimensions given by Kantro (1980). The inside of the cones had dimensions in the same proportion as those specified for a standard slump cone as given in ASTM C 143. These dimensions were 0.75 inches for the top diameter, 1.5 inches for the bottom diameter, and 2.25 inches for the height.

Figure 3.6, shows the two cones used in this study, along with other equipment used for performing this test, which included a Plexiglas board, plastic discs, and a spatula. The rectangular Plexiglas board was flat with a smooth surface and had dimensions of 39 inches by 13 inches by 0.2 inches. The plastic discs were cut from Zip-Lock bags and had diameters of about two inches. The stainless steel spatula had a length of four inches and a width of 0.7 inches.

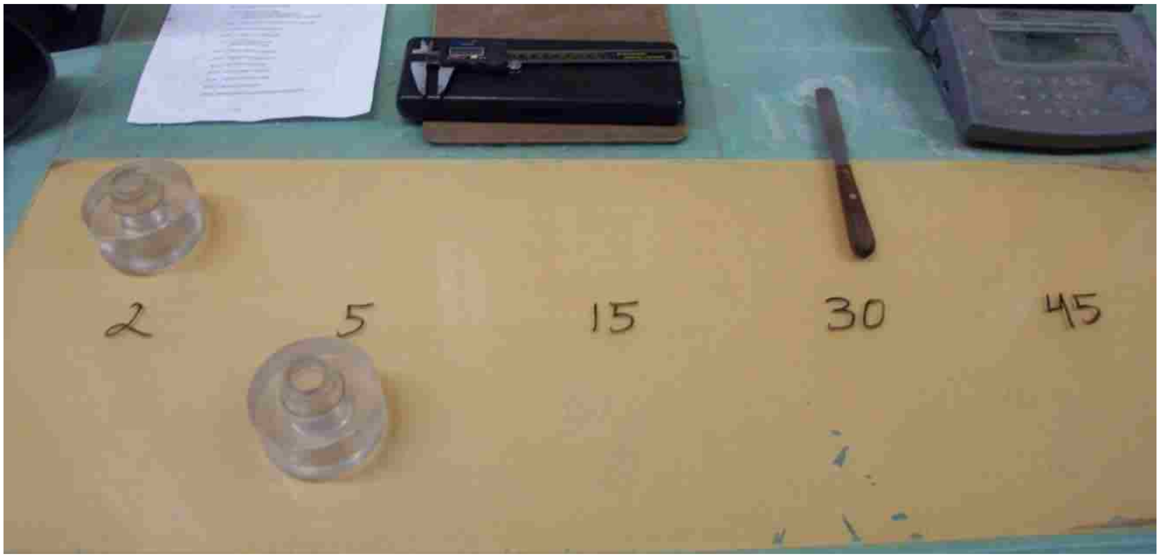

Figure 3.6. Miniature Slump Cones and Equipment

3.2.7. Vicat Setting Time and Normal Consistency Equipment. The Vicat apparatus described in ASTM C 191 and ASTM C 187 was used for both the Vicat setting time and normal consistency tests. The apparatus, shown in Figure 3.7, consists of a moveable rod that has one end with a diameter of 10 millimeters and another end with a removable needle that has a diameter of one millimeter. The rod is held in a frame that has a scale with a 50 millimeter length divided into one millimeter increments. An indicator attached to the rod moves along this scale and a set screw in the frame is used to hold the rod. The conical ring and base plate, which hold the paste, rest on the bottom portion of the frame. The conical ring is made of rigid plastic and the base plate is made of glass.

Figure 3.7. Vicat Apparatus with Ring and Glass Plate

The paste was mixed using a Hobart Model N50 mixer, bowl, and paddle, which conform to the requirements of ASTM C 305. The mixer has three speeds and moves the paddle in both planetary and revolving motions. Other equipment used to perform these tests included a bowl scraper with a semi-rigid rubber blade as specified in ASTM C 305, rubber gloves, and a steel trowel with a rectangular blade 4.25 inches long and two inches wide. Figure 3.8, below, shows the mixer and other equipment discussed above.

Figure 3.8. Hobart Mixer and Bowl Scraper

3.3 MATERIALS

3.3.1. Portland Cements. Five portland cements were chosen that were representative of those commonly used in the eastern and western portions of the State of Missouri. The cements were all either ASTM Type I or Type I/II. Oxide analyses were provided by the producers and are included below in Table 3.3.

Table 3.3. Cement Oxide Analyses (Screening Study)

Material	Type/Class	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	EqAlk (%)
Cement 1	Type I/II	20.40	4.21	3.62	63.83	2.49	0.20	0.45	0.52
Cement 2	Type I/II	19.90	5.10	3.80	62.60	3.00	-----	-----	0.50
Cement 3	Type I/II	20.30	4.69	3.22	63.00	2.82	-----	-----	0.50
Cement 4	Type I	19.85	4.63	3.23	64.08	3.28	0.18	0.48	0.49
Cement 5	Type I/II	19.80	4.80	3.10	63.20	3.10	-----	-----	0.55

The cement oxide analyses were performed on materials that were produced at a similar time as those received during the first shipment of materials. A second shipment of Cement 1 and Cement 4 were received approximately six months after the first delivery. As can be seen in Table 3.4, below, the analyses are quite similar.

Table 3.4. Cement Oxide Analyses (Main Effects Study)

Cement	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	EqAlk (%)	C_3S (%)	C_3A (%)	Fineness (cm^2/g)
1	20.29	4.05	3.64	63.43	2.91	0.2	0.47	0.54	57	4	4000
4	20	4.6	3.1	63.9	3.1	---	---	0.53	61	7	3900

3.3.2. Fly Ashes. Five fly ashes were chosen that were representative of those commonly used in the eastern and western portions of the State of Missouri. All of the fly ashes conformed to the requirements for ASTM Class C fly ash. The results of the oxide analyses for the fly ashes are included in Table 3.5.

Table 3.5. Fly Ash Oxide Analyses

Flyash	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	EqAlk (%)	Retained #325 (%)	LOI (%)
1	33.72	21.9	7.15	25.31	2.25	1.4	0.41	1.68	11.16	0.37
2	33.34	20.57	6.15	26.34	1.87	1.63	0.43	1.92	11.17	0.49
3	35.42	16.88	7.97	23.21	3.46	1.4	0.56	1.78	19.37	3.05
4	30.55	18.78	7.48	28.43	3.33	1.5	0.45	1.81	10.17	0.57
5	32.26	19.03	6.24	27.94	2.4	2.2	0.33	2.43	13.04	0.26

The fly ash oxide analyses were performed by the Materials Research Center (MRC), at the Missouri University of Science and Technology, on the first shipment of materials received. . Also, particle size distributions were analyzed by the Ash Grove Cement Company Technical Center on this initial shipment. A second shipment of Fly Ash 3 was received approximately six months after the first shipment. Fly Ash 1 was continually resupplied from bulk shipments to the Missouri University of Science and Technology.

3.3.3. Powder Additions. Three materials were used as powder additions in the paste mixtures. These included gypsum, hydrated lime, and rapid set cement. The gypsum was manufactured from recycled drywall by USA Gypsum. According to the manufacturer's website, the material has a calcium sulfate ($CaSO_4$) content of 96.0% and a moisture content no greater than 2.0%. The hydrated lime was Standard Hydrated Lime acquired from Mississippi Lime. Typical data from the manufacturer's website reported an available calcium hydroxide ($Ca(OH)_2$) content of 96.8%, $CaSO_4$ content of 0.1%, and free moisture content of 0.7%. The rapid set cement was Rapid Set Cement manufactured by CTS Cement Manufacturing Corporation. The advertised oxide analysis is shown in Table 3.6.

Table 3.6. Oxide Analysis of RSC

Parameter	**Percent**
Calcium oxide (CaO)	50.87
Silicon dioxide (SiO2)	15.40
Aluminum oxide (Al2O3)	13.74
Sulfur trioxide (SO3)	12.52
Iron oxide (FesO3)	2.38
Magnesium oxide (MgO)	1.26
Total alkalis (as Na2O)	0.56
Loss on ignition	2.84
Insoluble residue	0.78
Specific gravity	2.98

The manufacturer also provided results for modified ASTM C 109 tests performed with the material. These compressive strength results are given below in Table 3.7.

Table 3.7. CTS Rapid Set Cement Compressive Strength Results

Rapid Set Cement Compressive Strength (Modified ASTM C 109)	
Time	Compressive Strength (psi)
1.5 hours	2500
3 hours	5000
24 hours	6500
28 days	8000

3.3.4. Water Reducer. The water-reducing admixture used in this project was Glenium 7500 from BASF, which was a polycarboxylate and conformed to ASTM C 494/C 494M requirements for both a Type A, water-reducing admixture and a Type F, high-range water-reducing admixture. The recommended dosage range provided by the manufacturer was 2 to 15 fl. oz./cwt. of cementitious materials.

3.3.5. Water. The water used for all of the mixtures was supplied from a single source of deionized water.

3.4 TEST PROCEDURES

3.4.1. Pre-blending Dry Constituents. Prior to mixing of the paste batches, the dry constituents of the mixture were pre-blended. This was performed by transferring no more than 1200 grams of the materials into a 4 inchx8 inch plastic cylinder mold in similar proportions as those used in the mixture. The cap was then placed on the cylinder and the cylinder was held horizontally with one hand on each end. The cylinder was then shaken 25 cycles using a six inch throw. This procedure is included in all of the test procedures in Appendix A.

3.4.2. Determination of Rotational Speeds for Handheld Mixer. An adjustable rate strobe light was used to determine the rotational speeds for the various settings on the handheld mixer. To do this, a piece of white tape was attached to a fin of one paddle and a piece of orange tape was placed on the other paddle. The mixer was then started and the strobe light was adjusted to flash at different rates until the tape on the paddles appeared to stop moving. It was also noted that each fin appeared to stop when the proper rate was set on the light. This rate was read in RPMs from the dial used to adjust the flashing rate. The rates determined were between 390 and 700 RPM, which is a reasonable result for this appliance. Judgment had to be used to make sure that higher or lower speeds were not taken to be the actual speed of the blender, since the stopped-movement appearance can occur at higher or lower flashing rates on the strobe light that would be unreasonable for this type of device.

3.4.3. Combined Mixing Procedure. The paste for the cube compressive strength, semi-adiabatic calorimeter, and miniature slump tests was typically mixed in a single batch. In order to mix the materials adequately and within the time requirements of the tests being performed, a handheld kitchen mixer was used as recommended by Cost (T. Cost, personal communication, April 10, 2011). As noted by Cost (2009), the use of equipment and methods other than those given in ASTM C 305 can shorten mixing times to as little as 60 seconds. In this study, the initial mixing of the paste batch was performed in 90 seconds, which allowed the first miniature slump test to be performed at two minutes after mixing began. The initial mixing consisted of adding the water to the cementitious materials, allowing the cement to absorb the water for 10 seconds, mixing for 20 seconds at Speed 2 (440 rpm), and then mixing for 60 seconds at Speed 6 (670 rpm). As noted by Kantro (1980), brief setting of the paste mixture can be avoided by remixing the paste. This was done in this study by remixing the paste for 30 seconds at Speed 2 prior to each miniature slump test. The calorimeter specimens were prepared and inserted into the calorimeter after the 5-minute miniature slump test, which allowed for early data collection, and the cube specimens were molded after the 15-minute miniature slump test, so that molding began within 2 minutes and 30 seconds after remixing. In Table 3.8, on the following page, the complete sequence of testing can be seen.

In some cases, not all of the tests were performed using a single batch of paste. For these cases, the same mixing and remixing sequences were followed with the tests being performed at their respective times in the combined mixing procedure.

3.4.4. Cube Compressive Strength. All of the cube molds were sealed with vacuum grease to prevent the paste from leaking. Excess vacuum grease was removed from the interior of the molds to avoid deforming the shape of the cubes. The mixing procedure for the paste followed the combined mixing procedure, which was discussed previously, using the handheld mixer.

Table 3.8. Combined Mixing Procedure Sequence

Elapsed Time (mm:ss)	Action
0:00	Add water to mixing bowl with cementitious materials Record Time (Start Time)
0:10	Start mixing at Speed 2 (440 RPM)
0:30	Start mixing at Speed 6 (670 RPM)
1:30	Stop Mixing Record Temperature of Paste Prepare mini-slump test
2:00	Lift mini-slump cone
4:00	Remix paste at Speed 2
4:30	Prepare mini-slump test
5:00	Lift mini-slump cone Prepare calorimeter specimens Insert calorimeter specimens in F-Cal 4000
10:00	Close and latch the lid of the F-Cal 4000
13:00	Remix paste at Speed 2
13:30	Prepare mini-slump test
15:00	Lift mini-slump cone Mold cement cubes
28:00	Remix paste at Speed 2
28:30	Prepare mini-slump test
30:00	Lift mini-slump cone
43:00	Remix paste at Speed 2
43:30	Prepare mini-slump test
45:00	Lift mini-slump cone
60:00	Measure and record mini-slump diameters

The molding of the specimens followed the filling, tamping, and leveling procedures outlined in ASTM C 109 with a deviation of the time at which molding began. ASTM C 109 states that specimen molding should begin within two minutes and 30 seconds after completion of the original mixing of the batch. In this study, molding started after completion of the 15-minute miniature slump test, which would mean that molding started approximately fourteen minutes after completion of the initial mixing. However, this molding time was within two minutes and 30 seconds after completion of the remixing for the 15-minute miniature slump test. Also, it was noted that the paste at this time was sufficiently fluid to allow for complete consolidation. Following the completion of the molding procedures, the specimens were placed in the moist room. Further details on mold removal and specimen storage can be found in the “Compressive Strength of Cement Cubes” procedure in Appendix A.

The compressive strengths of the cubes were tested on the Tinius-Olsen load frame at a load rate of 200 pounds/second, which is within the range allowed by ASTM C 109. Prior to loading the specimens, the molded faces of the cubes that were to be loaded, were sanded to provide plane loading surfaces. The loading faces of the cubes and the load platens were cleaned of any debris prior to the start of loading.

The complete test procedure is titled “Compressive Strength of Cement Cubes” and is included in Appendix A.

3.4.5. Semi-adiabatic Calorimetry. Semi-adiabatic calorimetry was performed for the paste mixtures using an F-Cal 4000 calorimeter with CalCommander software from Calmetrix. Three paste specimens were inserted into the F-Cal 4000 for each mixture, with one receptacle containing an inert specimen. It was decided that three specimens should be used for each mixture, instead of testing multiple mixtures simultaneously, so that the results for a given specimen would not be affected by the temperature rise of other specimens with different compositions. The inert specimen consisted of high-silica sand and deionized water with a water-to-sand ratio equal to the water-to-cementitious materials ratio of 0.40 and mass similar to the paste specimens. The use of a water and sand combination is intended to better simulate the thermal conductivity of the paste specimens, when compared to a dry sand inert specimen (T. Cost, personal communication, April 10, 2011). The mass of the inert specimen was 1250.0 grams and the masses of the paste specimens were 1250.0 grams with a tolerance of 10.0 grams. This mass is recommended in the F-Cal 4000/8000 User Manual and fills approximately one-third of the cylinder's volume. As noted in a draft ASTM for evaluating hydration using thermal measurements (2011), the "masses of all specimens that will be compared with each other shall not differ by more than 5%". A tolerance of 10.0 grams was chosen because it was within this range, was easily accomplished, and could lessen the variability between specimens when compared to specimens differing in mass by 5%.

Once logging in the F-Cal 4000 was complete, the data was retrieved using the CalCommader software. From the software, the data for each logging channel was exported as a separate Text Document (.txt) file. These were then imported into Microsoft Excel and the Signal-to-Noise ratio (S/N) was calculated for each of the three specimens. The Signal is the difference between the highest and lowest temperatures recorded for the sample being tested. The Noise is the difference between the highest and lowest temperatures recorded for the inert specimen. Figure 3.9, below, shows an example of the temperature versus time curves resulting from the raw data for a typical hydrating cement paste sample and corresponding inert specimen. The Signal and Noise quantities are indicated in the figure. Use of this data will be discussed in a later section.

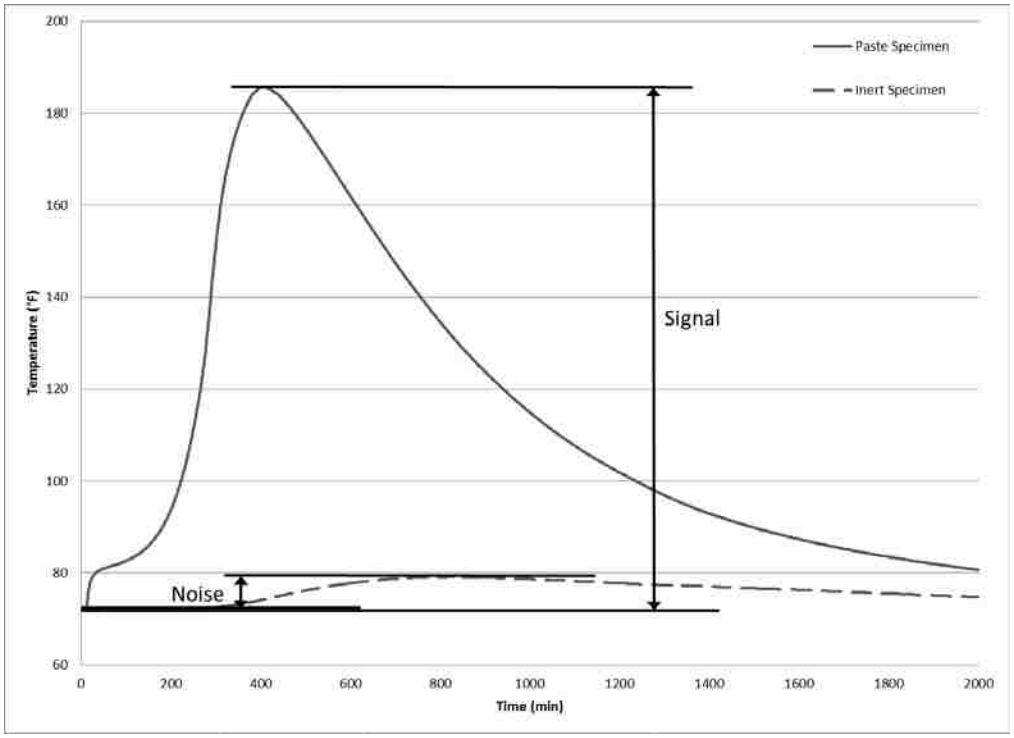

Figure 3.9. Examples of Signal and Noise Quantities

Cost (2009) noted that the curve generated for the inert specimen should be subtracted from the curve for the hydrating specimen, so that the resulting data represents only the heat evolution of the sample and not variances in the ambient temperature. Cost designated this quantity as ΔT, which is shown below in Figure 3.10. In this study, the curves for the three specimens were averaged to result in a single hydration curve for each paste mixture. The curve for the inert specimen was then subtracted from this averaged curve to result in a corrected average hydration curve.

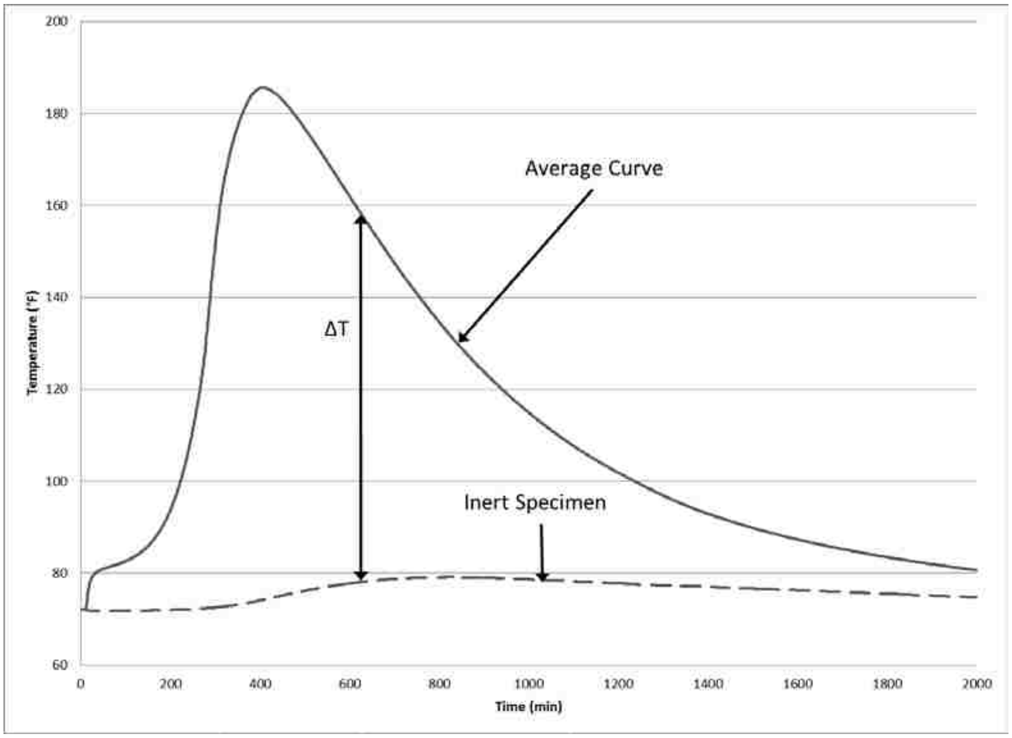

Figure 3.10. Representation of the ΔT Quantity

This corrected curve was then used to calculate predicted setting times using the Fractions Method and Derivatives Method, as discussed by Sandberg and Liberman (2007). For the Fractions Method, the main hydration response rise (M) is calculated, which is the difference between the peak temperature of the main hydration curve and the lowest temperature during the dormant period, and then two percentage values of the main hydration response rise are chosen to represent the initial and final set times. For this study, 20% of the main response was chosen for initial set and 50% was chosen for final set. A representation of the calculated values for the Fractions Method is shown below in Figure 3.11. For the Derivatives Method, initial set is taken as the time when the maximum second derivative of the main hydration curve occurs and final set is taken as the time when the maximum first derivative of the main hydration curve occurs.

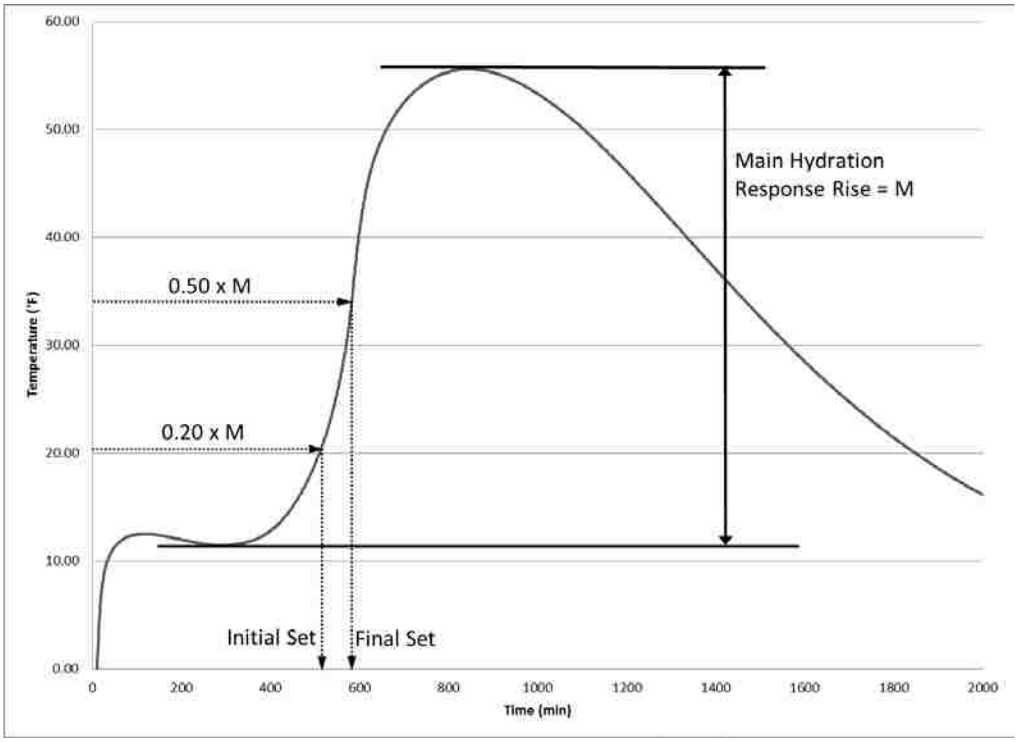

Figure 3.11. Example of Setting Time Prediction by the Fractions Method

The complete semi-adiabatic calorimetry procedure, including data reduction, is titled "Using the F-Cal 4000 & CalCommander Software for Testing Cement Paste" and is included in Appendix A.

Before testing began, a verification of the internal connections was performed, as suggested in the F-Cal 4000/8000 User Manual, to ensure that the connections had not been damaged during shipping. This was done by filling four cylinders with water at 110°F and inserting them into the F-Cal 4000. After thirty minutes, the temperature reading was checked for each of the sensors to ensure that no two sensors differed by more than 2°F.

3.4.6. Miniature Slump. The paste for the miniature slump test was mixed according to the combined mixing procedure previously discussed. The test was performed at 2, 5, 15, 30, and 45 minutes, as was done by Bhattacharja and Tang (2001). The tests at 2 and 5 minutes were performed 30 seconds after the end of mixing or remixing. The tests at 15, 30, and 45 minutes were performed one minute and 30 seconds after the end of remixing to allow for a longer period to fill the cone, which was needed for stiffer mixtures.

The cones were placed on thin plastic discs, as suggested by Bhattacharja and Tang (2001), to prevent leaking from the bottom of the cone. The discs had diameters of two inches and were cut from Zip-Lock sandwich bags.

Previous research (Kantro, 1980; Bhattacharja & Tang, 2001), discussed the use of a planimeter for measuring the area of the miniature slump pats. To do this, tracings of the pats were made on paper and measured after the pats had hardened and were removed. While this method gives more accurate results, time constraints and concerns about variability introduced by the paper led to the use of diameter measurements for area determination in this study, which has been found to be an accurate alternative for pat areas that remain nearly circular. In this study, this method involved taking four diameter measurements, separated by a rotation of 45 degrees, to obtain an average diameter from which the area was calculated.

The diameter measurements were taken at 60 minutes after the start of mixing. This time was chosen to allow the later miniature slump tests time to stabilize without allowing sufficient time for the results of the earlier tests to be affected by shrinkage from hydration and drying.

The complete test procedure, which was adapted from the procedures given by Kantro (1980) and Bhattacharja & Tang (2001), is titled “Miniature Slump Cone” and is included in Appendix A.

3.4.7. Normal Consistency and Vicat Time of Setting. The paste for the normal consistency test was mixed according the Procedure for Mixing Pastes given in ASTM C 305 with one deviation. In this study, the bowl and paddle were wetted before mixing commenced to provide a more constant surface condition of these items when multiple tests were run in succession. Care was taken to ensure that excess water was not present, which would affect the normal consistency results. Following the mixing procedure, normal consistency was determined according to ASTM C 187.

The paste from the normal consistency test was used to determine the time of setting by the Vicat method according to ASTM C 191 with one deviation. The specimen was kept in the moist room between penetration measurements and was covered with a plastic sheet while in the moist room to prevent damage to the surface of the specimen from dripping water. Similar modifications to ASTM C 191 have been made by other researchers (Bentz & Ferraris, 2010) to prevent evaporation from the surface of the specimen during the test.

For specimens that experienced initial set prior to the first penetration reading at 30 minutes, a penetration of 40 millimeters was assumed at time zero. This made possible the interpolation of initial set at a penetration of 25 millimeters, as described in ASTM C 191.

The complete test procedure is titled “Time of Setting by Vicat Needle” and is included in Appendix A.

4. RESULTS AND DISCUSSION

4.1 SCREENING STUDY RESULTS

In the Screening Study, paste mixtures were made from the five Type I or I/II cements, each in combination with the five Class C fly ashes at the 0, 25, 50, and 70 percent replacement levels. Testing of the paste in the Screening Study included cube compressive strength at one and 28 days, semi-adiabatic calorimetry, miniature slump, and Vicat setting time.

4.1.1. Cube Compressive Strength. The three cube compressive strength test results for each mixture were analyzed for outliers using ASTM E 178. Once the analysis indicated that a value was a possible outlier, the decision was made whether or not to remove the value from the data using the following criteria:

1. If two of the tests where identical or extremely similar, the ASMT E 178 analysis indicated that the other value was an outlier, even though it was reasonably close to the other two values. In this case, the indicated outlier was not considered to be an actual outlier.
2. Due to the nature of compressive strength testing, it is unlikely that an error in the procedure would occur which would result in an unreasonably high value. Because of this, high values, which were indicated to be outliers by the ASTM E 178 analysis, were generally not considered to be actual outliers.
3. In some cases, a value barely crossed the threshold of the ASTM E 178 analysis to be considered an outlier. In these cases, judgment was used to determine

whether the value was an actual outlier, by considering other factors such as standard deviation and overall magnitude of the values.

If no values were removed, the three results were averaged to obtain the cube compressive strength for the given mixture. If a value was determined to be an outlier, the cube compressive strength was taken as the average of the two remaining values. In the following outlier analysis tables, values that were discarded as actual outliers have been bolded and the cells containing the values have been shaded.

The outlier analyses for the one and 28 day cube strengths for the Cement 1 combinations are given below in Tables 4.1 and 4.2, respectively. The ASTM E 178 analysis indicated three possible outliers, but only one value, Test 3 of the 28-day tests for combination 1-2 with 50 percent fly ash replacement, was considered to be an actual outlier.

Table 4.1. 1-Day Cube Strength Outlier Analysis for Cement 1 Combinations

Combination	Proportions		Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 1	100	0	4917	4145	5018	4693	478	3	5018	4145	1.153	0.680	1.148	NO	NO	4693
1-1	75	25	2727	2709	2979	2805	151	3	2979	2709	1.153	1.152	0.639	NO	NO	2805
1-1	50	50	1176	1274	1288	1246	61	3	1288	1176	1.153	0.688	1.147	NO	NO	1246
1-1	30	70	341	347	310	332	20	3	347	310	1.153	0.720	1.142	NO	NO	332
1-2	75	25	2925	2840	2878	2881	43	3	2925	2840	1.153	1.035	0.961	NO	NO	2881
1-2	50	50	594	616	619	610	13	3	619	594	1.153	0.677	1.149	NO	NO	610
1-2	30	70	37	42	42	40	3	3	42	37	1.153	0.625	1.153	NO	YES	40
1-3	75	25	2790	2708	2825	2774	60	3	2825	2708	1.153	0.849	1.102	NO	NO	2774
1-3	50	50	626	656	683	655	29	3	683	626	1.153	0.982	1.017	NO	NO	655
1-3	30	70	21	11	16	16	5	3	21	11	1.153	1.000	1.000	NO	NO	16
1-4	75	25	2803	2753	2745	2767	31	3	2803	2745	1.153	1.145	0.703	NO	NO	2767
1-4	50	50	334	328	343	335	7	3	343	328	1.153	1.061	0.926	NO	NO	335
1-4	30	70	66	70	68	68	2	3	70	66	1.153	0.982	1.017	NO	NO	68
1-5	75	25	2802	2993	2977	2924	105	3	2993	2802	1.153	0.653	1.151	NO	NO	2924
1-5	50	50	497	538	510	515	21	3	538	497	1.153	1.099	0.855	NO	NO	515
1-5	30	70	101	101	96	100	3	3	101	96	1.153	0.620	1.154	NO	YES	100

Table 4.2. 28-Day Cube Strength Outlier Analysis for Cement 1 Combinations

Combination	Proportions		Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 1	100	0	11237	11165	11500	11300	176	3	11500	11165	1.153	1.131	0.769	NO	NO	11300
1-1	75	25	10566	11657	10754	10992	583	3	11657	10566	1.153	1.140	0.730	NO	NO	10992
1-1	50	50	8354	8021	7361	7912	506	3	8354	7361	1.153	0.874	1.090	NO	NO	7912
1-1	30	70	3984	4299	4039	4108	168	3	4299	3984	1.153	1.139	0.733	NO	NO	4108
1-2	75	25	10153	9645	9979	9925	258	3	10153	9645	1.153	0.880	1.087	NO	NO	9925
1-2	50	50	7980	7997	**7636**	7871	204	3	7997	7636	1.153	0.618	1.154	NO	YES	7989
1-2	30	70	4084	3956	4213	4084	128	3	4213	3956	1.153	1.002	0.998	NO	NO	4084
1-3	75	25	11641	10060	10407	10703	831	3	11641	10060	1.153	1.129	0.774	NO	NO	10703
1-3	50	50	7641	8195	7787	7874	287	3	8195	7641	1.153	1.117	0.813	NO	NO	7874
1-3	30	70	2522	2450	2455	2475	40	3	2522	2450	1.153	1.152	0.638	NO	NO	2475
1-4	75	25	9565	9396	10706	9889	712	3	10706	9396	1.153	1.147	0.692	NO	NO	9889
1-4	50	50	8588	8695	9127	8803	285	3	9127	8588	1.153	1.134	0.755	NO	NO	8803
1-4	30	70	5809	6234	6069	6037	214	3	6234	5809	1.153	0.918	1.066	NO	NO	6037
1-5	75	25	11121	11438	11468	11342	192	3	11468	11121	1.153	0.656	1.151	NO	NO	11342
1-5	50	50	8354	8073	8543	8323	236	3	8543	8073	1.153	0.930	1.058	NO	NO	8323
1-5	30	70	5556	5782	5727	5688	118	3	5782	5556	1.153	0.797	1.122	NO	NO	5688

Figure 4.1, given below, shows the cube strengths after one day for Cement 1 in combination with each fly ash. As can be seen, the strength decreased significantly with increasing fly ash replacement levels.

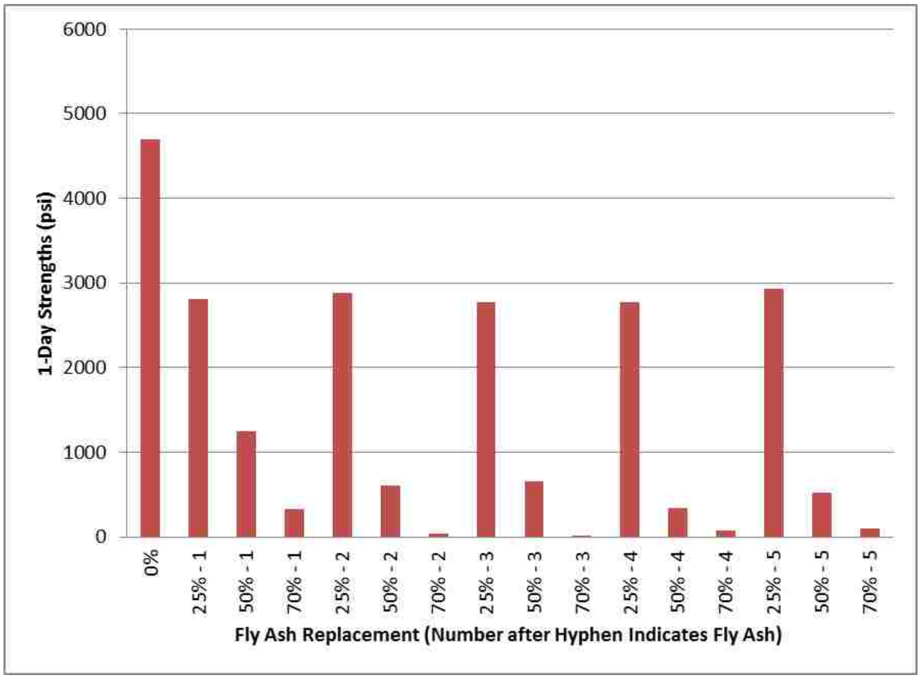

Figure 4.1. One-day Compressive Strengths for Cement 1 Combinations

Figure 4.2, below, shows the cube strengths after 28 days for Cement 1 in combination with each fly ash. The mixtures with 25 percent fly ash replacement generally show strengths comparable to the baseline and the combination with 25 percent of Fly Ash 5 exceeds the baseline strength by about 40 psi. The 70 percent fly ash mixtures show strengths much lower than the baseline, though not as severely as at one day.

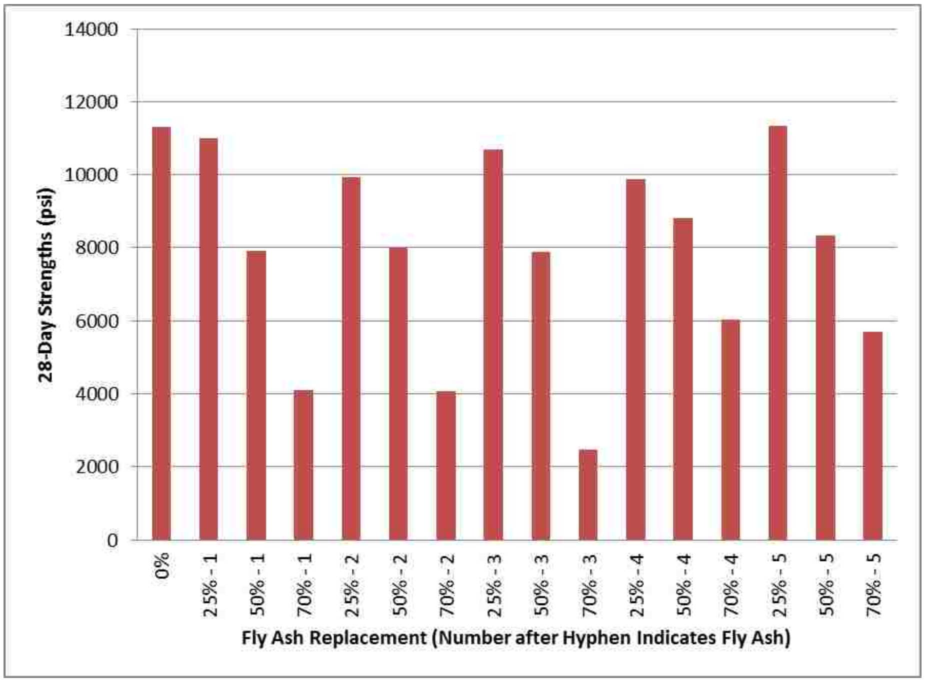

Figure 4.2. 28-day Compressive Strengths for Cement 1 Combinations

The outlier analyses for the one and 28 day cube strengths for the Cement 2 combinations are given, below, in Tables 4.3 and 4.4, respectively. The ASTM E 178 analysis indicated five possible outliers, but none of these were discarded as actual outliers.

Table 4.3. 1-Day Cube Strength Outlier Analysis for Cement 2 Combinations

Combination	Proportions		Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 2	100	0	4353	4527	4807	4562	229	3	4807	4353	1.153	1.068	0.914	NO	NO	4562
2-1	75	25	2809	2702	2657	2722	78	3	2809	2657	1.153	1.106	0.840	NO	NO	2722
2-1	50	50	1050	1055	1178	1094	73	3	1178	1050	1.153	1.154	0.615	YES	NO	1094
2-1	30	70	398	407	415	407	9	3	415	398	1.153	0.975	1.023	NO	NO	407
2-2	75	25	2325	2586	2562	2491	144	3	2586	2325	1.153	0.659	1.151	NO	NO	2491
2-2	50	50	929	944	930	934	8	3	944	929	1.153	1.154	0.608	YES	NO	934
2-2	30	70	168	186	179	178	9	3	186	168	1.153	0.886	1.084	NO	NO	178
2-3	75	25	2219	2338	2407	2321	95	3	2407	2219	1.153	0.900	1.077	NO	NO	2321
2-3	50	50	827	873	813	837	31	3	873	813	1.153	1.122	0.796	NO	NO	837
2-3	30	70	64	60	63	62	2	3	64	60	1.153	0.878	1.089	NO	NO	62
2-4	75	25	2677	2645	2649	2657	17	3	2677	2645	1.153	1.149	0.674	NO	NO	2657
2-4	50	50	1052	1063	1041	1052	11	3	1063	1041	1.153	1.012	0.987	NO	NO	1052
2-4	30	70	90	93	88	90	3	3	93	88	1.153	1.039	0.956	NO	NO	90
2-5	75	25	2580	2416	2635	2544	114	3	2635	2416	1.153	0.801	1.121	NO	NO	2544
2-5	50	50	1103	1071	1100	1091	18	3	1103	1071	1.153	0.673	1.149	NO	NO	1091
2-5	30	70	289	288	277	285	7	3	289	277	1.153	0.667	1.150	NO	NO	285

Table 4.4. 28-Day Cube Strength Outlier Analysis for Cement 2 Combinations

Combination	Proportions		Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?		
			Test 1	Test 2	Test 3	Avg.											
Baseline 2	100	0	12299	12217	10609	11708	953	3	12299	10609	1.153	0.620	1.154	NO	YES		11708
2-1	75	25	10180	9864	10278	10107	217	3	10278	9864	1.153	0.788	1.125	NO	NO		10107
2-1	50	50	6321	7584	7818	7241	805	3	7818	6321	1.153	0.717	1.142	NO	NO		7241
2-1	30	70	3076	3065	3093	3078	14	3	3093	3065	1.153	1.067	0.916	NO	NO		3078
2-2	75	25	6159	6464	5124	5916	702	3	6464	5124	1.153	0.781	1.127	NO	NO		5916
2-2	50	50	3860	4589	4214	4221	364	3	4589	3860	1.153	1.009	0.991	NO	NO		4221
2-2	30	70	2681	2720	2540	2647	95	3	2720	2540	1.153	0.770	1.130	NO	NO		2647
2-3	75	25	8928	8828	8907	8888	53	3	8928	8828	1.153	0.763	1.132	NO	NO		8888
2-3	50	50	6835	6561	7154	6850	297	3	7154	6561	1.153	1.024	0.974	NO	NO		6850
2-3	30	70	2708	2700	2699	2702	5	3	2708	2699	1.153	1.153	0.629	YES	NO		2702
2-4	75	25	10209	10718	10351	10426	263	3	10718	10209	1.153	1.111	0.827	NO	NO		10426
2-4	50	50	7981	8100	7638	7906	240	3	8100	7638	1.153	0.807	1.119	NO	NO		7906
2-4	30	70	4339	4480	4480	4433	81	3	4480	4339	1.153	0.580	1.155	NO	YES		4433
2-5	75	25	8291	8069	7384	7915	473	3	8291	7384	1.153	0.796	1.122	NO	NO		7915
2-5	50	50	7923	8003	7557	7828	238	3	8003	7557	1.153	0.738	1.138	NO	NO		7828
2-5	30	70	4193	4151	4450	4264	162	3	4450	4151	1.153	1.145	0.704	NO	NO		4264

Figure 4.3, given below, shows the cube strengths after one day for Cement 2 in combination with each fly ash. As can be seen, the strength decreased significantly with increasing fly ash replacement levels.

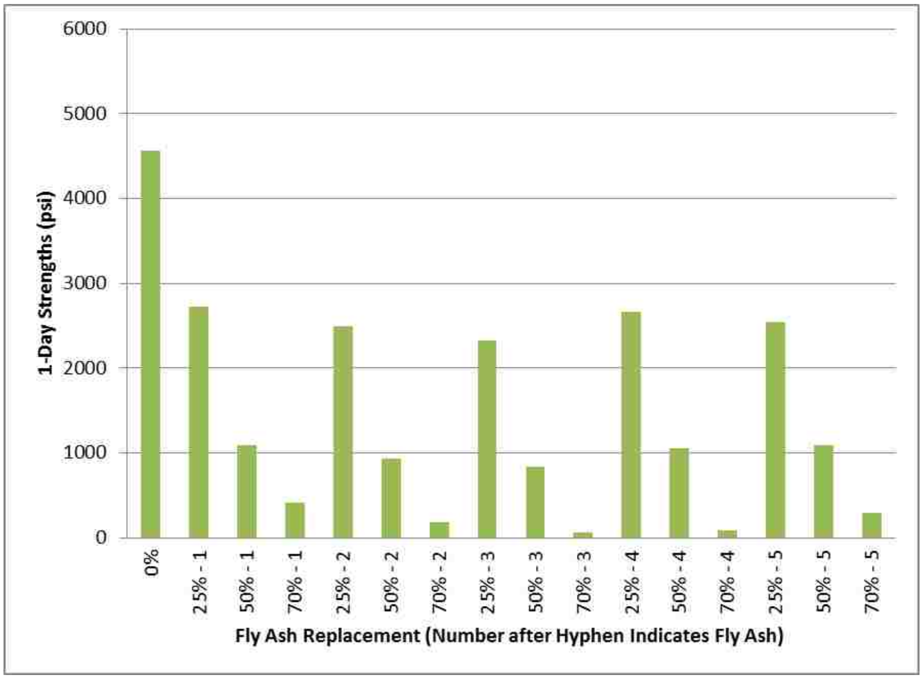

Figure 4.3. One-day Compressive Strengths for Cement 2 Combinations

Figure 4.4, below, shows the cube strengths after 28 days for Cement 2 in combination with each fly ash. Here, almost all of the fly ash mixtures show greatly decreased strengths compared to the baseline, with only combination 2-4 at 25 percent replacement being within 2000 psi of the baseline.

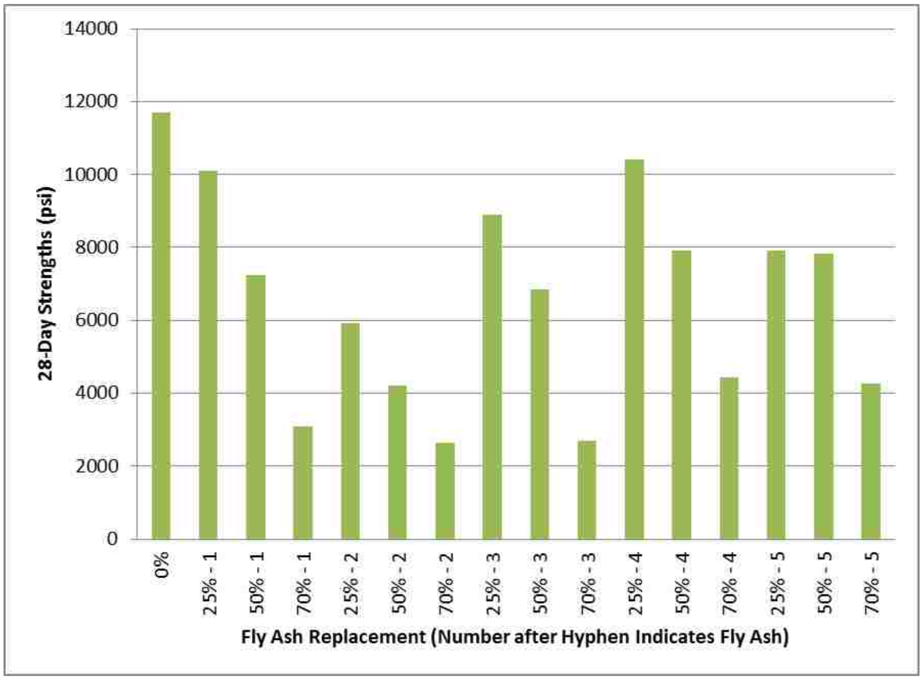

Figure 4.4. 28-day Compressive Strengths for Cement 2 Combinations

The outlier analyses for the one and 28 day cube strengths for the Cement 3 combinations are given, below, in Tables 4.5 and 4.6, respectively. The ASTM E 178 analysis indicated two possible outliers, but neither of these where discarded as actual outliers.

Table 4.5. 1-Day Cube Strength Outlier Analysis for Cement 3 Combinations

Combination	Proportions		Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 3	100	0	5052	5406	5088	5182	195	3	5406	5052	1.153	1.150	0.666	NO	NO	5182
3-1	75	25	3124	3135	3287	3182	91	3	3287	3124	1.153	1.153	0.633	NO	NO	3182
3-1	50	50	1233	1300	1281	1271	35	3	1300	1233	1.153	0.837	1.107	NO	NO	1271
3-1	30	70	289	316	319	308	16	3	319	289	1.153	0.681	1.148	NO	NO	308
3-2	75	25	3300	3746	3519	3522	223	3	3746	3300	1.153	1.007	0.993	NO	NO	3522
3-2	50	50	795	814	802	804	9	3	814	795	1.153	1.064	0.920	NO	NO	804
3-2	30	70	58	53	55	55	3	3	58	53	1.153	1.024	0.974	NO	NO	55
3-3	75	25	3152	2987	3324	3154	169	3	3324	2987	1.153	1.006	0.994	NO	NO	3154
3-3	50	50	912	923	915	917	5	3	923	912	1.153	1.124	0.792	NO	NO	917
3-3	30	70	23	24	21	22	1	3	24	21	1.153	0.908	1.072	NO	NO	22
3-4	75	25	3336	3005	2983	3108	198	3	3336	2983	1.153	1.153	0.632	NO	NO	3108
3-4	50	50	316	353	347	339	20	3	353	316	1.153	0.715	1.143	NO	NO	339
3-4	30	70	137	141	140	139	2	3	141	137	1.153	0.926	1.060	NO	NO	139
3-5	75	25	3413	3262	3310	3329	77	3	3413	3262	1.153	1.098	0.859	NO	NO	3329
3-5	50	50	936	930	911	926	13	3	936	911	1.153	0.785	1.126	NO	NO	926
3-5	30	70	141	131	140	137	5	3	141	131	1.153	0.645	1.152	NO	NO	137

Table 4.6. 28-Day Cube Strength Outlier Analysis for Cement 3 Combinations

Combination	Proportions		Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 3	100	0	12430	11309	11679	11806	571	3	12430	11309	1.153	1.092	0.870	NO	NO	11806
3-1	75	25	9235	10653	9769	9886	716	3	10653	9235	1.153	1.072	0.908	NO	NO	9886
3-1	50	50	7068	6931	6979	6993	69	3	7068	6931	1.153	1.084	0.886	NO	NO	6993
3-1	30	70	3647	4595	4715	4319	585	3	4715	3647	1.153	0.677	1.149	NO	NO	4319
3-2	75	25	10797	10371	10376	10514	244	3	10797	10371	1.153	1.155	0.588	YES	NO	10514
3-2	50	50	6864	7011	6278	6718	388	3	7011	6278	1.153	0.757	1.134	NO	NO	6718
3-2	30	70	3768	3832	3855	3818	45	3	3855	3768	1.153	0.814	1.116	NO	NO	3818
3-3	75	25	9491	10100	9438	9676	368	3	10100	9438	1.153	1.152	0.648	NO	NO	9676
3-3	50	50	6730	6798	6911	6813	91	3	6911	6730	1.153	1.071	0.909	NO	NO	6813
3-3	30	70	2326	2383	2346	2351	29	3	2383	2326	1.153	1.086	0.882	NO	NO	2351
3-4	75	25	10871	10499	9894	10421	493	3	10871	9894	1.153	0.912	1.069	NO	NO	10421
3-4	50	50	7450	7688	7937	7692	243	3	7937	7450	1.153	1.007	0.993	NO	NO	7692
3-4	30	70	5019	5644	5396	5353	315	3	5644	5019	1.153	0.925	1.061	NO	NO	5353
3-5	75	25	8594	9648	8732	8991	573	3	9648	8594	1.153	1.146	0.694	NO	NO	8991
3-5	50	50	5824	6302	6048	6058	239	3	6302	5824	1.153	1.020	0.978	NO	NO	6058
3-5	30	70	5455	5451	5522	5476	40	3	5522	5451	1.153	1.154	0.620	YES	NO	5476

The cube strengths at one day for combinations with Cement 3 are shown below in Figure 4.5. It can be seen that the strength decreased significantly with increasing fly ash replacement levels.

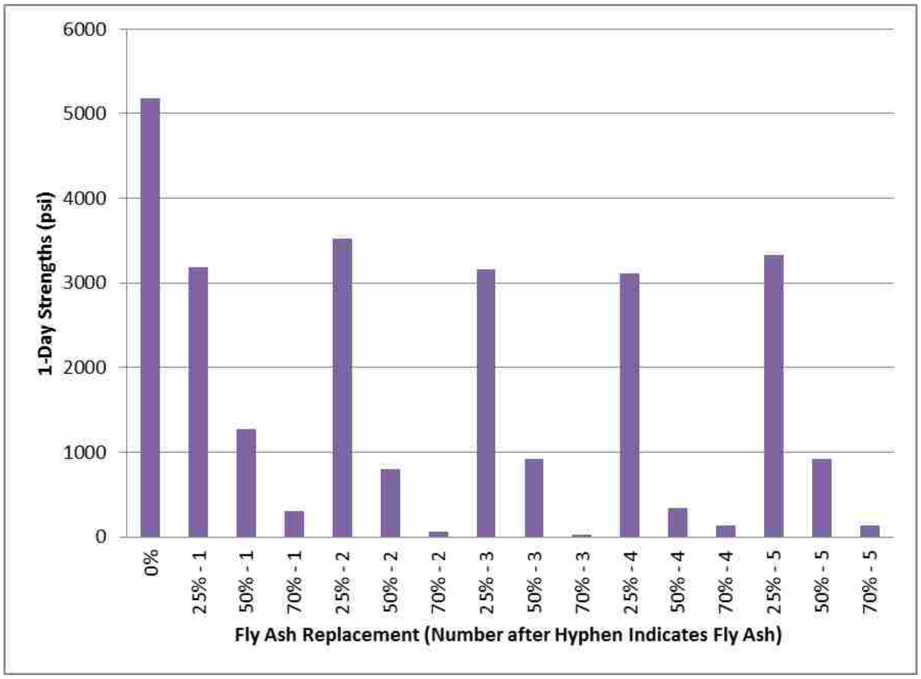

Figure 4.5. One-day Compressive Strengths for Cement 3 Combinations

Figure 4.6, below, shows the cube strengths after 28 days for Cement 3 in combination with each fly ash. These combinations show decreasing strength with increasing fly ash replacement, though not as severely as some of the combinations with Cement 2.

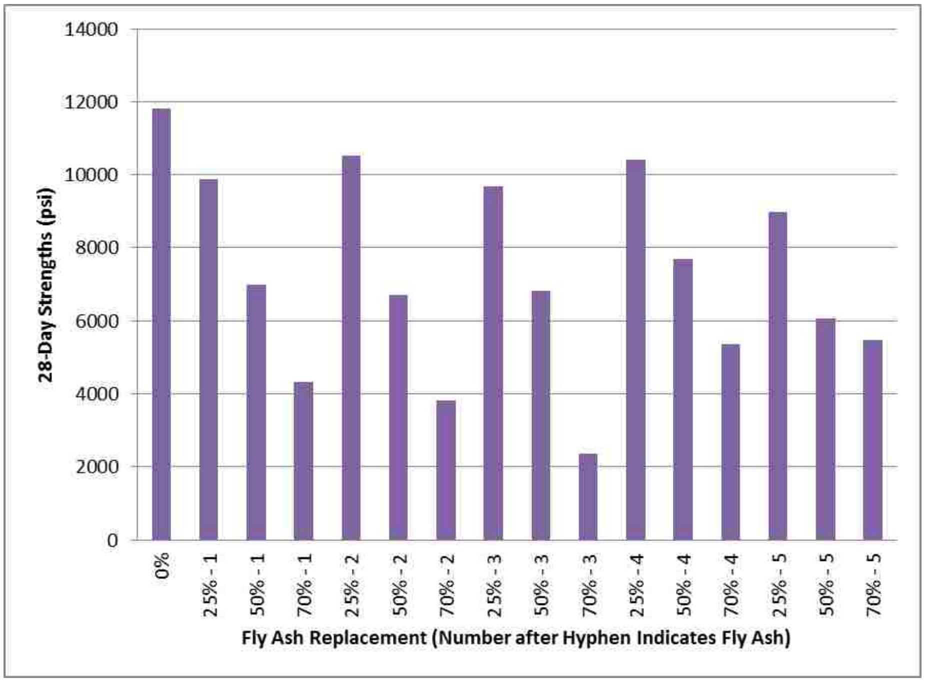

Figure 4.6. 28-day Compressive Strengths for Cement 3 Combinations

The outlier analyses for the one and 28 day cube strengths for the Cement 4 combinations are given, below, in Tables 4.7 and 4.8, respectively. The ASTM E 178 analysis indicated five possible outliers. Only Test 2 of the 1-day strengths for combination 4-4 with 25 percent fly ash was discarded as an actual outlier.

Table 4.7. 1-Day Cube Strength Outlier Analysis for Cement 4 Combinations

Combination	Proportions		Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 4	100	0	4037	4280	4025	4114	144	3	4280	4025	1.153	1.154	0.620	YES	NO	4114
4-1	75	25	3757	3799	3458	3671	186	3	3799	3458	1.153	0.686	1.147	NO	NO	3671
4-1	50	50	1925	1966	1914	1935	27	3	1966	1914	1.153	1.133	0.758	NO	NO	1935
4-1	30	70	678	628	689	665	32	3	689	628	1.153	0.742	1.137	NO	NO	665
4-2	75	25	3625	3632	3618	3625	7	3	3632	3618	1.153	1.006	0.994	NO	NO	3625
4-2	50	50	1298	1346	1261	1302	42	3	1346	1261	1.153	1.040	0.954	NO	NO	1302
4-2	30	70	286	271	274	277	8	3	286	271	1.153	1.137	0.743	NO	NO	277
4-3	75	25	2973	3503	3216	3230	265	3	3503	2973	1.153	1.027	0.971	NO	NO	3230
4-3	50	50	1376	1357	1358	1364	11	3	1376	1357	1.153	1.151	0.656	NO	NO	1364
4-3	30	70	320	308	320	316	7	3	320	308	1.153	0.587	1.155	NO	YES	316
4-4	75	25	3601	**3151**	3614	3455	264	3	3614	3151	1.153	0.600	1.154	NO	YES	3608
4-4	50	50	1511	1498	1440	1483	38	3	1511	1440	1.153	0.736	1.138	NO	NO	1483
4-4	30	70	333	341	321	332	10	3	341	321	1.153	0.926	1.060	NO	NO	332
4-5	75	25	3807	3761	3782	3783	23	3	3807	3761	1.153	1.019	0.979	NO	NO	3783
4-5	50	50	1617	1755	1693	1688	69	3	1755	1617	1.153	0.965	1.031	NO	NO	1688
4-5	30	70	535	527	536	533	5	3	536	527	1.153	0.630	1.153	NO	YES	533

Table 4.8. 28-Day Cube Strength Outlier Analysis for Cement 4 Combinations

Combination	Proportions		Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 4	100	0	11479	11002	11303	11261	241	3	11479	11002	1.153	0.903	1.075	NO	NO	11261
4-1	75	25	10736	10658	10210	10535	284	3	10736	10210	1.153	0.709	1.144	NO	NO	10535
4-1	50	50	8562	8701	8238	8500	238	3	8701	8238	1.153	0.843	1.105	NO	NO	8500
4-1	30	70	4246	4231	3954	4144	164	3	4246	3954	1.153	0.623	1.153	NO	YES	4144
4-2	75	25	10180	10425	9554	10053	449	3	10425	9554	1.153	0.829	1.111	NO	NO	10053
4-2	50	50	7813	8023	8192	8009	190	3	8192	7813	1.153	0.962	1.034	NO	NO	8009
4-2	30	70	3917	3893	3715	3842	110	3	3917	3715	1.153	0.682	1.148	NO	NO	3842
4-3	75	25	10102	9943	9719	9921	192	3	10102	9719	1.153	0.938	1.052	NO	NO	9921
4-3	50	50	7953	7849	7744	7849	105	3	7953	7744	1.153	0.997	1.003	NO	NO	7849
4-3	30	70	2884	2913	2893	2897	15	3	2913	2884	1.153	1.100	0.855	NO	NO	2897
4-4	75	25	11129	10070	10897	10698	556	3	11129	10070	1.153	0.773	1.129	NO	NO	10698
4-4	50	50	7924	8464	7878	8088	326	3	8464	7878	1.153	1.152	0.646	NO	NO	8088
4-4	30	70	4877	5012	4971	4953	69	3	5012	4877	1.153	0.851	1.102	NO	NO	4953
4-5	75	25	10048	10812	10716	10525	416	3	10812	10048	1.153	0.689	1.147	NO	NO	10525
4-5	50	50	8153	7880	8412	8148	266	3	8412	7880	1.153	0.991	1.008	NO	NO	8148
4-5	30	70	4907	4943	4929	4926	18	3	4943	4907	1.153	0.925	1.061	NO	NO	4926

Figure 4.7, below, shows the cube strengths after one day for Cement 4 in combination with each fly ash. The 25 percent combinations do not show as great of a decrease from the baseline compared to the 25 percent combinations with other cements. It should also be noted that the baseline mixture for Cement 4 had the lowest strength of all the baseline mixtures.

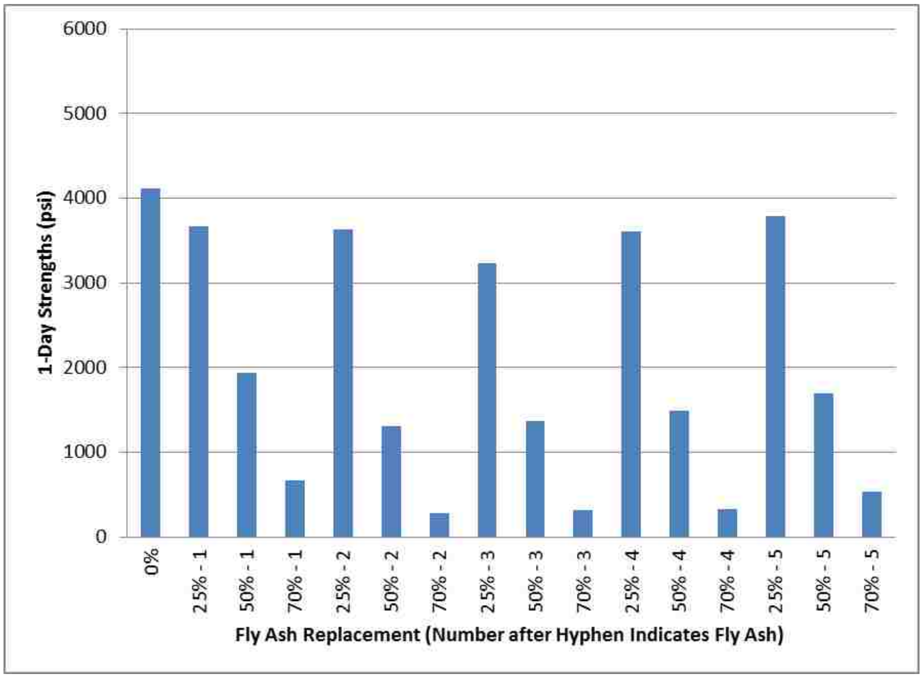

Figure 4.7. One-day Compressive Strengths for Cement 4 Combinations

The cube strengths at 28 days for combinations with Cement 4 are shown, below, in Figure 4.8. Here, the 25 percent fly ash mixtures show strengths within 1500 psi of the baseline. The 70 percent fly ash combinations continue to show significantly decreased strengths, when compared to the baseline.

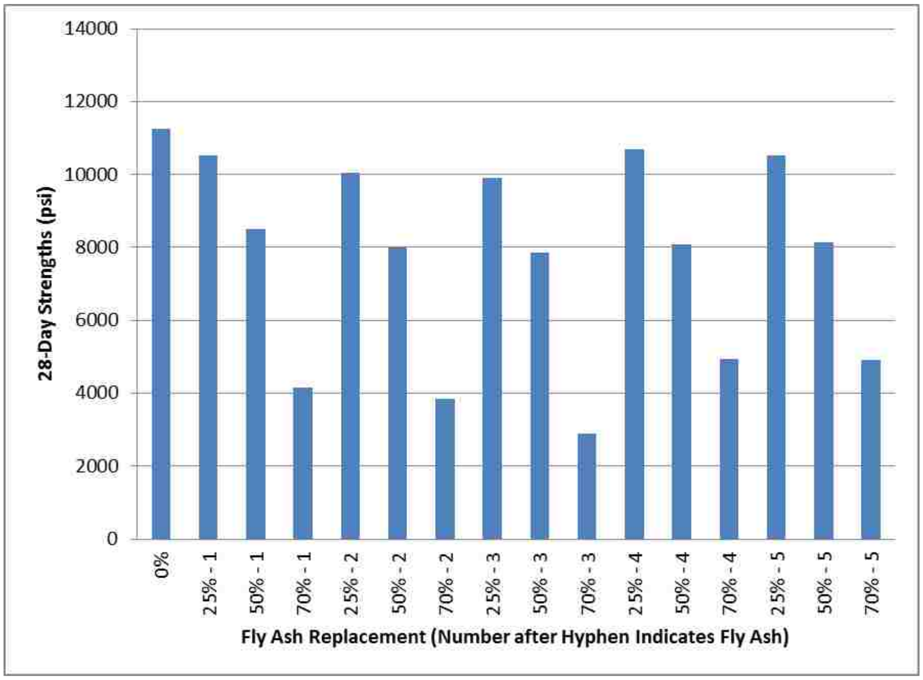

Figure 4.8. 28-day Compressive Strengths for Cement 4 Combinations

The outlier analyses for the one and 28 day cube strengths for the Cement 5 combinations are given, below, in Tables 4.9 and 4.10, respectively. The ASTM E 178 analysis indicated three possible outliers. Only Test 2 of the 28-day tests for combination 5-2 with 50 percent fly ash was discarded as an actual outlier.

Table 4.9. 1-Day Cube Strength Outlier Analysis for Cement 5 Combinations

Combination	Proportions		Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 5	100	0	4963	4588	4894	4815	200	3	4963	4588	1.153	0.741	1.137	NO	NO	4815
5-1	75	25	3196	3028	3209	3144	101	3	3209	3028	1.153	0.637	1.153	NO	NO	3144
5-1	50	50	1380	1408	1433	1407	26	3	1433	1380	1.153	0.983	1.017	NO	NO	1407
5-1	30	70	610	595	631	612	18	3	631	595	1.153	1.044	0.949	NO	NO	612
5-2	75	25	3054	3308	2845	3069	232	3	3308	2845	1.153	1.030	0.967	NO	NO	3069
5-2	50	50	934	1012	1049	998	59	3	1049	934	1.153	0.862	1.096	NO	NO	998
5-2	30	70	192	198	189	193	5	3	198	189	1.153	1.100	0.854	NO	NO	193
5-3	75	25	2735	2832	2663	2743	85	3	2832	2663	1.153	1.045	0.948	NO	NO	2743
5-3	50	50	874	852	847	858	14	3	874	847	1.153	1.139	0.733	NO	NO	858
5-3	30	70	109	102	104	105	3	3	109	102	1.153	1.133	0.759	NO	NO	105
5-4	75	25	2941	3034	2928	2968	58	3	3034	2928	1.153	1.147	0.687	NO	NO	2968
5-4	50	50	1086	1094	1124	1101	20	3	1124	1086	1.153	1.132	0.763	NO	NO	1101
5-4	30	70	96	98	106	100	5	3	106	96	1.153	1.147	0.689	NO	NO	100
5-5	75	25	3065	3014	3210	3096	102	3	3210	3014	1.153	1.119	0.808	NO	NO	3096
5-5	50	50	1207	1175	1159	1180	24	3	1207	1159	1.153	1.088	0.880	NO	NO	1180
5-5	30	70	310	334	330	325	13	3	334	310	1.153	0.729	1.140	NO	NO	325

Table 4.10. 28-Day Cube Strength Outlier Analysis for Cement 5 Combinations

Combination	Proportions		Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
			Test 1	Test 2	Test 3	Avg.										
Baseline 5	100	0	12240	12086	12295	12207	109	3	12295	12086	1.153	0.811	1.117	NO	NO	12207
5-1	75	25	11241	9997	12025	11087	1023	3	12025	9997	1.153	0.917	1.066	NO	NO	11087
5-1	50	50	7990	8061	7964	8005	50	3	8061	7964	1.153	1.115	0.817	NO	NO	8005
5-1	30	70	4230	4366	4366	4321	78	3	4366	4230	1.153	0.579	1.155	NO	YES	4321
5-2	75	25	11486	10830	10416	10911	539	3	11486	10416	1.153	1.066	0.917	NO	NO	10911
5-2	50	50	8006	**7388**	7997	7797	354	3	8006	7388	1.153	0.590	1.155	NO	YES	8001
5-2	30	70	3775	3683	3732	3730	46	3	3775	3683	1.153	0.980	1.019	NO	NO	3730
5-3	75	25	11659	11322	11462	11481	169	3	11659	11322	1.153	1.052	0.939	NO	NO	11481
5-3	50	50	7747	7551	7809	7703	135	3	7809	7551	1.153	0.793	1.123	NO	NO	7703
5-3	30	70	2398	2348	2490	2412	72	3	2490	2348	1.153	1.083	0.888	NO	NO	2412
5-4	75	25	12625	11969	11644	12079	500	3	12625	11644	1.153	1.092	0.872	NO	NO	12079
5-4	50	50	7813	7405	7656	7625	206	3	7813	7405	1.153	0.915	1.067	NO	NO	7625
5-4	30	70	4133	3913	4010	4019	110	3	4133	3913	1.153	1.037	0.958	NO	NO	4019
5-5	75	25	11871	11933	11217	11674	397	3	11933	11217	1.153	0.653	1.151	NO	NO	11674
5-5	50	50	8807	8652	8716	8725	78	3	8807	8652	1.153	1.053	0.936	NO	NO	8725
5-5	30	70	4324	4322	4281	4309	24	3	4324	4281	1.153	0.613	1.154	NO	YES	4309

Figure 4.9, below, shows the cube strengths after one day for Cement 5 in combination with each fly ash. It can be seen that strength decreased significantly with increasing fly ash replacement levels.

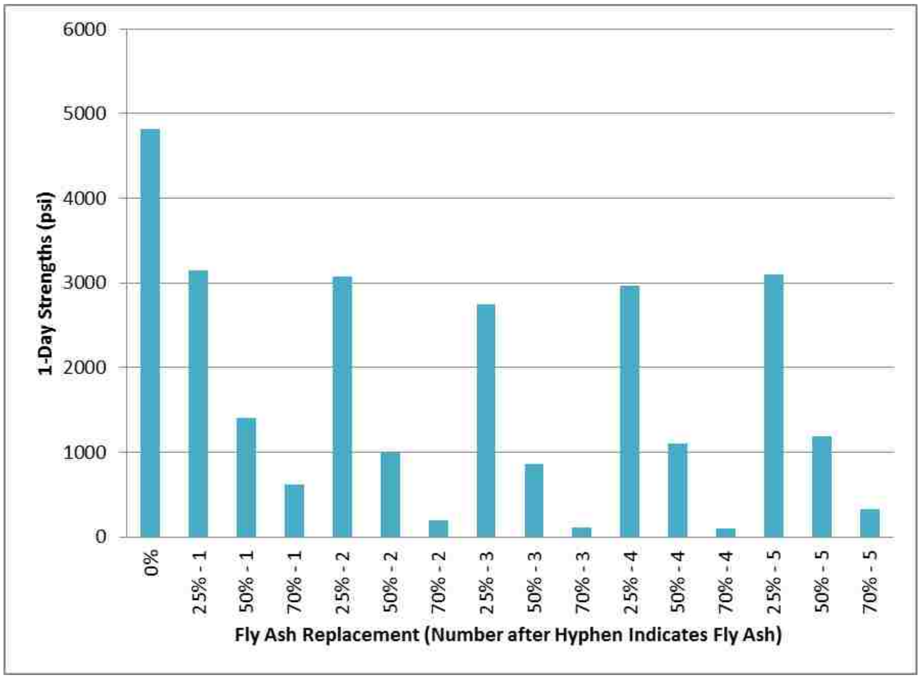

Figure 4.9. One-day Compressive Strengths for Cement 5 Combinations

The cube strengths at 28 days for combinations with Cement 5 are shown, below, in Figure 4.10. The 25 percent fly ash combinations shows strengths within 1500 psi of the baseline and the 25 percent combination with Fly Ash 4 is only 128 psi less than the baseline. The 50 and 70 percent fly ash combinations continue to show significantly decreased strength levels, compared to the baseline.

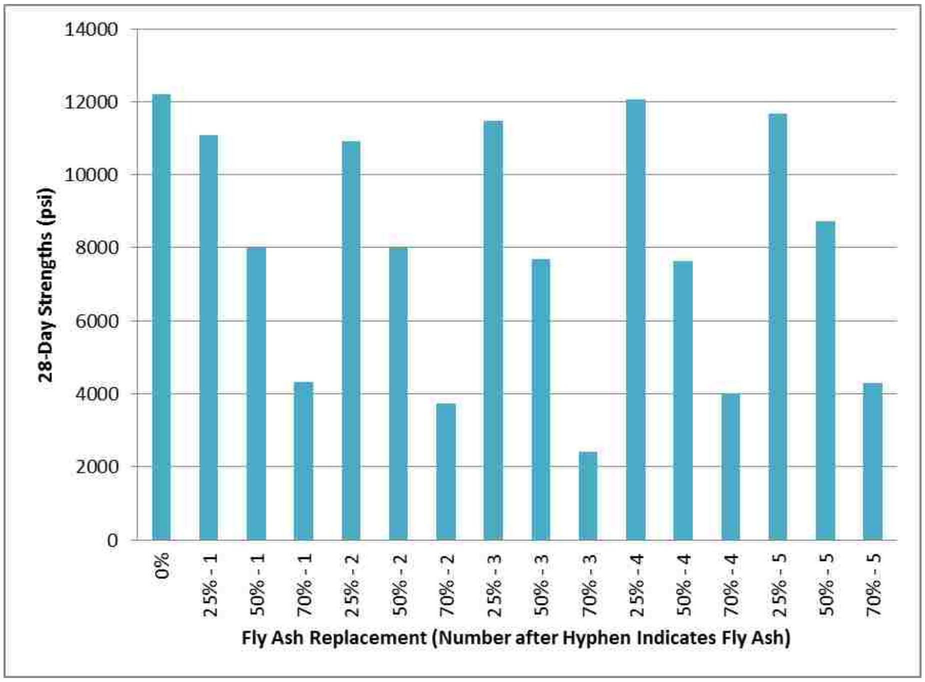

Figure 4.10. 28-day Compressive Strengths for Cement 5 Combinations

It can be seen from the results above that increasing fly ash contents leads to significant reductions in one day strengths. While these strengths are still significantly reduced at 28 days for mixtures with 50 and 70 percent fly ash, noticeable strength gain has occurred since the testing at one day. At 28 days, all of the mixtures with 50 percent fly ash had strengths between approximately 6000 and 8000 psi, except for Cement 2 in combination with Fly Ash 2 which had a compressive strength closer to 4000 psi. This shows that particular cement-fly ash combinations may perform much differently than combinations of similar materials.

The strength gain behavior shown in the results above is typical for mixtures containing a pozzolan and correlates well with the results of previous researchers (Jiang et al., 1999; Bentz et al., 2010). During the first day, the pozzolanic reaction has not begun to contribute to the strength of the paste. Between one and 28 days, the slow pozzolanic reaction has begun to contribute to the strength of the paste. Also, if the increased aluminate levels have created a sulfate imbalance, rapid aluminate hydration, in combination with a lack of sulfate, may have led to much slower silicate hydration. This would lead to significantly slower strength gain.

4.1.2. Semi-adiabatic Calorimetry. Calculations were performed on the raw temperature log data, from the F-Cal 4000, as discussed in the Laboratory Investigation. These included the calculation of the Signal-to-Noise Ratios (S/N) for the individual temperature logs and the prediction of setting times by two methods.

The three Signal-to-Noise Ratios for each test were used as a measure of resolution of the test and as a means of performing an outlier analysis on the temperature logs. According to a draft ASTM for evaluating hydration using thermal measurements (2011), the signal-to-noise ratio “shall be a minimum of 5.0.” While a few of the mixtures had S/N less than 5.0, it was determined that this was due to low signal values resulting from mixtures which produced little heat, rather than high levels of noise which would have significantly affected the results. The outlier analysis was performed using ASTM E 178, which indicated three possible outliers. These values were indicated falsely as outliers because the other two values in each data set were extremely similar. Due to this, none of the values were discarded as outliers. The outlier analysis of the calorimetry results can be found in Appendix B.

Following the evaluation of the S/N for each temperature log, the three logs were averaged and then corrected for the inert specimen log to obtain the corrected average thermal curve for each mixture. The values determined from the thermal curve for each mixture included the maximum temperature rise (ΔT_{max}), the time at which the maximum temperature rise occurs, and the main hydration response rise (M). The predicted initial and final set times were also calculated by the Fractions Method and Derivatives Method. These values are summarized in Tables 4.11 through 4.15, below, for each mixture.

As can be seen in these results, M decreases with increasing fly ash replacement for most combinations. Two exceptions are combination 1-5 with 70 percent fly ash and combination 3-5 with 70 percent fly ash.

The predicted final set by the Percentage Method is the time at which 50 percent of the main hydration response rise has occurred. This value was used to compare the placement of the curves with respect to time. For the most part, with increasing fly ash replacement the predicted final set by the Percentage Method occurs at a later time for fly ash replacements up to 50 percent. The only exception to this is combination 4-5 at 50 percent fly ash replacement, which has a predicted final set 22 minutes earlier than the combination with 25 percent fly ash replacement. Many of the combinations with 70 percent fly ash replacement showed predicted final set times that occurred earlier than at 50 percent fly ash replacement.

These results correlate well with the findings of Schindler and Folliard (2003) and Bentz (2010), who noted that up to 50 percent cement replacement with Class C fly ash resulted in retarded silicate hydration and a decrease in the main hydration peak, as illustrated in Figure 4.11, below.

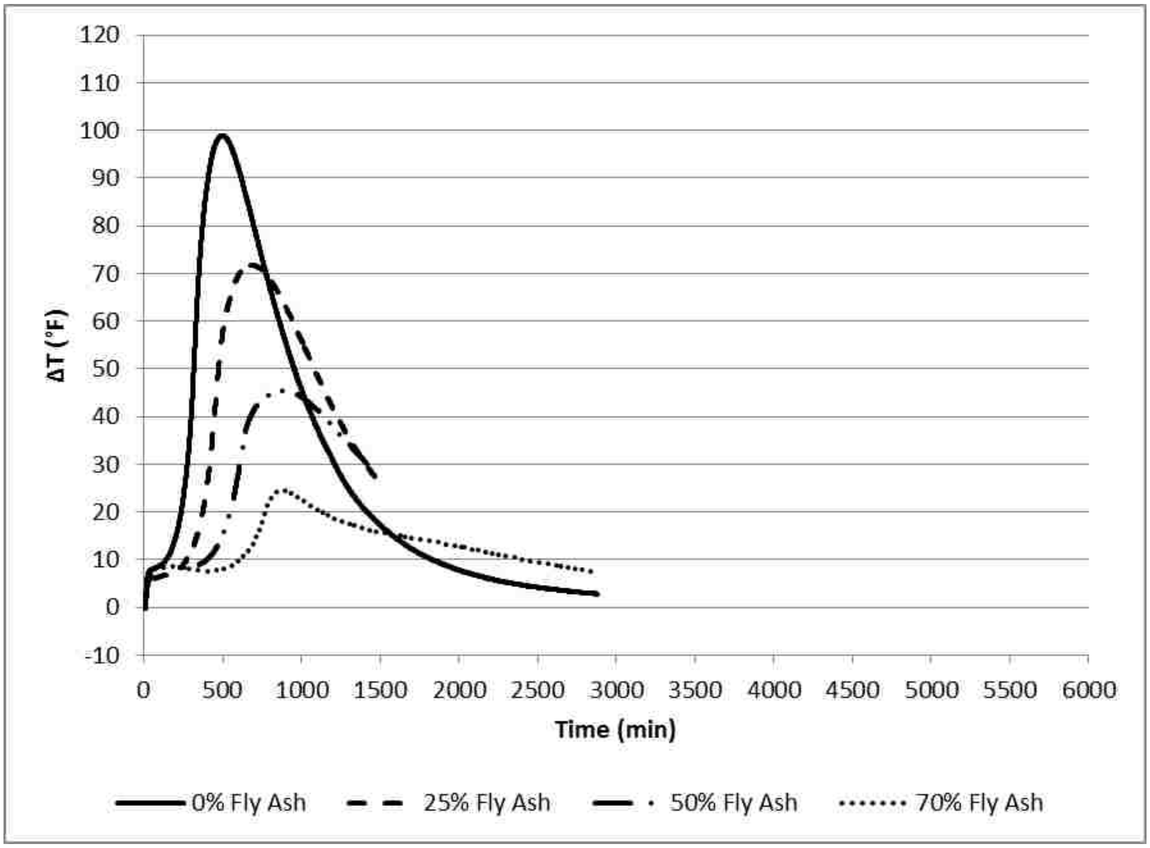

Figure 4.11. Typical Series of Thermal Curves Showing Delayed Silicate Hydration and Decreased Main Hydration Peaks

The earlier predicted set times seen with the 70 percent fly ash mixtures, as shown in Figure 4.12, below, may be explained by sulfate imbalances, which could lead to rapid aluminate hydration and flash setting behavior. In this case the peak from which the setting time calculations were made would have been the aluminate hydration peak.

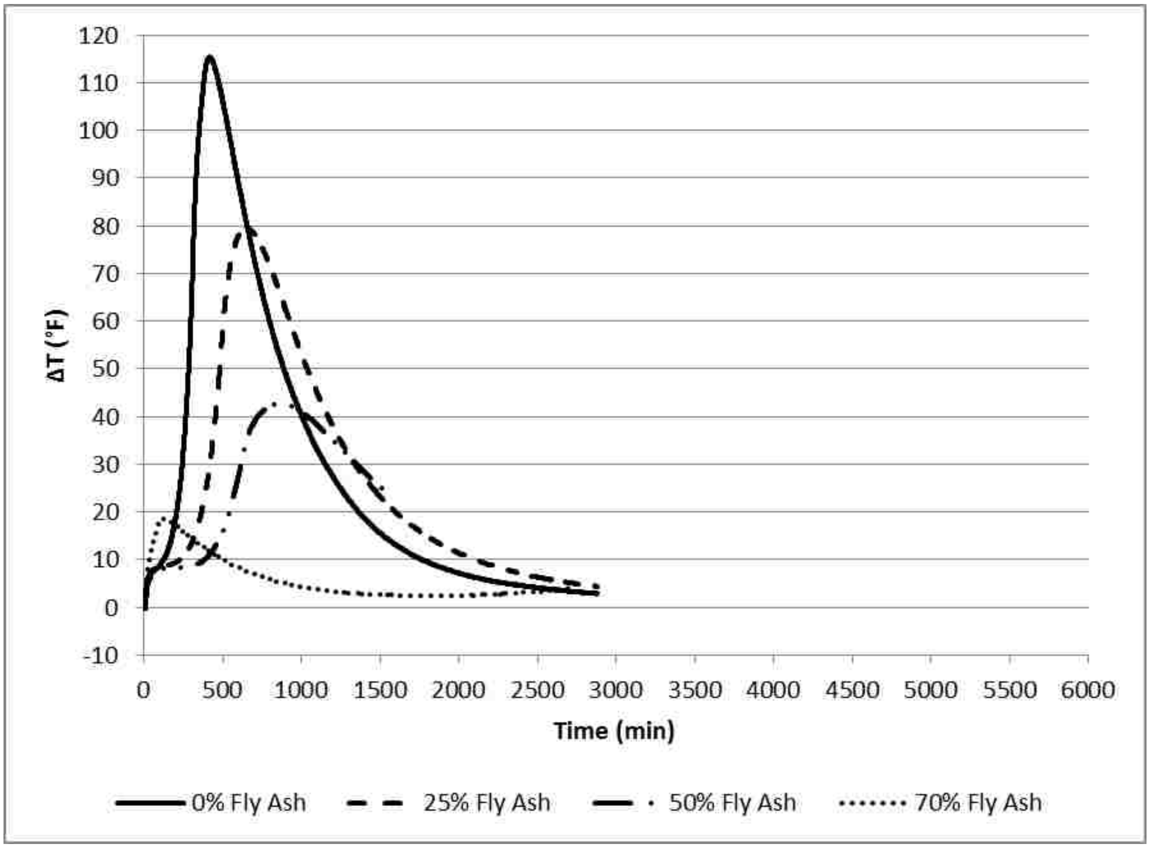

Figure 4.12. Series of Thermal Curves Showing Accelerated Hydration at 70% Fly Ash Replacement

Table 4.11. Thermal Curve Data for Cement 1 Combinations

Combination	Proportions		Curve Type	ΔT_{max} (°F)	Time at ΔT_{max} (min)	M (°F)	Setting Time Predictions			
	Cement (%)	Fly Ash (%)					Percentage Method		Derivatives	
							Initial Set (min)	Final Set (min)	Initial Set (min)	Final Set (min)
Baseline 1	100	0	A	98.91	501	91.62	264	321	303	325
1-1	75	25	A	71.81	685	65.54	369	445	246	458
1-1	50	50	A	45.50	883	37.46	506	592	577	613
1-1	30	70	B	24.45	882	16.85	641	730	755	769
1-2	75	25	A	75.56	713	68.02	354	426	385	420
1-2	50	50	C	31.59	1256	22.73	488	571	510	562
1-2	30	70	B	10.05	599	2.47	493	519	499	519
1-3	75	25	A	72.96	749	63.27	392	469	444	471
1-3	50	50	C	33.58	1050	24.27	477	572	512	560
1-3	30	70	G	22.25	94	12.50	26	41	33	43
1-4	75	25	A	78.15	829	69.00	425	500	443	478
1-4	50	50	D	20.04	642	9.30	445	511	513	530
1-4	30	70	G	19.99	197	9.32	61	104	77	117
1-5	75	25	A	83.17	756	72.22	391	463	410	443
1-5	50	50	D	19.41	597	7.24	426	486	491	500
1-5	30	70	G	21.68	204	14.30	64	108	70	110

Table 4.12. Thermal Curve Data for Cement 2 Combinations

Combination	Proportions		Curve Type	ΔT_{max} (°F)	Time at ΔT_{max} (min)	M (°F)	Setting Time Predictions			
	Cement (%)	Fly Ash (%)					Percentage Method		Derivatives	
							Initial Set (min)	Final Set (min)	Initial Set (min)	Final Set (min)
Baseline 2	100	0	A	96.40	521	91.84	305	374	366	386
2-1	75	25	A	81.29	705	74.01	380	455	448	468
2-1	50	50	A	53.69	763	45.27	455	548	550	569
2-1	30	70	B	30.52	819	22.03	573	671	696	711
2-2	75	25	A	80.25	714	74.55	374	452	436	457
2-2	50	50	A	47.50	822	41.16	438	520	508	528
2-2	30	70	E	17.39	757	10.42	541	612	619	638
2-3	75	25	A	72.43	644	65.40	376	452	436	464
2-3	50	50	A	38.92	861	31.75	462	552	476	575
2-3	30	70	E	11.41	627	2.86	471	526	439	539
2-4	75	25	A	83.87	744	75.83	413	484	461	482
2-4	50	50	C	45.47	927	35.42	481	556	520	548
2-4	30	70	E	14.71	588	3.44	471	512	381	527
2-5	75	25	A	85.44	738	77.19	414	486	458	483
2-5	50	50	C	49.62	977	39.13	508	581	547	565
2-5	30	70	-----	-----	-----	-----	-----	-----	-----	-----

Table 4.13. Thermal Curve Data for Cement 3 Combinations

Combination	Proportions		Curve Type	ΔT_{max} (°F)	Time at ΔT_{max} (min)	M (°F)	Setting Time Predictions			
	Cement (%)	Fly Ash (%)					Percentage Method		Derivatives	
							Initial Set (min)	Final Set (min)	Initial Set (min)	Final Set (min)
Baseline 3	100	0	A	111.88	413	104.13	228	284	279	292
3-1	75	25	A	94.29	622	84.57	364	427	412	428
3-1	50	50	A	55.64	839	44.21	512	581	571	589
3-1	30	70	B	28.24	767	16.15	582	652	655	669
3-2	75	25	A	94.90	632	87.45	369	429	399	422
3-2	50	50	C	43.65	1010	35.26	521	582	547	573
3-2	30	70	G	12.26	664	5.09	546	576	556	569
3-3	75	25	A	89.61	635	80.68	364	428	409	425
3-3	50	50	C	39.26	966	29.80	506	583	544	582
3-3	30	70	F	12.15	400	1.86	179	316	259	366
3-4	75	25	A	101.17	664	92.04	413	469	433	451
3-4	50	50	D	25.77	660	14.02	500	550	533	561
3-4	30	70	F	20.99	185	13.23	38	86	73	149
3-5	75	25	A	99.82	703	88.10	446	505	456	477
3-5	50	50	D	24.73	607	12.11	452	493	474	492
3-5	30	70	G	23.04	232	12.19	62	116	71	73

Table 4.14. Thermal Curve Data for Cement 4 Combinations

Combination	Proportions		Curve Type	ΔT_{max} (°F)	Time at ΔT_{max} (min)	M (°F)	Setting Time Predictions			
	Cement (%)	Fly Ash (%)					Percentage Method		Derivatives	
							Initial Set (min)	Final Set (min)	Initial Set (min)	Final Set (min)
Baseline 4	100	0	A	108.25	486	102.35	288	353	352	376
4-1	75	25	A	99.92	567	90.53	306	374	365	390
4-1	50	50	A	58.97	785	50.61	475	573	579	599
4-1	30	70	B	35.17	794	25.68	537	640	669	687
4-2	75	25	A	81.61	713	77.95	412	513	517	542
4-2	50	50	A	57.41	837	50.65	483	578	575	598
4-2	30	70	E	17.74	885	12.68	591	696	721	743
4-3	75	25	A	78.41	705	71.82	431	526	535	555
4-3	50	50	A	45.85	917	37.34	545	642	614	671
4-3	30	70	E	16.53	1489	8.42	561	649	623	662
4-4	75	25	A	106.63	649	97.37	391	462	449	466
4-4	50	50	C	73.23	980	61.22	477	553	514	536
4-4	30	70	E	23.63	1150	10.70	503	570	555	583
4-5	75	25	A	91.93	791	86.69	474	563	546	569
4-5	50	50	A	72.94	881	62.02	463	541	515	540
4-5	30	70	E	19.85	681	7.17	512	562	561	574

Table 4.15. Thermal Curve Data for Cement 5 Combinations

Combination	**Proportions**		**Curve Type**	**ΔT_{max} (°F)**	**Time at ΔT_{max} (min)**	**M (°F)**	**Setting Time Predictions**			
							Percentage Method		**Derivatives**	
	Cement (%)	**Fly Ash (%)**					**Initial Set (min)**	**Final Set (min)**	**Initial Set (min)**	**Final Set (min)**
Baseline 5	100	0	A	115.40	414	109.28	237	298	299	313
5-1	75	25	A	83.82	678	78.40	382	471	471	494
5-1	50	50	A	55.05	844	48.54	494	605	615	639
5-1	30	70	B	29.81	868	21.08	619	720	754	766
5-2	75	25	A	91.18	674	84.30	372	452	441	461
5-2	50	50	A	45.15	909	39.35	488	583	568	599
5-2	30	70	E	16.81	789	10.55	548	632	386	672
5-3	75	25	A	79.41	657	71.89	378	464	470	490
5-3	50	50	A	42.77	854	34.77	487	584	610	625
5-3	30	70	G	18.46	129	9.85	36	58	41	51
5-4	75	25	A	85.66	788	79.33	446	534	512	543
5-4	50	50	C	46.15	980	35.01	544	625	598	628
5-4	30	70	G	14.80	530	1.96	448	476	434	493
5-5	75	25	A	91.67	743	85.84	434	518	493	518
5-5	50	50	C	50.45	1063	39.70	533	617	570	700
5-5	30	70	-----	-----	-----	-----	-----	-----	-----	-----

Along with the data discussed previously, the thermal curve for each combination was categorized as one of seven curve types based on the general shape of the curve. The general curve shapes were chosen as those which commonly occurred and had distinct attributes from the other curve shapes. It should be noted that since the specimens were not inserted into the calorimeter until approximately 10 minutes following the start of hydration, the dormant period may or may not be well defined. Also, each curve initially shows a sharp rise in temperature. This is due to the rapid increase in temperature of the thermistors, which were at the ambient temperature prior to coming in contact with the hydrating specimens that had already begun to rise in temperature.

In Appendix C, plots are included that show the curve for the baseline mixture, along with the curves for the three fly ash replacement levels of each portland cement and fly ash combination. The curve type for each mixture has been included here in Tables

4.11 through 4.15, above. Examples of the curve shapes are shown below in Figures 4.13 through 4.19. Defining characteristics of the seven curve shapes are as follows:

- Type A: Typical curve shape for normally hydrating portland cement. The dormant period may or may not be well-defined before the main hydration temperature rise. The main hydration temperature rise is, for the most part, symmetrical about a vertical line at the time where the peak of the curve occurs.
- Type B: Extremely low magnitude, but abrupt, peak following the dormant period. This curve is not symmetrical, as Type A was, but shows a sharp rise before the peak with a lower slope descent following the peak.
- Type C: Lower magnitude and wider overall shape of the main hydration curve, with an abrupt change in the rate of temperature rise occurring prior to the peak of the curve.
- Type D: Two separate peaks following a dormant period. The second peak is significantly larger in magnitude and occurs shortly after the first peak.
- Type E: Abrupt, but low magnitude, rise following a dormant period. Following the rise, the temperature may remain nearly unchanged for a period or show two peaks of similar magnitudes. The second peak occurs shortly after the first peak and may indicate two overlapping hydration peaks.
- Type F: Immediate, but low magnitude, rise which is not followed by a second peak and appears to approach a ΔT of zero.
- Type G: Abrupt, but low magnitude, initial rise followed by an extended dormant period and a low magnitude second rise. These curves do not approach a ΔT of zero during the dormant period.

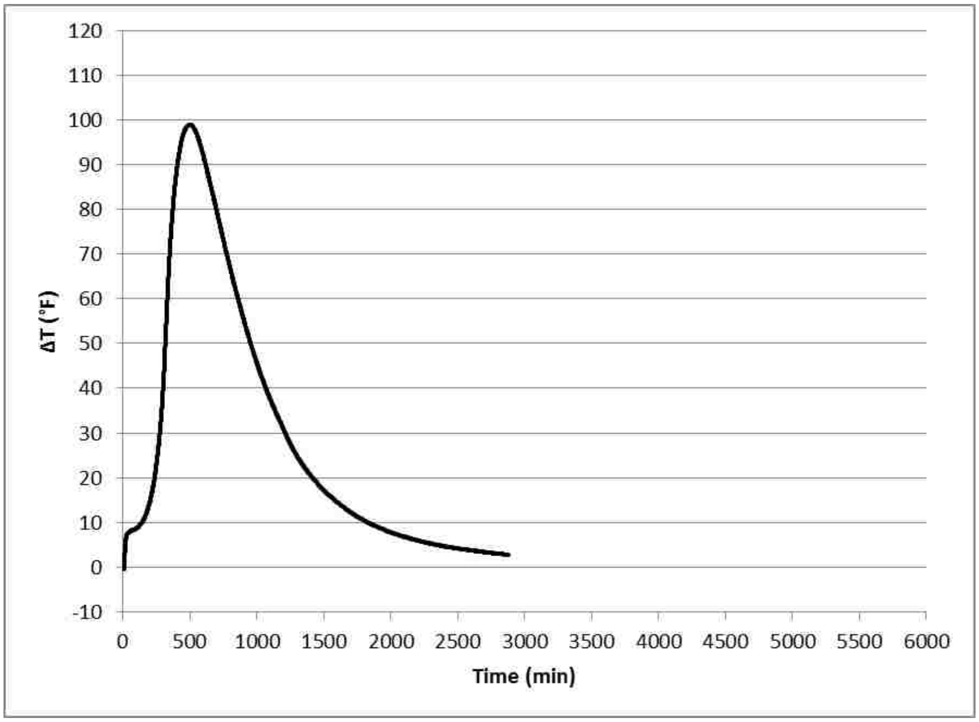

Figure 4.13. Example of Type A Thermal Curve Shape

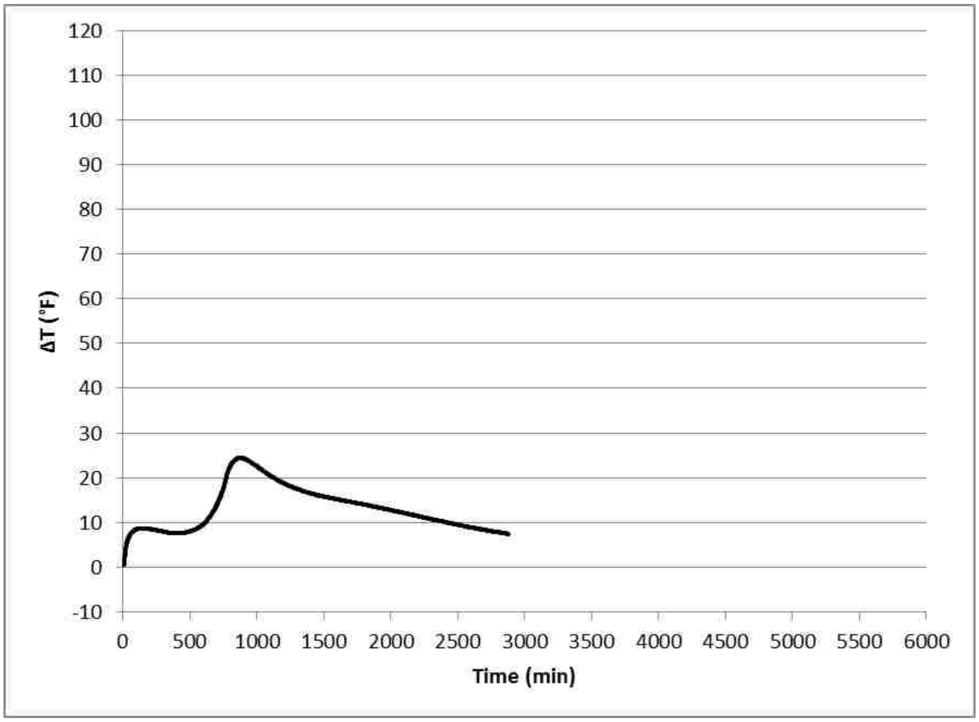

Figure 4.14. Example of Type B Thermal Curve Shape

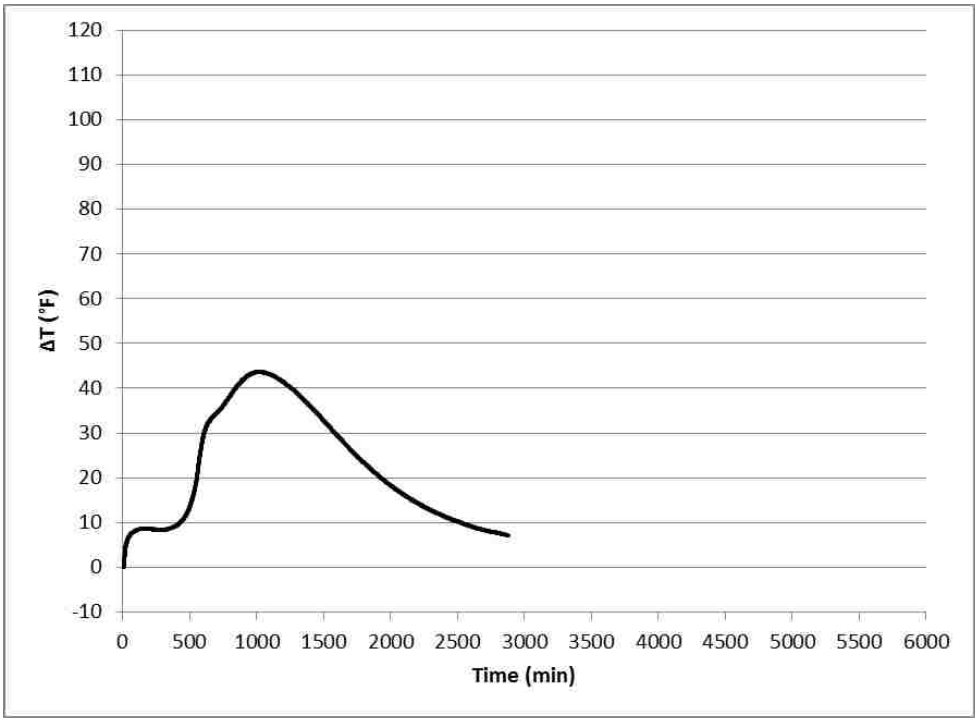

Figure 4.15. Example of Type C Thermal Curve Shape

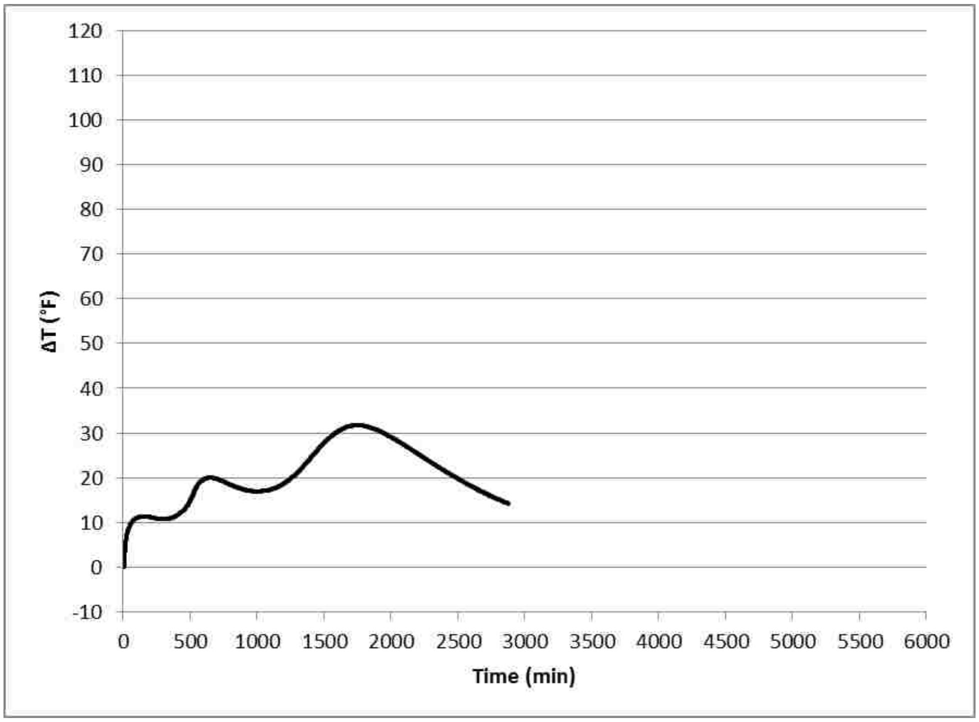

Figure 4.16. Example of Type D Thermal Curve Shape

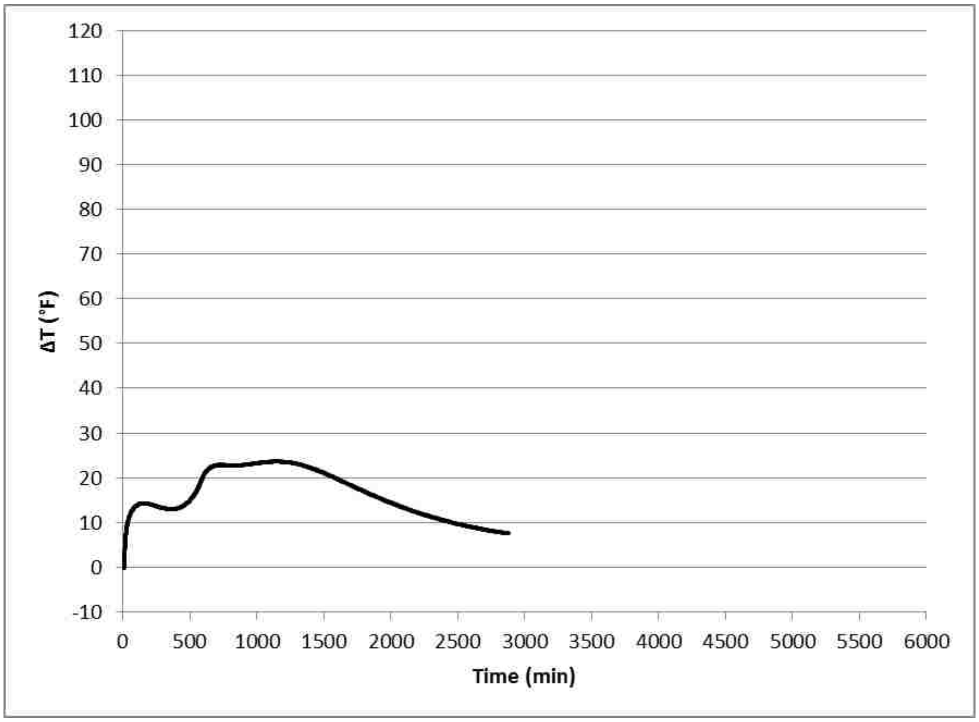

Figure 4.17. Example of Type E Thermal Curve Shape

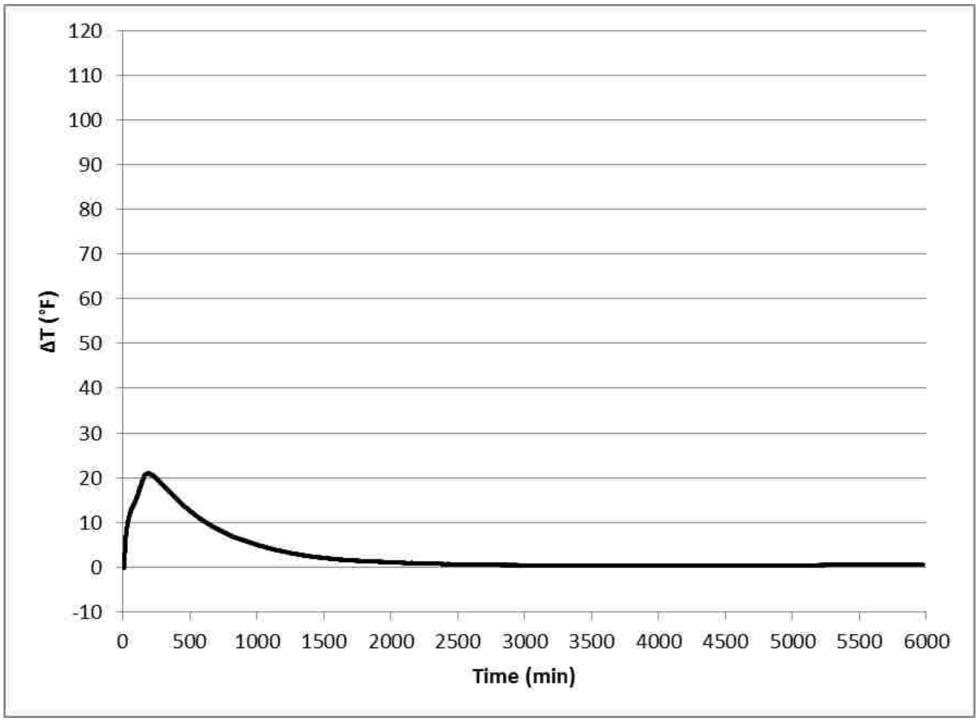

Figure 4.18. Example of Type F Thermal Curve Shape

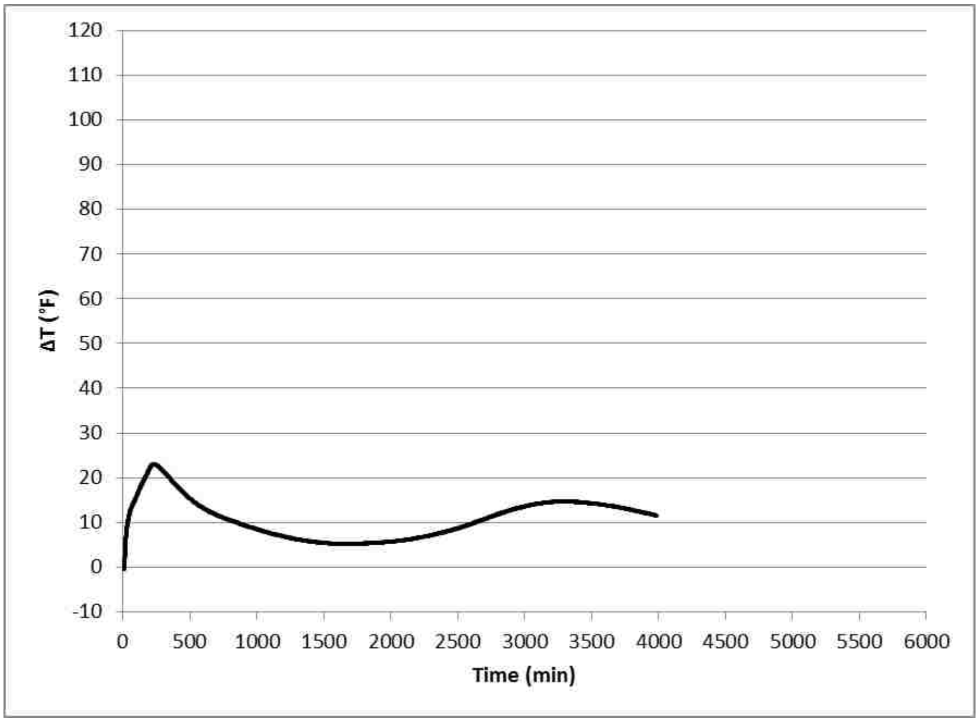

Figure 4.19. Example of Type G Thermal Curve Shape

To explain the curve shapes shown above, a few points which should first be emphasized include: (1) the role of sulfate in hydration; (2) the effect of rapid aluminate hydration on the cementitious system; and (3) the effect of alkali content. (1) As discussed by Lerch (1946), aluminates are less soluble and silicates are more soluble in solutions containing sulfates. This results in aluminate hydration being retarded and silicate hydration being accelerated once the sulfates go into solution. Also, it is thought that rapidly forming ettringite around the particles may assist in slowing the aluminate reactions. When available sulfate is depleted form the system, renewed aluminate hydration will occur rapidly and silicate hydration will occur at a significantly slower rate. (2) If hydration of the aluminates is not controlled at early ages by sulfate, calcium will be rapidly consumed by the aluminates. This results in a lack of available calcium for silicate hydration and will result in extremely slow or nonexistent silicate hydration (Roberts & Taylor, 2007). (3) According to Lerch (1946), high alkali concentrations can result in more rapid reactions between the aluminates and gypsum. This may account for differences in the heat evolution characteristics of systems which may otherwise appear to be chemically similar.

Type A curves result from normally hydrating paste systems. When water first comes in contact with the cement, aluminates go into solution and begin reacting rapidly. As sulfate goes into solution, the solubility of the aluminates decreases which results in a dormant period. A contribution to this effect is also made by the formation of ettringite around the particles. Following the dormant period, the high calcium concentration of the pore solution causes the silicates to begin hydrating, which is accompanied by a large rise in temperature. This rise reaches a peak when the hydration products have formed around the particles sufficiently to slow further hydration, at which point the rate of heat evolution decreases. With the addition of fly ash, Type A curves will decrease in magnitude and occur at later times, because the content of the more reactive cement has been decreased. xThis curve type is associated with fly ash replacement levels of 0 and 25 percent. Also, some 50 percent fly ash mixtures may result in Type A curves.

Type B and E curves occur due to similar processes. In the case of Type B curves, the sulfate has been consumed and the remaining aluminates being reacting rapidly, which results in significant heat generation. After the aluminate peak occurs, the thermal curve decreases abnormally slowly. This may be caused by extremely slow silicate hydration, which would result from a lack of calcium and sulfate. Type E curves suggest similar behavior, but with less severe sulfate depletion. The plateau shape of these curves may be the result of partially overlapping aluminate and silicate hydration peaks. Both Type B and Type E curves are associated with 70 percent fly ash mixtures.

Type C, D, and G curves can be viewed as increasingly severe forms of the same behavior. For Type C curves, a lack of sulfate results in a rapid aluminate hydration rise, which occurs during hydration of the silicates. Sufficient calcium is still available for silicate hydration, but it is retarded by a lack of sulfate, increasing the period over which the curve occurs. Type D curves may result from a similar process, but with a more delayed silicate peak due to an even greater lack of sulfate. Type G curves can be attributed to a severe lack of sulfate, resulting in extremely rapid aluminate hydration followed by extremely delayed and suppressed silicate hydration. So, as unmet sulfate demand increases, the aluminate peak occurs earlier and the silicate peak occurs later. Type C and D curves occur for mixtures with 50 percent fly ash, while Type G curves occur for 70 percent fly ash mixtures.

Type F curves result from conditions similar to those seen with Type G curves, except that silicate hydration is severely suppressed or nonexistent. This results from the consumption of the available calcium by the aluminates during early hydration. As can be seen, the curve approaches zero following the aluminate reactions, which indicates that very little or no heat is being generated by the paste. Type F curves are associated with mixtures containing 70 percent fly ash.

Shown below, in Figure 4.20, are all of the previously discussed curve types on a single plot for comparison to a typical, Type A, curve. When compared to Type A, Type

B curves have a slightly delayed and severely decreased peak. Type C curves are significantly shorter, broader, and have a “shoulder” occurring before the peak of the curve. The peak for this curve type is significantly delayed, when compared to a Type A. Type D curves have two separate peaks, where the second peak is larger than the first and occurs after the first. Here, the first peak may occur at a similar time as the main peak of a Type A curve. Type E curves have a delayed, but abrupt, low magnitude rise. Following the rise, the temperature may show a plateau or two extremely close peaks of similar magnitude. Type F curves show a sharp, low magnitude peak, which occurs earlier than the peak of a Type A curve. Following the peak, the ΔT appears to approach zero. Type G curves have an abrupt, early peak, which is similar to Type F and is followed by an extended dormant period. Following the dormant period, a second peak occurs at a time much later than the peaks of the other curve types.

4.1.3. Miniature Slump. The miniature slump test was performed for each mixture at 2, 5, 15, 30, and 45 minutes after mixing began. Four diameter measurements were taken for each miniature slump test and then averaged. The average diameter was used to calculate the area of the paste pat. These values are summarized for each mixture in Tables 4.16 through 4.20, below. It can been seen from the results that as fly ash replacement increases the pat area typically increases considerably at 2, 5, and 15 minutes. The results also show that the miniature slump area decreases more rapidly over time with increasing fly ash levels. From 15 to 45 minutes, the miniature slump results for a given combination, at 50 and 70 percent fly ash replacement, tend to converge on the baseline mixture results and either remain above the baseline or drop below the baseline. The 25 percent fly ash mixtures generally remain higher than the baseline. A typical plot of miniature slump pat area over time for increasing fly ash replacement levels is shown below in Figure 4.21. Plots of the results for all mixtures can be found in Appendix E.

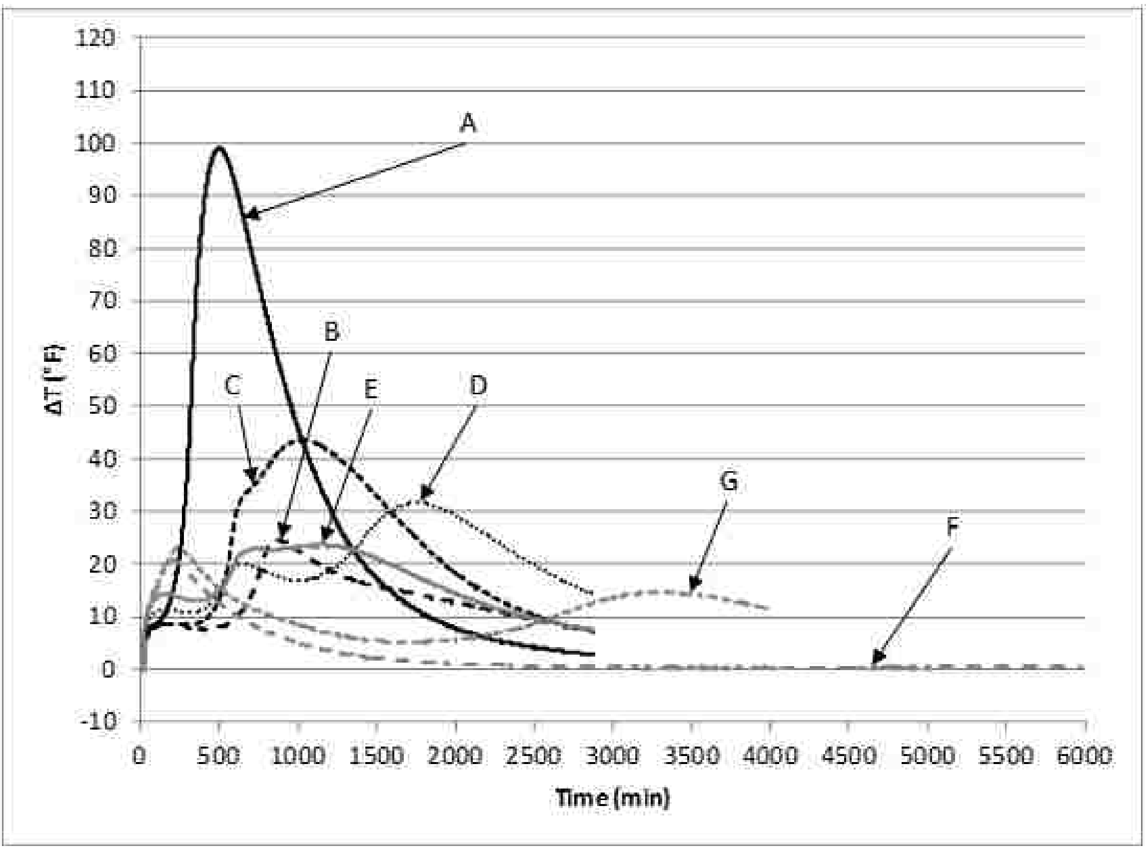

Figure 4.20. Comparison of Curve Types

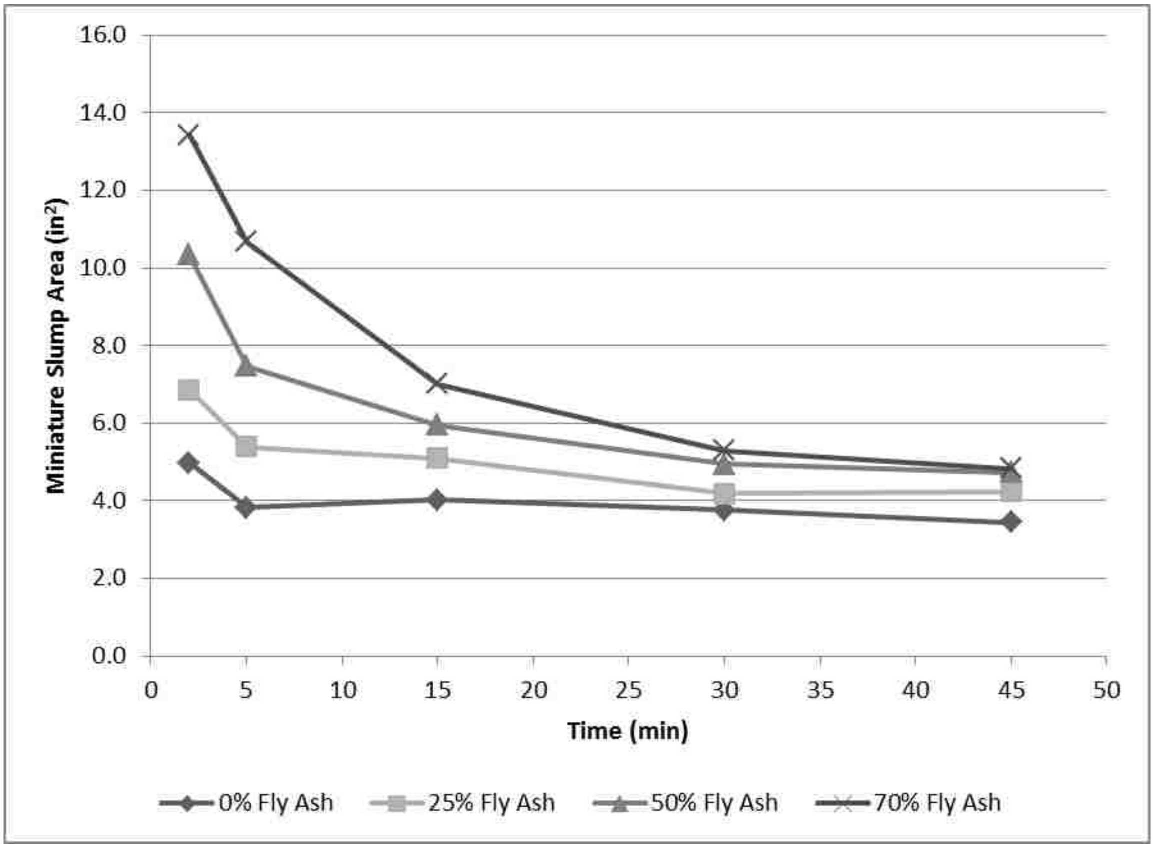

Figure 4.21. Example of Miniature Slump Results for Increasing Fly Ash Contents

Roberts & Taylor (2007) discussed the use of an early stiffening index, which is calculated by dividing the pat area at 30 minutes by the pat area at 5 minutes. Rapid stiffening is indicated by an index value less than 0.85. This index value was calculated for each mixture and is also included in the tables below. For all of the combinations with 50 and 70 percent fly ash, a value less than 0.85 was obtained. Cement 5 had the only 100 percent cement mixture with a value less than 0.85. It should also be noted that, for Cements 2 and 5, a majority of the mixtures had values indicating early stiffening behavior.

Table 4.16. Miniature Slump Results for Cement 1

Combination	Proportions		Miniature Slump Area (in^2)					Early Stiffening Index
	Cement (%)	Fly Ash (%)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	(30-min/5-min)
Baseline 1	100	0	2.0	2.7	2.8	2.5	2.7	0.93
1-1	75	25	3.1	3.8	3.7	3.8	3.5	1.02
1-1	50	50	5.5	4.9	4.8	4.1	4.2	0.84
1-1	30	70	6.0	4.8	3.9	3.3	3.2	0.69
1-2	75	25	3.4	3.7	3.6	3.3	3.5	0.87
1-2	50	50	6.1	5.5	4.9	4.3	4.1	0.79
1-2	30	70	11.2	8.4	5.6	4.6	4.5	0.55
1-3	75	25	2.6	3.4	3.4	3.2	3.3	0.95
1-3	50	50	5.9	4.8	3.8	3.9	3.8	0.83
1-3	30	70	8.2	6.3	4.5	3.7	3.7	0.59
1-4	75	25	2.6	3.1	3.1	2.8	2.8	0.89
1-4	50	50	5.1	4.4	3.2	2.6	2.7	0.59
1-4	30	70	6.9	5.7	3.3	2.8	2.6	0.50
1-5	75	25	3.1	3.3	3.1	2.9	3.0	0.87
1-5	50	50	7.0	5.4	4.4	3.6	3.6	0.68
1-5	30	70	10.2	10.6	5.5	3.8	3.4	0.36

Table 4.17. Miniature Slump Results for Cement 2

Combination	Proportions		Miniature Slump Area (in^2)					Early Stiffening Index
	Cement (%)	Fly Ash (%)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	(30-min/5-min)
Baseline 2	100	0	5.0	3.8	4.0	3.8	3.4	0.98
2-1	75	25	6.8	5.4	6.0	5.1	4.8	0.95
2-1	50	50	11.6	7.9	7.0	6.0	5.9	0.75
2-1	30	70	13.3	9.2	5.8	4.5	4.7	0.49
2-2	75	25	6.9	5.4	5.1	4.2	4.2	0.78
2-2	50	50	10.3	7.5	5.9	5.0	4.7	0.66
2-2	30	70	13.4	10.7	7.0	5.3	4.8	0.50
2-3	75	25	6.2	5.2	4.5	3.9	3.9	0.76
2-3	50	50	9.2	7.0	5.1	4.1	4.1	0.58
2-3	30	70	13.1	7.5	4.7	3.7	3.7	0.49
2-4	75	25	6.3	5.2	4.3	3.8	3.7	0.72
2-4	50	50	7.8	6.5	3.9	3.2	3.1	0.49
2-4	30	70	9.9	8.7	3.5	2.6	2.7	0.30
2-5	75	25	7.1	5.6	4.8	4.2	3.9	0.75
2-5	50	50	11.7	9.1	5.3	4.2	3.8	0.46
2-5	30	70	14.3	12.7	4.8	3.5	3.3	0.27

Table 4.18. Miniature Slump Results for Cement 3

Combination	Proportions		Miniature Slump Area (in^2)					Early Stiffening Index
	Cement (%)	Fly Ash (%)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	(30-min/5-min)
Baseline 3	100	0	2.2	2.4	2.4	2.4	2.4	1.00
3-1	75	25	2.1	3.1	3.1	2.8	2.9	0.90
3-1	50	50	3.7	4.1	4.0	3.3	3.5	0.81
3-1	30	70	5.0	4.6	3.4	2.9	2.8	0.63
3-2	75	25	2.1	3.1	2.9	2.7	2.9	0.90
3-2	50	50	3.6	4.4	4.0	3.6	3.4	0.83
3-2	30	70	7.7	6.0	5.3	4.5	4.3	0.75
3-3	75	25	2.2	2.9	2.8	2.8	2.9	0.96
3-3	50	50	4.4	4.2	3.9	3.3	3.4	0.79
3-3	30	70	6.8	6.0	4.5	3.7	3.6	0.61
3-4	75	25	1.9	2.7	2.6	2.5	2.5	0.93
3-4	50	50	3.9	3.4	2.9	2.7	2.5	0.79
3-4	30	70	6.5	5.1	2.9	2.4	2.4	0.47
3-5	75	25	2.2	3.1	2.9	2.7	2.5	0.86
3-5	50	50	4.6	4.9	3.6	3.0	2.9	0.61
3-5	30	70	8.4	6.1	4.1	3.1	3.1	0.50

Table 4.19. Miniature Slump Results for Cement 4

Combination	Proportions		Miniature Slump Area (in^2)					Early Stiffening Index
	Cement (%)	Fly Ash (%)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	(30-min/5-min)
Baseline 4	100	0	3.8	3.8	3.8	3.5	3.7	0.92
4-1	75	25	5.4	4.6	4.6	4.2	3.9	0.91
4-1	50	50	8.3	7.4	6.0	5.4	5.2	0.72
4-1	30	70	9.2	7.3	5.7	4.7	4.3	0.64
4-2	75	25	3.0	3.3	4.0	3.5	3.4	1.08
4-2	50	50	6.8	6.2	4.7	4.5	4.3	0.73
4-2	30	70	9.3	9.7	6.4	5.3	4.6	0.54
4-3	75	25	5.0	4.6	4.4	4.1	3.7	0.88
4-3	50	50	6.2	5.5	4.4	3.9	3.7	0.71
4-3	30	70	8.8	6.1	4.4	3.5	3.5	0.57
4-4	75	25	4.5	4.4	3.7	3.3	3.2	0.77
4-4	50	50	6.9	4.7	3.2	3.0	2.7	0.65
4-4	30	70	8.0	4.8	2.9	2.7	2.4	0.57
4-5	75	25	6.4	5.8	4.9	3.7	3.5	0.64
4-5	50	50	8.9	6.9	4.9	3.8	4.0	0.55
4-5	30	70	10.0	9.8	4.9	3.4	3.3	0.35

Table 4.20. Miniature Slump Results for Cement 5

Combination	Proportions		Miniature Slump Area (in^2)					Early Stiffening Index
	Cement (%)	Fly Ash (%)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	(30-min/5-min)
Baseline 5	100	0	3.1	3.7	3.0	2.8	2.8	0.77
5-1	75	25	5.2	4.8	4.7	4.1	3.9	0.85
5-1	50	50	6.7	5.9	5.0	4.2	4.0	0.71
5-1	30	70	9.0	5.0	3.3	2.8	2.7	0.56
5-2	75	25	5.2	4.8	4.2	3.7	3.6	0.77
5-2	50	50	8.2	6.7	5.6	4.6	4.4	0.69
5-2	30	70	11.4	8.3	5.8	4.3	4.2	0.51
5-3	75	25	5.2	4.7	4.3	3.6	3.8	0.77
5-3	50	50	6.9	5.8	5.0	4.3	4.1	0.74
5-3	30	70	10.3	6.6	4.8	3.9	3.5	0.58
5-4	75	25	4.4	4.3	3.6	3.0	3.0	0.71
5-4	50	50	6.2	4.7	3.1	2.7	2.8	0.58
5-4	30	70	8.4	4.8	2.6	2.3	2.1	0.48
5-5	75	25	5.6	5.3	4.5	3.8	3.5	0.72
5-5	50	50	8.8	6.9	5.0	3.9	3.7	0.57
5-5	30	70	14.9	12.2	5.0	3.2	3.2	0.26

The increase in miniature slump area with increasing fly ash replacement is expected, because it is known that fly ash increases workability, due to the spherical and glassy characteristics of fly ash particles. The more rapid loss in slump area and lower early stiffening indices seen with increasing fly ash replacement may be explained by increased aluminate levels and sulfate imbalance, which would lead to rapid setting behavior.

4.1.4. Vicat Setting Time. The initial and final setting times for each mixture were determined by the Vicat method according to ASTM C 191. As part of the Vicat setting time method, the water required to achieve normal consistency of the paste was determined according to ASTM C 187. The results of the normal consistency and setting time tests are summarized in Tables 4.21 through 4.25, below, for each mixture. The results show that, except for Cement 2 combinations, initial set generally increases with 25 percent fly ash replacement and then decreases with 50 and 70 percent fly ash replacement. For mixtures made with Fly Ashes 1, 2, or 3, final set tended to increase with fly ash replacement up to 50 percent. For mixtures made with Fly Ashes 4 and 5, final set generally increased at 25 percent fly ash replacement and then decreased at the 50 and 70 percent replacement levels, similar to initial set. The increases in setting times for mixtures with 25 to 50 percent fly ash is explained by the retarding effect of fly ash noted by other researchers including Bentz (2010). The decrease in setting times can be attributed to sulfate imbalances which are significant enough to produce flash setting behavior. The differences in the fly ash replacement level at which setting times began to decrease could be explained by differing sulfate requirements, which would lead to varying degrees of sulfate imbalance for each system. It should also be noted that the required water for normal consistency decreased with increasing fly ash replacement levels for all combinations. This is explained by the increased fluidity achieved when replacing portland cement with fly ash, which is composed of spherical, glassy particles.

Table 4.21. Vicat Setting Time Results for Cement 1

Combination	Proportions		Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)		Initial Set (min)	Final Set (min)
Baseline 1	100	0	26.0	110	210
1-1	75	25	23.0	184	345
1-1	50	50	20.5	95	390
1-1	30	70	19.5	34	405
1-2	75	25	24.0	218	390
1-2	50	50	21.0	208	510
1-2	30	70	19.5	87	450
1-3	75	25	24.5	171	375
1-3	50	50	21.5	142	435
1-3	30	70	20.0	49	525
1-4	75	25	23.0	203	450
1-4	50	50	21.0	47	360
1-4	30	70	19.0	15	135
1-5	75	25	22.5	178	480
1-5	50	50	19.0	33	180
1-5	30	70	17.5	11	45

Table 4.22. Vicat Setting Time Results for Cement 2

Combination	Proportions		Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)		Initial Set (min)	Final Set (min)
Baseline 2	100	0	25.0	158	255
2-1	75	25	22.0	182	360
2-1	50	50	19.0	67	375
2-1	30	70	18.0	20	420
2-2	75	25	21.5	154	345
2-2	50	50	20.0	71	435
2-2	30	70	19.0	57	495
2-3	75	25	22.5	151	390
2-3	50	50	21.0	40	650
2-3	30	70	19.0	12	150
2-4	75	25	21.5	92	360
2-4	50	50	20.0	35	300
2-4	30	70	18.5	12	90
2-5	75	25	21.0	80	345
2-5	50	50	19.0	13	90
2-5	30	70	17.5	11	45

Table 4.23. Vicat Setting Time Results for Cement 3

Combination	Proportions		Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)		Initial Set (min)	Final Set (min)
Baseline 3	100	0	25.0	78	180
3-1	75	25	23.0	170	315
3-1	50	50	20.5	85	360
3-1	30	70	19.0	31	225
3-2	75	25	23.0	146	315
3-2	50	50	20.5	101	435
3-2	30	70	19.0	59	435
3-3	75	25	23.0	123	300
3-3	50	50	21.0	96	450
3-3	30	70	19.5	40	375
3-4	75	25	23.0	172	375
3-4	50	50	21.0	33	300
3-4	30	70	19.0	12	60
3-5	75	25	22.5	124	345
3-5	50	50	20.0	12	75
3-5	30	70	18.5	11	30

Table 4.24. Vicat Setting Time Results for Cement 4

Combination	Proportions		Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)		Initial Set (min)	Final Set (min)
Baseline 4	100	0	24.0	81	180
4-1	75	25	23.0	132	270
4-1	50	50	21.5	107	300
4-1	30	70	20.5	14	285
4-2	75	25	23.0	213	450
4-2	50	50	21.0	78	525
4-2	30	70	19.0	53	480
4-3	75	25	23.0	238	435
4-3	50	50	21.5	101	660
4-3	30	70	20.5	48	300
4-4	75	25	22.5	125	360
4-4	50	50	20.0	34	270
4-4	30	70	19.5	12	105
4-5	75	25	22.5	123	255
4-5	50	50	21.0	15	195
4-5	30	70	19.5	11	60

Table 4.25. Vicat Setting Time Results for Cement 5

Combination	Proportions		Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)		Initial Set (min)	Final Set (min)
Baseline 5	100	0	26.0	146	285
5-1	75	25	23.0	158	300
5-1	50	50	20.5	100	405
5-1	30	70	19.0	21	465
5-2	75	25	24.0	179	330
5-2	50	50	21.0	175	435
5-2	30	70	19.0	59	495
5-3	75	25	24.0	149	315
5-3	50	50	21.0	54	390
5-3	30	70	20.0	13	150
5-4	75	25	23.0	167	345
5-4	50	50	21.0	48	375
5-4	30	70	19.0	14	120
5-5	75	25	22.5	136	345
5-5	50	50	19.0	13	135
5-5	30	70	18.0	11	45

The results of the Screening Study show some general trends in the properties of paste mixtures with increasing fly ash replacement levels. Cube compressive strengths were severely decreased at early ages, but experienced significant increases at later ages, indicating slower rates of strength gain. The thermal curves illustrated that the silicate hydration peaks were delayed and decreased in magnitude, due to the slower rate and lower heat production of the pozzolanic reaction. The miniature slump results showed increasing pat areas at times up to 15 minutes, which can be attributed to the spherical, glassy characteristics of fly ash. The effects of the fly ash particles were also seen in the decreased water required to achieve normal consistency, when performing the Vicat setting time test. Also, many of the Vicat results indicated increases in setting times. These results are typical for fly ash mixtures, which have slower reaction rates, due to the pozzolanic reaction, resulting in slower strength gain, decreased heat generation, and delayed setting times.

Some of the results in the Screening Study contradict the generalizations made in the previous paragraph. These results may be attributed to sulfate imbalances, which are increasingly likely at higher fly ash replacement levels. Sulfate imbalances, which cause accelerated early hydration of the aluminates, can lead to severely slow strength gain, rapid losses in fluidity, and decreased setting times. The changes in the hydration reactions of mixtures experiencing sulfate imbalances can also been observed in the unusual curve shapes obtained from the calorimetry results for these mixtures.

4.2 MAIN STUDY RESULTS

In the Main Study, two cement and fly ash combinations were chosen from the Screening Study for further study with powder additions and a water reducer. The two combinations, 4-1 and 1-3, were chosen as the most and least reactive combinations based on one-day cube strength results from the Screening Study. The effect of adding a water reducer was evaluated at the 0, 25, 50, and 70 percent fly ash replacement levels. The effects of gypsum, lime, and rapid set cement additions were evaluated at the 50 and 70 percent fly ash replacement levels. Paste testing for the Main Study included cube compressive strength, semi-adiabatic calorimetry, miniature slump, and Vicat setting time. Compressive strength testing was performed at 1, 3, 7, 28, and 56 days.

4.2.1. Outlier Analysis. The three cube compressive strength results for each mixture were evaluated for outliers as discussed above in Section 4.1.1. The results of the outlier analyses for Combination 4-1 mixtures are shown below in Tables 4.26 through 4.30. The results of the outlier analyses for Combination 1-3 mixtures are shown below in Tables 4.31 through 4.35. Values which were discarded as outliers have been bolded and the cell has been shaded. For Combination 4-1, the ASTM E 178 analysis indicated 16 possible outliers. Of these, two values were discarded as actual outliers, while the others were falsely indicated as outlying values. Two additional values, which were not indicated as outliers by the ASTM E 178 analysis, were discarded as outliers. For Combination 1-3, the ASTM E 178 analysis indicated 10 possible outliers. Of these, one value was discarded as an actual outlier. No other values were discarded as outlying values. An outlier analysis was also run on the calorimeter data for the Main Study and has been included in Appendix B.

Table 4.26. Outlier Analysis of 1-Day Cube Strengths for Combination 4-1 Mixtures.

Combination	Nominal Proportions						Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
4-1	100	0	0	0	0	0.00	4037	4280	4025	4114	144	3	4280	4025	1.153	1.154	0.620	YES	NO	4114
4-1	100	0	0	0	0	2.75	3597	4577	4424	4199	527	3	4577	3597	1.153	0.717	1.142	NO	NO	4199
4-1	100	0	0	0	0	5.00	5045	5406	5278	5243	183	3	5406	5045	1.153	0.891	1.081	NO	NO	5243
4-1	75	25	0	0	0	0.00	3757	3799	3458	3671	186	3	3799	3458	1.153	0.686	1.147	NO	NO	3671
4-1	75	25	0	0	0	2.75	3436	3396	3327	3387	55	3	3436	3327	1.153	0.900	1.076	NO	NO	3387
4-1	75	25	0	0	0	5.00	2926	2752	2894	2857	93	3	2926	2752	1.153	0.746	1.136	NO	NO	2857
4-1	50	50	0	0	0	0.00	1925	1966	1914	1935	27	3	1966	1914	1.153	1.133	0.758	NO	NO	1935
4-1	50	50	0	0	0	2.75	1370	1375	1399	1381	15	3	1399	1370	1.153	1.144	0.710	NO	NO	1381
4-1	50	50	0	0	0	5.00	1219	1256	1176	1217	40	3	1256	1176	1.153	0.969	1.028	NO	NO	1217
4-1	50	50	2	0	0	2.75	1324	1277	1250	1284	37	3	1324	1250	1.153	1.075	0.902	NO	NO	1284
4-1	50	50	4	0	0	2.75	714	694	722	710	14	3	722	694	1.153	0.829	1.110	NO	NO	710
4-1	50	50	4	5	0	2.75	609	631	626	622	11	3	631	609	1.153	0.786	1.126	NO	NO	622
4-1	50	50	4	10	0	2.75	1249	1195	1257	1234	34	3	1257	1195	1.153	0.689	1.147	NO	NO	1234
4-1	50	50	4	0	10	2.75	755	783	784	774	17	3	784	755	1.153	0.606	1.154	NO	YES	774
4-1	50	50	4	0	20	2.75	1170	1199	1238	1202	34	3	1238	1170	1.153	1.044	0.950	NO	NO	1202
4-1	30	70	0	0	0	0.00	678	628	689	665	32	3	689	628	1.153	0.742	1.137	NO	NO	665
4-1	30	70	0	0	0	2.75	300	307	321	309	10	3	321	300	1.153	1.098	0.858	NO	NO	309
4-1	30	70	0	0	0	5.00	362	364	381	369	10	3	381	362	1.153	1.152	0.645	NO	NO	369
4-1	30	70	2	0	0	2.75	453	457	477	462	13	3	477	453	1.153	1.145	0.704	NO	NO	462
4-1	30	70	4	0	0	2.75	204	207	225	212	11	3	225	204	1.153	1.142	0.720	NO	NO	212
4-1	30	70	4	5	0	2.75	556	561	554	557	3	3	561	554	1.153	1.135	0.750	NO	NO	557
4-1	30	70	4	10	0	2.75	556	546	529	544	13	3	556	529	1.153	0.899	1.077	NO	NO	544
4-1	30	70	4	0	10	2.75	679	655	693	675	19	3	693	655	1.153	0.906	1.073	NO	NO	675
4-1	30	70	4	0	20	2.75	816	794	795	802	13	3	816	794	1.153	1.154	0.606	YES	NO	802

Table 4.27. Outlier Analysis of 3-Day Cube Strengths for Combination 4-1 Mixtures.

Combination	Nominal Proportions						Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
4-1	100	0	0	0	0	0.00	8341	8015	7977	8111	200	3	8341	7977	1.153	1.150	0.668	NO	NO	8111
4-1	100	0	0	0	0	2.75	8423	8187	7965	8192	229	3	8423	7965	1.153	1.010	0.989	NO	NO	8192
4-1	100	0	0	0	0	5.00	8908	8708	-----	8808	-----	--	-----	-----	-----	-----	-----	-----	-----	8808
4-1	75	25	0	0	0	0.00	6179	6156	6235	6190	41	3	6235	6156	1.153	1.108	0.836	NO	NO	6190
4-1	75	25	0	0	0	2.75	6754	6807	6775	6779	27	3	6807	6754	1.153	1.063	0.923	NO	NO	6779
4-1	75	25	0	0	0	5.00	6124	6235	6048	6136	94	3	6235	6048	1.153	1.055	0.934	NO	NO	6136
4-1	50	50	0	0	0	0.00	3530	3485	3589	3535	52	3	3589	3485	1.153	1.044	0.949	NO	NO	3535
4-1	50	50	0	0	0	2.75	2937	3372	3534	3281	309	3	3534	2937	1.153	0.820	1.114	NO	NO	3281
4-1	50	50	0	0	0	5.00	3515	3623	3603	3580	57	3	3623	3515	1.153	0.743	1.137	NO	NO	3580
4-1	50	50	2	0	0	2.75	3257	3461	3333	3351	103	3	3461	3257	1.153	1.073	0.906	NO	NO	3351
4-1	50	50	4	0	0	2.75	3416	3334	3237	3329	90	3	3416	3237	1.153	0.970	1.027	NO	NO	3329
4-1	50	50	4	5	0	2.75	3100	3206	3183	3163	56	3	3206	3100	1.153	0.775	1.129	NO	NO	3163
4-1	50	50	4	10	0	2.75	3104	3025	3272	3134	126	3	3272	3025	1.153	1.097	0.860	NO	NO	3134
4-1	50	50	4	0	10	2.75	2978	2973	2871	2940	61	3	2978	2871	1.153	0.617	1.154	NO	YES	2940
4-1	50	50	4	0	20	2.75	3377	3257	3394	3343	75	3	3394	3257	1.153	0.687	1.147	NO	NO	3343
4-1	30	70	0	0	0	0.00	1109	1074	1120	1101	24	3	1120	1074	1.153	0.787	1.125	NO	NO	1101
4-1	30	70	0	0	0	2.75	946	1083	1080	1036	78	3	1083	946	1.153	0.598	1.154	NO	YES	1036
4-1	30	70	0	0	0	5.00	1117	1148	1207	1157	46	3	1207	1117	1.153	1.091	0.873	NO	NO	1157
4-1	30	70	2	0	0	2.75	1261	1284	1323	1289	31	3	1323	1261	1.153	1.069	0.912	NO	NO	1289
4-1	30	70	4	0	0	2.75	1586	1721	1622	1643	70	3	1721	1586	1.153	1.116	0.814	NO	NO	1643
4-1	30	70	4	5	0	2.75	1404	1443	1451	1433	25	3	1451	1404	1.153	0.727	1.140	NO	NO	1433
4-1	30	70	4	10	0	2.75	1291	1255	1247	1264	23	3	1291	1247	1.153	1.140	0.730	NO	NO	1264
4-1	30	70	4	0	10	2.75	1667	1690	1665	1674	14	3	1690	1665	1.153	1.150	0.664	NO	NO	1674
4-1	30	70	4	0	20	2.75	1896	1907	1852	1885	29	3	1907	1852	1.153	0.756	1.134	NO	NO	1885

Table 4.28. Outlier Analysis of 7-Day Cube Strengths for Combination 4-1 Mixtures.

Combination	Nominal Proportions						Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
4-1	100	0	0	0	0	0.00	9152	9630	10236	9672	543	3	10236	9152	1.153	1.037	0.958	NO	NO	9672
4-1	100	0	0	0	0	2.75	10274	10604	9818	10232	394	3	10604	9818	1.153	0.943	1.049	NO	NO	10232
4-1	100	0	0	0	0	5.00	11053	9988	10764	10602	551	3	11053	9988	1.153	0.820	1.114	NO	NO	10602
4-1	75	25	0	0	0	0.00	7738	7761	8027	7842	160	3	8027	7738	1.153	1.152	0.648	NO	NO	7842
4-1	75	25	0	0	0	2.75	7003	7577	8261	7613	630	3	8261	7003	1.153	1.028	0.969	NO	NO	7613
4-1	75	25	0	0	0	5.00	7214	7812	-----	7513	-----	--	-----	-----	-----	-----	-----	-----	-----	7513
4-1	50	50	0	0	0	0.00	5007	4882	5000	4963	70	3	5007	4882	1.153	0.628	1.153	NO	YES	4963
4-1	50	50	0	0	0	2.75	4926	4737	4901	4855	102	3	4926	4737	1.153	0.694	1.146	NO	NO	4855
4-1	50	50	0	0	0	5.00	4840	5013	5082	4978	125	3	5082	4840	1.153	0.832	1.109	NO	NO	4978
4-1	50	50	2	0	0	2.75	4919	4853	4660	4811	135	3	4919	4660	1.153	0.805	1.119	NO	NO	4811
4-1	50	50	4	0	0	2.75	5135	5032	5188	5118	80	3	5188	5032	1.153	0.878	1.088	NO	NO	5118
4-1	50	50	4	5	0	2.75	4791	4910	4912	4871	69	3	4912	4791	1.153	0.596	1.155	NO	YES	4871
4-1	50	50	4	10	0	2.75	4697	4671	4552	4640	77	3	4697	4552	1.153	0.741	1.137	NO	NO	4640
4-1	50	50	4	0	10	2.75	5386	5066	5444	5299	203	3	5444	5066	1.153	0.713	1.143	NO	NO	5299
4-1	50	50	4	0	20	2.75	5290	5300	5345	5311	30	3	5345	5290	1.153	1.139	0.735	NO	NO	5311
4-1	30	70	0	0	0	0.00	1785	1704	1731	1740	42	3	1785	1704	1.153	1.091	0.873	NO	NO	1740
4-1	30	70	0	0	0	2.75	2075	2073	2020	2056	31	3	2075	2020	1.153	0.610	1.154	NO	YES	2056
4-1	30	70	0	0	0	5.00	2071	2101	2054	2075	24	3	2101	2054	1.153	1.076	0.900	NO	NO	2075
4-1	30	70	2	0	0	2.75	2085	2110	2068	2088	21	3	2110	2068	1.153	1.053	0.937	NO	NO	2088
4-1	30	70	4	0	0	2.75	2352	2481	2490	2441	77	3	2490	2352	1.153	0.631	1.153	NO	NO	2441
4-1	30	70	4	5	0	2.75	2140	2198	2134	2157	35	3	2198	2134	1.153	1.151	0.659	NO	NO	2157
4-1	30	70	4	10	0	2.75	1952	2015	2010	1992	35	3	2015	1952	1.153	0.648	1.152	NO	NO	1992
4-1	30	70	4	0	10	2.75	2710	2885	2785	2793	88	3	2885	2710	1.153	1.044	0.949	NO	NO	2793
4-1	30	70	4	0	20	2.75	2983	3040	3178	3067	100	3	3178	2983	1.153	1.107	0.838	NO	NO	3067

Table 4.29. Outlier Analysis of 28-Day Cube Strengths for Combination 4-1 Mixtures.

Combination	Nominal Proportions						Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
4-1	100	0	0	0	0	0.00	11479	11002	11303	11261	241	3	11479	11002	1.153	0.903	1.075	NO	NO	11261
4-1	100	0	0	0	0	2.75	12541	11329	10859	11576	867	3	12541	10859	1.153	1.112	0.826	NO	NO	11576
4-1	100	0	0	0	0	5.00	13147	**10736**	13085	12323	1374	3	13147	10736	1.153	0.600	1.154	NO	YES	13116
4-1	75	25	0	0	0	0.00	10736	10658	10210	10535	284	3	10736	10210	1.153	0.709	1.144	NO	NO	10535
4-1	75	25	0	0	0	2.75	10641	11270	11133	11015	331	3	11270	10641	1.153	0.772	1.130	NO	NO	11015
4-1	75	25	0	0	0	5.00	11332	10349	10968	10883	497	3	11332	10349	1.153	0.903	1.075	NO	NO	10883
4-1	50	50	0	0	0	0.00	8562	8701	8238	8500	238	3	8701	8238	1.153	0.843	1.105	NO	NO	8500
4-1	50	50	0	0	0	2.75	6453	6491	6038	6327	252	3	6491	6038	1.153	0.651	1.151	NO	NO	6327
4-1	50	50	0	0	0	5.00	6861	6300	6563	6574	281	3	6861	6300	1.153	1.020	0.979	NO	NO	6574
4-1	50	50	2	0	0	2.75	6739	6933	6821	6831	97	3	6933	6739	1.153	1.048	0.944	NO	NO	6831
4-1	50	50	4	0	0	2.75	6747	7220	6781	6916	264	3	7220	6747	1.153	1.152	0.641	NO	NO	6916
4-1	50	50	4	5	0	2.75	6468	6599	6463	6510	77	3	6599	6463	1.153	1.154	0.605	YES	NO	6510
4-1	50	50	4	10	0	2.75	6123	6125	6231	6160	62	3	6231	6123	1.153	1.155	0.593	YES	NO	6160
4-1	50	50	4	0	10	2.75	6945	7426	7203	7191	241	3	7426	6945	1.153	0.976	1.023	NO	NO	7191
4-1	50	50	4	0	20	2.75	7794	8019	7859	7891	116	3	8019	7794	1.153	1.109	0.834	NO	NO	7891
4-1	30	70	0	0	0	0.00	4246	4231	3954	4144	164	3	4246	3954	1.153	0.623	1.153	NO	YES	4144
4-1	30	70	0	0	0	2.75	2928	2970	3335	3078	224	3	3335	2928	1.153	1.149	0.670	NO	NO	3078
4-1	30	70	0	0	0	5.00	3419	3115	3138	3224	169	3	3419	3115	1.153	1.152	0.642	NO	NO	3224
4-1	30	70	2	0	0	2.75	3184	3201	3118	3168	44	3	3201	3118	1.153	0.755	1.134	NO	NO	3168
4-1	30	70	4	0	0	2.75	3558	3762	3612	3644	106	3	3762	3558	1.153	1.115	0.817	NO	NO	3644
4-1	30	70	4	5	0	2.75	3152	3219	3316	3229	82	3	3316	3152	1.153	1.056	0.932	NO	NO	3229
4-1	30	70	4	10	0	2.75	2765	2808	2748	2774	31	3	2808	2748	1.153	1.112	0.825	NO	NO	2774
4-1	30	70	4	0	10	2.75	3829	3967	3766	3854	103	3	3967	3766	1.153	1.100	0.855	NO	NO	3854
4-1	30	70	4	0	20	2.75	4465	4397	4460	4441	38	3	4465	4397	1.153	0.646	1.152	NO	NO	4441

Table 4.30. Outlier Analysis of 56-Day Cube Strengths for Combination 4-1 Mixtures.

Combination	**Nominal Proportions**						**Outlier Analysis**														**Average Cube Strength (psi)**
	Cement (%)	**Fly Ash (%)**	**Gypsum (%)**	**Lime (%)**	**RSC (%)**	**WR (fl.oz./cwt)**	**Cube Strengths (psi)**				**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**Outlier$_{MAX}$?**	**Outlier$_{MIN}$?**		
							Test 1	**Test 2**	**Test 3**	**Avg.**											
4-1	100	0	0	0	0	0.00	13126	12662	12802	12863	238	3	13126	12662	1.153	1.104	0.845	NO	NO		12863
4-1	100	0	0	0	0	2.75	13887	13475	13513	13625	227	3	13887	13475	1.153	1.151	0.660	NO	NO		13625
4-1	100	0	0	0	0	5.00	13996	13474	12402	13291	813	3	13996	12402	1.153	0.868	1.094	NO	NO		13291
4-1	75	25	0	0	0	0.00	12184	10893	10299	11125	963	3	12184	10299	1.153	1.098	0.858	NO	NO		11125
4-1	75	25	0	0	0	2.75	12278	12722	12659	12553	240	3	12722	12278	1.153	0.703	1.145	NO	NO		12553
4-1	75	25	0	0	0	5.00	12838	**11237**	13140	12405	1022	3	13140	11237	1.153	0.718	1.142	NO	NO		12989
4-1	50	50	0	0	0	0.00	8664	8606	8860	8710	133	3	8860	8606	1.153	1.126	0.784	NO	NO		8710
4-1	50	50	0	0	0	2.75	7725	8220	8268	8071	301	3	8268	7725	1.153	0.656	1.151	NO	NO		8071
4-1	50	50	0	0	0	5.00	8534	8504	8332	8457	109	3	8534	8332	1.153	0.708	1.144	NO	NO		8457
4-1	50	50	2	0	0	2.75	8071	8199	8238	8169	87	3	8238	8071	1.153	0.789	1.125	NO	NO		8169
4-1	50	50	4	0	0	2.75	**7896**	8369	8359	8208	270	3	8369	7896	1.153	0.596	1.154	NO	YES		8364
4-1	50	50	4	5	0	2.75	6907	7353	7351	7204	257	3	7353	6907	1.153	0.580	1.155	NO	YES		7204
4-1	50	50	4	10	0	2.75	7396	7655	7511	7521	130	3	7655	7396	1.153	1.035	0.961	NO	NO		7521
4-1	50	50	4	0	10	2.75	7597	8470	8588	8218	542	3	8588	7597	1.153	0.683	1.148	NO	NO		8218
4-1	50	50	4	0	20	2.75	8494	7692	8371	8186	432	3	8494	7692	1.153	0.714	1.143	NO	NO		8186
4-1	30	70	0	0	0	0.00	4110	4090	4176	4125	45	3	4176	4090	1.153	1.125	0.789	NO	NO		4125
4-1	30	70	0	0	0	2.75	4322	4325	4433	4360	63	3	4433	4322	1.153	1.154	0.598	YES	NO		4360
4-1	30	70	0	0	0	5.00	4447	4451	4368	4422	47	3	4451	4368	1.153	0.619	1.154	NO	YES		4422
4-1	30	70	2	0	0	2.75	3464	3623	3791	3626	163	3	3791	3464	1.153	1.009	0.991	NO	NO		3626
4-1	30	70	4	0	0	2.75	4251	4282	**4027**	4187	139	3	4282	4027	1.153	0.686	1.147	NO	NO		4267
4-1	30	70	4	5	0	2.75	3304	3572	3338	3405	146	3	3572	3304	1.153	1.147	0.691	NO	NO		3405
4-1	30	70	4	10	0	2.75	3091	3282	3396	3256	155	3	3396	3091	1.153	0.906	1.073	NO	NO		3256
4-1	30	70	4	0	10	2.75	4457	4720	4745	4641	160	3	4745	4457	1.153	0.655	1.151	NO	NO		4641
4-1	30	70	4	0	20	2.75	5287	5125	5210	5207	81	3	5287	5125	1.153	0.982	1.017	NO	NO		5207

Table 4.31. Outlier Analysis of 1-Day Cube Strengths for Combination 1-3 Mixtures.

	Nominal Proportions						Outlier Analysis													
Combination	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	Average Cube Strength (psi)
							Test 1	Test 2	Test 3	Avg.										
1-3	100	0	0	0	0	0.00	4917	4145	5018	4693	478	3	5018	4145	1.153	0.680	1.148	NO	NO	4693
1-3	100	0	0	0	0	2.75	4088	4336	4103	4176	139	3	4336	4088	1.153	1.153	0.628	YES	NO	4176
1-3	100	0	0	0	0	5.00	3030	3092	3137	3086	54	3	3137	3030	1.153	0.941	1.050	NO	NO	3086
1-3	75	25	0	0	0	0.00	2790	2708	2825	2774	60	3	2825	2708	1.153	0.849	1.102	NO	NO	2774
1-3	75	25	0	0	0	2.75	2064	2002	2028	2031	31	3	2064	2002	1.153	1.052	0.938	NO	NO	2031
1-3	75	25	0	0	0	5.00	1622	1646	1659	1642	19	3	1659	1622	1.153	0.877	1.089	NO	NO	1642
1-3	50	50	0	0	0	0.00	626	656	683	655	29	3	683	626	1.153	0.982	1.017	NO	NO	655
1-3	50	50	0	0	0	2.75	237	238	242	239	3	3	242	237	1.153	1.080	0.893	NO	NO	239
1-3	50	50	0	0	0	5.00	131	138	137	135	4	3	138	131	1.153	0.660	1.151	NO	NO	135
1-3	50	50	2	0	0	2.75	347	351	346	348	3	3	351	346	1.153	1.129	0.774	NO	NO	348
1-3	50	50	4	0	0	2.75	322	314	309	315	6	3	322	309	1.153	1.078	0.898	NO	NO	315
1-3	50	50	4	5	0	2.75	659	663	648	656	8	3	663	648	1.153	0.816	1.116	NO	NO	656
1-3	50	50	4	10	0	2.75	684	685	722	697	22	3	722	684	1.153	1.155	0.594	YES	NO	697
1-3	50	50	4	0	10	2.75	666	656	660	660	5	3	666	656	1.153	1.080	0.894	NO	NO	660
1-3	50	50	4	0	20	2.75	622	599	597	606	13	3	622	597	1.153	1.152	0.649	NO	NO	606
1-3	30	70	0	0	0	0.00	21	11	16	16	5	3	21	11	1.153	1.000	1.000	NO	NO	16
1-3	30	70	0	0	0	2.75	55	58	61	58	3	3	61	55	1.153	1.042	0.952	NO	NO	58
1-3	30	70	0	0	0	5.00	58	56	62	59	3	3	62	56	1.153	1.130	0.772	NO	NO	59
1-3	30	70	2	0	0	2.75	63	65	63	64	1	3	65	63	1.153	1.152	0.641	NO	NO	64
1-3	30	70	4	0	0	2.75	219	207	209	212	6	3	219	207	1.153	1.134	0.755	NO	NO	212
1-3	30	70	4	5	0	2.75	241	247	244	244	3	3	247	241	1.153	0.945	1.048	NO	NO	244
1-3	30	70	4	10	0	2.75	231	235	255	240	13	3	255	231	1.153	1.134	0.756	NO	NO	240
1-3	30	70	4	0	10	2.75	270	286	268	275	10	3	286	268	1.153	1.149	0.672	NO	NO	275
1-3	30	70	4	0	20	2.75	431	455	444	443	12	3	455	431	1.153	0.959	1.037	NO	NO	443

Table 4.32. Outlier Analysis of 3-Day Cube Strengths for Combination 1-3 Mixtures.

Combination	Nominal Proportions						Outlier Analysis														Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
1-3	100	0	0	0	0	0.00	8091	7844	7742	7892	179	3	8091	7742	1.153	1.107	0.838	NO	NO	7892
1-3	100	0	0	0	0	2.75	7842	8004	7867	7905	87	3	8004	7842	1.153	1.142	0.718	NO	NO	7905
1-3	100	0	0	0	0	5.00	7641	7684	8046	7790	222	3	8046	7641	1.153	1.149	0.673	NO	NO	7790
1-3	75	25	0	0	0	0.00	4422	5298	4566	4762	470	3	5298	4422	1.153	1.141	0.724	NO	NO	4762
1-3	75	25	0	0	0	2.75	5308	5406	5447	5387	71	3	5447	5308	1.153	0.840	1.106	NO	NO	5387
1-3	75	25	0	0	0	5.00	4815	4989	5079	4961	134	3	5079	4815	1.153	0.878	1.088	NO	NO	4961
1-3	50	50	0	0	0	0.00	2405	2217	2389	2337	104	3	2405	2217	1.153	0.652	1.151	NO	NO	2337
1-3	50	50	0	0	0	2.75	2500	2425	2326	2417	87	3	2500	2326	1.153	0.949	1.044	NO	NO	2417
1-3	50	50	0	0	0	5.00	2182	2125	2169	2159	30	3	2182	2125	1.153	0.775	1.129	NO	NO	2159
1-3	50	50	2	0	0	2.75	2017	2191	2186	2131	99	3	2191	2017	1.153	0.604	1.154	NO	YES	2131
1-3	50	50	4	0	0	2.75	2261	2197	2238	2232	33	3	2261	2197	1.153	0.890	1.082	NO	NO	2232
1-3	50	50	4	5	0	2.75	2563	2608	2677	2616	57	3	2677	2563	1.153	1.059	0.928	NO	NO	2616
1-3	50	50	4	10	0	2.75	2808	2783	2638	2743	92	3	2808	2638	1.153	0.705	1.145	NO	NO	2743
1-3	50	50	4	0	10	2.75	3021	2796	2886	2901	114	3	3021	2796	1.153	1.058	0.929	NO	NO	2901
1-3	50	50	4	0	20	2.75	2997	2948	2848	2931	76	3	2997	2848	1.153	0.865	1.095	NO	NO	2931
1-3	30	70	0	0	0	0.00	74	70	82	75	6	3	82	70	1.153	1.103	0.847	NO	NO	75
1-3	30	70	0	0	0	2.75	70	72	71	71	1	3	72	70	1.153	0.816	1.115	NO	NO	71
1-3	30	70	0	0	0	5.00	78	69	82	76	6	3	82	69	1.153	0.894	1.080	NO	NO	76
1-3	30	70	2	0	0	2.75	453	460	457	457	3	3	460	453	1.153	0.987	1.012	NO	NO	457
1-3	30	70	4	0	0	2.75	1020	983	991	998	20	3	1020	983	1.153	1.127	0.782	NO	NO	998
1-3	30	70	4	5	0	2.75	918	929	893	913	18	3	929	893	1.153	0.839	1.107	NO	NO	913
1-3	30	70	4	10	0	2.75	747	782	813	781	33	3	813	747	1.153	0.977	1.021	NO	NO	781
1-3	30	70	4	0	10	2.75	1009	1008	1019	1012	6	3	1019	1008	1.153	1.151	0.654	NO	NO	1012
1-3	30	70	4	0	20	2.75	539	630	533	567	54	3	630	533	1.153	1.153	0.628	YES	NO	567

Table 4.33. Outlier Analysis of 7-Day Cube Strengths for Combination 1-3 Mixtures.

Combination	Nominal Proportions						Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
1-3	100	0	0	0	0	0.00	8746	8851	9396	8998	349	3	9396	8746	1.153	1.142	0.721	NO	NO	8998
1-3	100	0	0	0	0	2.75	9602	8946	8498	9015	555	3	9602	8498	1.153	1.057	0.931	NO	NO	9015
1-3	100	0	0	0	0	5.00	9755	8727	8694	9059	603	3	9755	8694	1.153	1.154	0.604	YES	NO	9059
1-3	75	25	0	0	0	0.00	7086	7253	6762	7034	249	3	7253	6762	1.153	0.878	1.089	NO	NO	7034
1-3	75	25	0	0	0	2.75	7334	7427	7789	7517	241	3	7789	7334	1.153	1.133	0.761	NO	NO	7517
1-3	75	25	0	0	0	5.00	8453	8363	8012	8276	233	3	8453	8012	1.153	0.760	1.133	NO	NO	8276
1-3	50	50	0	0	0	0.00	4050	4287	4318	4218	147	3	4318	4050	1.153	0.680	1.148	NO	NO	4218
1-3	50	50	0	0	0	2.75	4387	4246	4233	4289	85	3	4387	4233	1.153	1.152	0.650	NO	NO	4289
1-3	50	50	0	0	0	5.00	4017	3926	3851	3932	83	3	4017	3851	1.153	1.031	0.966	NO	NO	3932
1-3	50	50	2	0	0	2.75	3954	3981	3978	3971	15	3	3981	3954	1.153	0.659	1.151	NO	NO	3971
1-3	50	50	4	0	0	2.75	4106	4314	4159	4193	108	3	4314	4106	1.153	1.119	0.806	NO	NO	4193
1-3	50	50	4	5	0	2.75	4480	4356	4360	4399	70	3	4480	4356	1.153	1.154	0.605	YES	NO	4399
1-3	50	50	4	10	0	2.75	4170	4102	4282	4185	91	3	4282	4102	1.153	1.071	0.910	NO	NO	4185
1-3	50	50	4	0	10	2.75	4502	4672	4589	4587	85	3	4672	4502	1.153	0.994	1.006	NO	NO	4587
1-3	50	50	4	0	20	2.75	4857	4926	4571	4785	188	3	4926	4571	1.153	0.750	1.135	NO	NO	4785
1-3	30	70	0	0	0	0.00	91	95	94	93	2	3	95	91	1.153	0.899	1.077	NO	NO	93
1-3	30	70	0	0	0	2.75	87	107	114	103	14	3	114	87	1.153	0.795	1.123	NO	NO	103
1-3	30	70	0	0	0	5.00	103	85	106	98	11	3	106	85	1.153	0.723	1.141	NO	NO	98
1-3	30	70	2	0	0	2.75	1393	1513	1471	1459	61	3	1513	1393	1.153	0.889	1.083	NO	NO	1459
1-3	30	70	4	0	0	2.75	1651	1708	1729	1696	40	3	1729	1651	1.153	0.817	1.115	NO	NO	1696
1-3	30	70	4	5	0	2.75	1584	1659	1545	1596	58	3	1659	1545	1.153	1.089	0.878	NO	NO	1596
1-3	30	70	4	10	0	2.75	1403	1456	1437	1432	27	3	1456	1403	1.153	0.899	1.077	NO	NO	1432
1-3	30	70	4	0	10	2.75	1860	1816	1949	1875	68	3	1949	1816	1.153	1.094	0.867	NO	NO	1875
1-3	30	70	4	0	20	2.75	2432	2435	2427	2431	4	3	2435	2427	1.153	0.881	1.087	NO	NO	2431

Table 4.34. Outlier Analysis of 28-Day Cube Strengths for Combination 1-3 Mixtures.

Combination	Nominal Proportions						Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	$Outlier_{MAX}$?	$Outlier_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
1-3	100	0	0	0	0	0.00	11237	11165	11500	11300	176	3	11500	11165	1.153	1.131	0.769	NO	NO	11300
1-3	100	0	0	0	0	2.75	12902	12812	12291	12668	330	3	12902	12291	1.153	0.709	1.144	NO	NO	12668
1-3	100	0	0	0	0	5.00	11127	12223	11667	11673	548	3	12223	11127	1.153	1.005	0.995	NO	NO	11673
1-3	75	25	0	0	0	0.00	11641	10060	10407	10703	831	3	11641	10060	1.153	1.129	0.774	NO	NO	10703
1-3	75	25	0	0	0	2.75	10421	10604	10706	10577	144	3	10706	10421	1.153	0.892	1.081	NO	NO	10577
1-3	75	25	0	0	0	5.00	11553	10807	11245	11201	375	3	11553	10807	1.153	0.937	1.053	NO	NO	11201
1-3	50	50	0	0	0	0.00	7641	8195	7787	7874	287	3	8195	7641	1.153	1.117	0.813	NO	NO	7874
1-3	50	50	0	0	0	2.75	6015	5570	5900	5828	231	3	6015	5570	1.153	0.807	1.119	NO	NO	5828
1-3	50	50	0	0	0	5.00	6086	6193	5928	6069	133	3	6193	5928	1.153	0.929	1.059	NO	NO	6069
1-3	50	50	2	0	0	2.75	5669	5602	5595	5622	41	3	5669	5595	1.153	1.151	0.659	NO	NO	5622
1-3	50	50	4	0	0	2.75	5855	5724	5905	5828	94	3	5905	5724	1.153	0.823	1.113	NO	NO	5828
1-3	50	50	4	5	0	2.75	5909	6025	5974	5969	58	3	6025	5909	1.153	0.956	1.039	NO	NO	5969
1-3	50	50	4	10	0	2.75	5509	5240	5448	5399	141	3	5509	5240	1.153	0.782	1.127	NO	NO	5399
1-3	50	50	4	0	10	2.75	6600	6651	6732	6661	67	3	6732	6600	1.153	1.065	0.919	NO	NO	6661
1-3	50	50	4	0	20	2.75	7198	7103	7149	7150	47	3	7198	7103	1.153	1.011	0.988	NO	NO	7150
1-3	30	70	0	0	0	0.00	2522	2450	2455	2475	40	3	2522	2450	1.153	1.152	0.638	NO	NO	2475
1-3	30	70	0	0	0	2.75	2523	2679	2560	2588	81	3	2679	2523	1.153	1.124	0.790	NO	NO	2588
1-3	30	70	0	0	0	5.00	2470	2595	2446	2504	80	3	2595	2446	1.153	1.142	0.720	NO	NO	2504
1-3	30	70	2	0	0	2.75	2897	2771	2825	2831	64	3	2897	2771	1.153	1.045	0.948	NO	NO	2831
1-3	30	70	4	0	0	2.75	2705	2995	2970	2890	161	3	2995	2705	1.153	0.652	1.151	NO	NO	2890
1-3	30	70	4	5	0	2.75	2663	2601	2742	2669	70	3	2742	2601	1.153	1.037	0.958	NO	NO	2669
1-3	30	70	4	10	0	2.75	2673	2653	2728	2685	39	3	2728	2653	1.153	1.118	0.808	NO	NO	2685
1-3	30	70	4	0	10	2.75	3594	3436	3601	3544	93	3	3601	3436	1.153	0.612	1.154	NO	YES	3544
1-3	30	70	4	0	20	2.75	4330	4351	4403	4362	38	3	4403	4330	1.153	1.110	0.831	NO	NO	4362

Table 4.35. Outlier Analysis of 56-Day Cube Strengths for Combination 1-3 Mixtures.

Combination	Nominal Proportions						Outlier Analysis													Average Cube Strength (psi)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Cube Strengths (psi)				σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	
							Test 1	Test 2	Test 3	Avg.										
1-3	100	0	0	0	0	0.00	11599	11509	11856	11655	180	3	11856	11509	1.153	1.118	0.809	NO	NO	11655
1-3	100	0	0	0	0	2.75	13994	14006	13937	13979	37	3	14006	13937	1.153	0.738	1.138	NO	NO	13979
1-3	100	0	0	0	0	5.00	14060	13435	13948	13814	333	3	14060	13435	1.153	0.738	1.138	NO	NO	13814
1-3	75	25	0	0	0	0.00	11716	11789	12010	11838	153	3	12010	11716	1.153	1.121	0.799	NO	NO	11838
1-3	75	25	0	0	0	2.75	11884	11944	11805	11877	69	3	11944	11805	1.153	0.952	1.042	NO	NO	11877
1-3	75	25	0	0	0	5.00	11869	12037	11833	11913	108	3	12037	11833	1.153	1.139	0.735	NO	NO	11913
1-3	50	50	0	0	0	0.00	7466	7650	7323	7480	164	3	7650	7323	1.153	1.039	0.956	NO	NO	7480
1-3	50	50	0	0	0	2.75	6999	6652	7093	6915	232	3	7093	6652	1.153	0.767	1.131	NO	NO	6915
1-3	50	50	0	0	0	5.00	7374	7076	7245	7232	149	3	7374	7076	1.153	0.951	1.043	NO	NO	7232
1-3	50	50	2	0	0	2.75	7172	7494	7395	7354	165	3	7494	7172	1.153	0.852	1.101	NO	NO	7354
1-3	50	50	4	0	0	2.75	6919	7044	6994	6986	63	3	7044	6919	1.153	0.931	1.057	NO	NO	6986
1-3	50	50	4	5	0	2.75	6375	6401	6403	6393	16	3	6403	6375	1.153	0.634	1.153	NO	NO	6393
1-3	50	50	4	10	0	2.75	6156	5881	5878	5972	159	3	6156	5878	1.153	1.155	0.588	YES	NO	5972
1-3	50	50	4	0	10	2.75	8155	8332	8259	8249	89	3	8332	8155	1.153	0.937	1.053	NO	NO	8249
1-3	50	50	4	0	20	2.75	8391	8396	8653	8480	150	3	8653	8391	1.153	1.155	0.595	YES	NO	8480
1-3	30	70	0	0	0	0.00	3126	3210	-----	3168	-----	--	-----	-----	-----	-----	-----	-----	-----	3168
1-3	30	70	0	0	0	2.75	3596	3958	4048	3867	239	3	4048	3596	1.153	0.755	1.134	NO	NO	3867
1-3	30	70	0	0	0	5.00	3316	3504	3423	3414	94	3	3504	3316	1.153	0.951	1.043	NO	NO	3414
1-3	30	70	2	0	0	2.75	3629	3928	3747	3768	151	3	3928	3629	1.153	1.062	0.923	NO	NO	3768
1-3	30	70	4	0	0	2.75	3632	3860	3757	3750	114	3	3860	3632	1.153	0.966	1.031	NO	NO	3750
1-3	30	70	4	5	0	2.75	3224	3321	3329	3291	58	3	3329	3224	1.153	0.643	1.152	NO	NO	3291
1-3	30	70	4	10	0	2.75	3030	3099	3226	3118	100	3	3226	3030	1.153	1.084	0.887	NO	NO	3118
1-3	30	70	4	0	10	2.75	4341	4217	4435	4331	110	3	4435	4217	1.153	0.951	1.043	NO	NO	4331
1-3	30	70	4	0	20	2.75	**5507**	5977	5955	5813	265	3	5977	5507	1.153	0.619	1.154	NO	YES	5966

4.2.2. Effects of Water Reducer Addition. The effects of a Type A/F water reducing admixture were evaluated at a low dose, 2.75 fluid ounces/hundredweight, and a high dose, 5.00 fluid ounces/hundredweight. These dosages were added to the paste mixtures at the 0, 25, 50, and 70 percent fly ash replacement levels.

The effect of the water reducer on compressive strength was varied for both combinations. Figures 4.22 and 4.23 show the effect of the water reducer on one-day cube strengths for Combinations 4-1 and 1-3, respectively. The 100 percent cement mixture for Combination 4-1 shows increasing strengths with greater water reducer dosage. This is expected, because the addition of a water reducer is generally known to increase dispersion of cement particles, resulting in greater strengths. For Combination 1-3, however, increasing dosages led to decreased strengths. Also, for the mixtures containing fly ash, increasing water reducer dosages typically resulted in lower strengths at one day.

The results of the 56-day cube compressive strength tests with increasing water reducer dosages for Combinations 4-1 and 1-3 are shown below in Figures 4.24 and 4.25, respectively. As can be seen, the addition of the water reducer resulted in 56-day strengths that were similar to or exceeded the baseline mixtures with no water reducer addition. At ages between one and 56 days, the results generally trended from those at one day to those at 56 days with respect to the mixtures that did not include the water reducer.

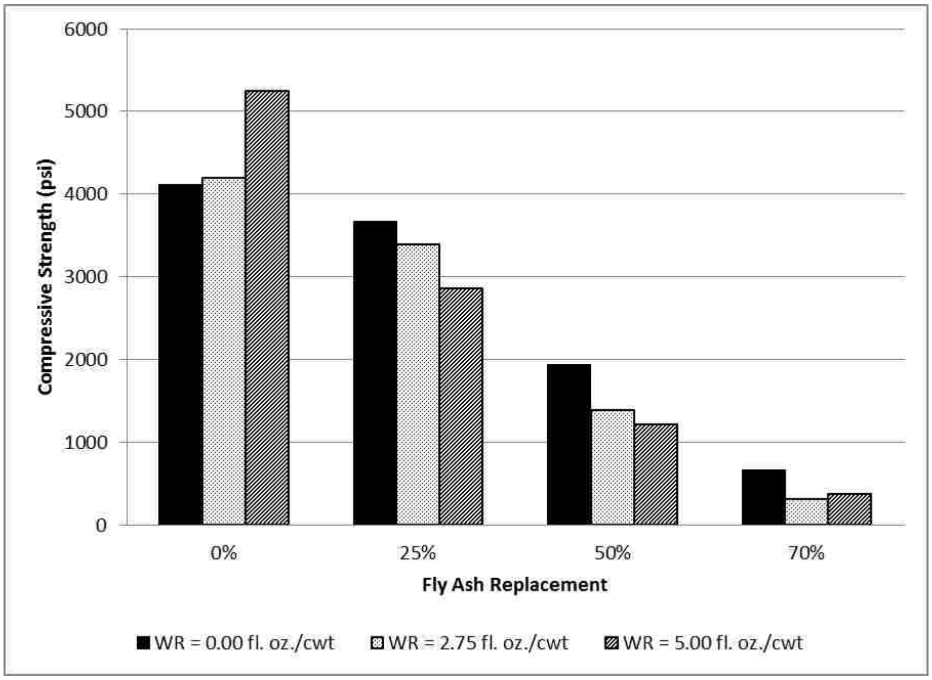

Figure 4.22. Effect of Water Reducer on One-Day Cube Strengths for Combination 4-1

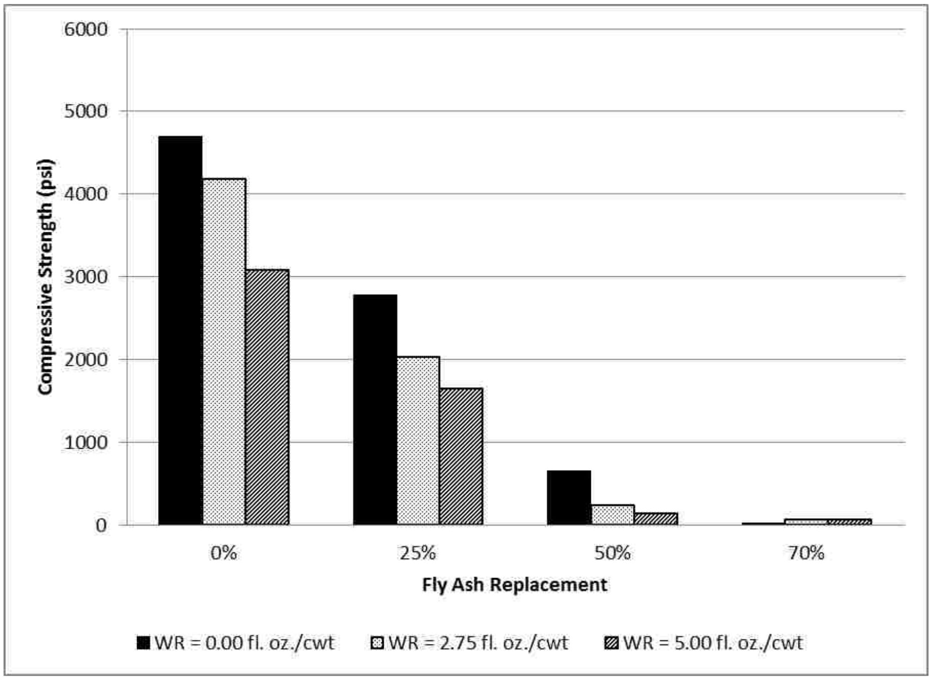

Figure 4.23. Effect of Water Reducer on One-Day Cube Strengths for Combination 1-3

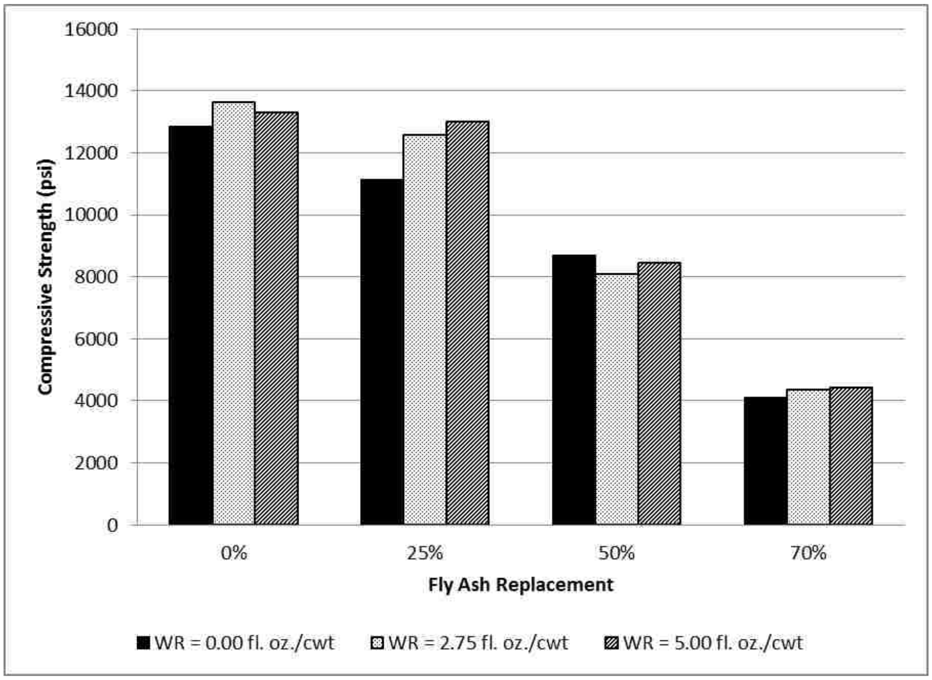

Figure 4.24. Effect of Water Reducer on 56-Day Cube Strengths for Combination 4-1

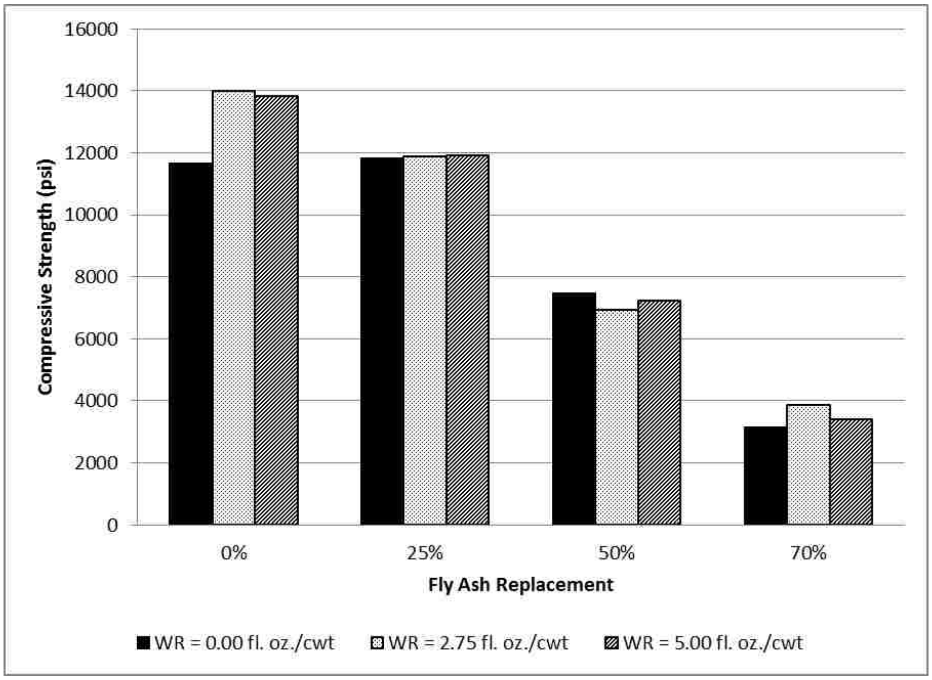

Figure 4.25. Effect of Water Reducer on 56-Day Cube Strengths for Combination 1-3

The calorimetry results are shown in Table 4.36 for mixtures with the two water reducer dosages and corresponding mixtures without the water reducer. As can be seen, the water reducer addition did not result in significant changes in curve shape for the mixtures. The exception to this is Combination 1-3 with 70 percent fly ash, which changed from a Type G to Type F curve with the addition of a water reducer. This may be explained by the increased dispersion, and therefore increased hydration rate, caused by the water reducer. This would lead to increased aluminate hydration, which may suppress silicate hydration if a majority of the calcium was consumed by the aluminates. The results also show that increased dosages led to a delay in the main hydration curve for all fly ash replacement levels, based on the predicted final set by the Percentage Method. An example of this effect is shown in the series of curves in Figure 4.26, below.

Similar effects were found by Bentz (2010) with the addition of a water-reducing admixture. Two exceptions in this study were Combination 4-1 with 100 percent cement, which decreased by 39 minutes with the high dosage, and Combination 1-3 with 70 percent fly ash, which decreased 5 minutes with the low dosage. This may be caused by the effects of sulfate imbalance, as discussed in the Screening Study Results section. The curves for all mixtures are included in Appendix D.

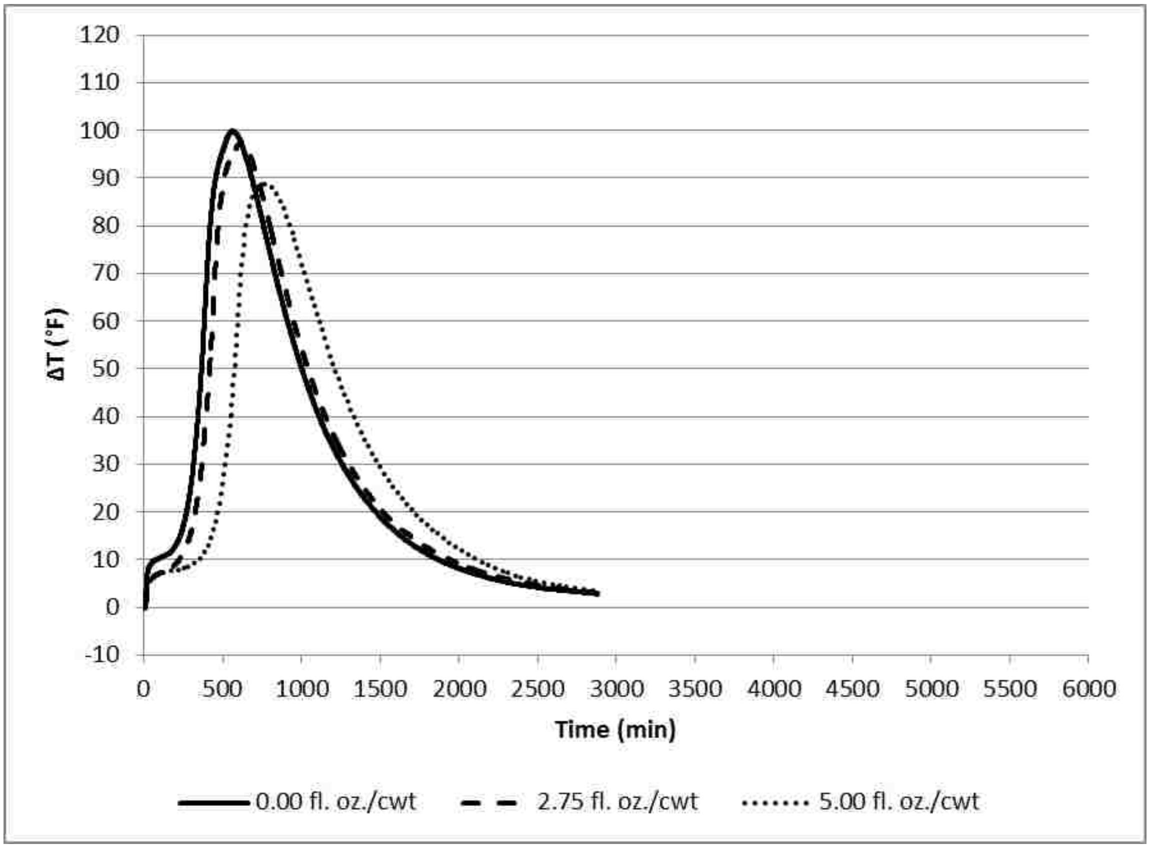

Figure 4.26. Thermal Curves Showing the Retarding Effect of Water Reducer

Table 4.36. Calorimetry Results for Mixtures with Increasing Water Reducer Dosages

Combination	Nominal Proportions						Curve Type	ΔT_{max} (°F)	Time at ΔT_{max} (min)	M (°F)	Setting Time Predictions			
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)					Percentage Method		Derivatives	
											Initial Set (min)	Final Set (min)	Initial Set (min)	Final Set (min)
4-1	100	0	0	0	0	0.00	A	108.25	486	102.35	288	353	352	376
4-1	100	0	0	0	0	2.75	A	107.74	551	105.17	347	413	407	435
4-1	100	0	0	0	0	5.00	A	116.16	501	112.74	314	374	373	395
4-1	75	25	0	0	0	0.00	A	99.92	567	90.53	306	374	365	390
4-1	75	25	0	0	0	2.75	A	97.39	618	91.73	345	420	424	440
4-1	75	25	0	0	0	5.00	A	88.80	753	82.75	483	569	572	592
4-1	50	50	0	0	0	0.00	A	58.97	785	50.61	475	573	579	599
4-1	50	50	0	0	0	2.75	A	59.37	846	50.66	543	639	642	663
4-1	50	50	0	0	0	5.00	A	57.82	948	50.06	621	722	722	744
4-1	30	70	0	0	0	0.00	B	35.17	794	25.68	537	640	669	687
4-1	30	70	0	0	0	2.75	B	28.98	964	20.25	680	796	833	851
4-1	30	70	0	0	0	5.00	B	30.61	984	22.88	707	812	473	853
1-3	100	0	0	0	0	0.00	A	98.91	501	91.62	264	321	303	325
1-3	100	0	0	0	0	2.75	A	103.14	532	95.84	314	378	361	388
1-3	100	0	0	0	0	5.00	A	92.43	636	83.58	407	481	477	496
1-3	75	25	0	0	0	0.00	A	72.96	749	63.27	392	469	444	471
1-3	75	25	0	0	0	2.75	A	80.95	757	70.36	423	490	457	480
1-3	75	25	0	0	0	5.00	A	72.64	836	62.53	502	577	544	575
1-3	50	50	0	0	0	0.00	C	33.58	1050	24.27	477	572	512	560
1-3	50	50	0	0	0	2.75	C	34.69	1245	23.07	493	778	335	498
1-3	50	50	0	0	0	5.00	C	30.88	1497	20.77	564	1020	522	561
1-3	30	70	0	0	0	0.00	G	22.25	94	12.50	26	41	33	43
1-3	30	70	0	0	0	2.75	F	19.85	92	12.13	27	36	32	36
1-3	30	70	0	0	0	5.00	F	19.26	96	12.44	27	38	33	38

The results of the miniature slump testing for mixtures with the low and high water reducer dosages are shown below in Table 4.37. Plots of the results can be found in Appendix E. Generally, as was expected, an increase in water reducer dosage resulted in increased pat area at all test times. Exceptions to this are the 50% and 70% fly ash mixtures for Combination 1-3. The low dosage with 50% fly ash and both dosages with 70% fly ash both show rapidly decreasing pat areas over time. For the 70% fly ash mixtures, some tests at later times were not able to be performed due to the stiffness of the paste. A sulfate imbalance, which resulted in rapid aluminate hydration, could explain the rapid setting behavior of some of these mixtures. For the zero and 25 percent fly ash mixtures at both water reducer dosages, the pat area typically increased at early ages and then began to gradually decrease, starting at five or fifteen minutes. This may have occurred because, even though the water reducer was added with the mixing water, it may have taken a period of time for the admixture to become active. However, Combination 1-3 with zero percent fly ash had increasing pat areas through 45 minutes for both dosages. An explanation for this behavior has not yet been found. The 50 and 70 percent fly ash mixtures showed decreasing pat areas over time, except for the 50 percent fly ash mixtures with the high water reducer dosage, which both increased from two to five minutes. A majority of the mixtures showed early stiffening behavior according to the guidelines presented by Roberts & Taylor (2007). Also, many of the mixtures had early stiffening indices greater than 1.00, which means that the pat areas for these mixtures increased from five to thirty minutes.

Table 4.37. Miniature Slump Results for Mixtures with Increasing Water Reducer Dosages.

Combination	Nominal Proportions						Miniature Slump Area (in^2)					Early Stiffening Index (30-min/5-min)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	
4-1	100	0	0	0	0	0.00	3.8	3.8	3.8	3.5	3.7	0.92
4-1	100	0	0	0	0	2.75	6.1	7.3	7.9	6.1	5.7	0.83
4-1	100	0	0	0	0	5.00	12.6	16.6	20.2	19.0	18.5	1.14
4-1	75	25	0	0	0	0.00	5.4	4.6	4.6	4.2	3.9	0.91
4-1	75	25	0	0	0	2.75	13.3	15.8	13.7	11.6	10.0	0.73
4-1	75	25	0	0	0	5.00	17.4	20.1	22.3	20.3	20.3	1.01
4-1	50	50	0	0	0	0.00	8.3	7.4	6.0	5.4	5.2	0.72
4-1	50	50	0	0	0	2.75	21.1	18.0	16.4	13.7	12.0	0.76
4-1	50	50	0	0	0	5.00	23.5	24.9	23.7	23.4	21.1	0.94
4-1	30	70	0	0	0	0.00	9.2	7.3	5.7	4.7	4.3	0.64
4-1	30	70	0	0	0	2.75	24.4	20.1	12.3	9.6	8.9	0.48
4-1	30	70	0	0	0	5.00	26.9	25.0	21.1	20.4	20.6	0.81
1-3	100	0	0	0	0	0.00	2.0	2.7	2.8	2.5	2.7	0.93
1-3	100	0	0	0	0	2.75	4.8	8.1	11.3	10.9	12.4	1.35
1-3	100	0	0	0	0	5.00	6.4	16.9	24.3	27.9	28.4	1.65
1-3	75	25	0	0	0	0.00	2.6	3.4	3.4	3.2	3.3	0.95
1-3	75	25	0	0	0	2.75	7.3	8.7	8.4	7.3	6.4	0.84
1-3	75	25	0	0	0	5.00	8.7	14.5	17.1	17.1	16.8	1.17
1-3	50	50	0	0	0	0.00	5.9	4.8	3.8	3.9	3.8	0.83
1-3	50	50	0	0	0	2.75	10.8	6.7	4.4	3.2	3.4	0.47
1-3	50	50	0	0	0	5.00	15.6	16.0	14.2	12.8	10.7	0.80
1-3	30	70	0	0	0	0.00	8.2	6.3	4.5	3.7	3.7	0.59
1-3	30	70	0	0	0	2.75	12.2	6.2	2.8	-----	-----	-----
1-3	30	70	0	0	0	5.00	18.9	14.8	7.7	2.5	-----	0.17

Table 4.38, below, summarizes the results of the Vicat setting time test for mixtures with increasing water reducer dosages. It shows that, generally, as the water reducer dosage increases, initial set increases, except for Combination 1-3 mixtures with 50 and 70 percent fly ash. Final set also increases with increased water reducer dosage, except for Combination 1-3 with 70 percent fly ash. Also, the final set time for Combination 4-1 with 25 percent fly ash decreased by 15 minutes with the low dose, but increased significantly with the high dose. Sulfate imbalance, resulting in rapid setting behavior, would explain the decrease in setting times for the mixtures with higher fly ash contents. The results also show that, as expected, the water required to achieve normal consistency usually decreased with increased dosages of the water reducer. The mixtures with 50 and 70 percent fly ash for Combination 1-3 showed little or no change in water requirement with the addition of the water reducer.

4.2.3. Effects of Gypsum Addition. The effects of gypsum addition were evaluated for both combinations at the 50 and 70 percent fly ash replacement levels. The two levels of gypsum addition were two and four percent, nominally.

Table 4.38. Vicat Results for Mixtures with Increasing Water Reducer Dosages

Combination	Nominal Proportions						Water for Normal	Vicat Results	
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	Consistency (0.5%)	Initial Set (min)	Final Set (min)
4-1	100	0	0	0	0	0.00	24.0	81	180
4-1	100	0	0	0	0	2.75	24.5	138	255
4-1	100	0	0	0	0	5.00	23.5	167	375
4-1	75	25	0	0	0	0.00	23.0	132	270
4-1	75	25	0	0	0	2.75	22.5	137	255
4-1	75	25	0	0	0	5.00	21.0	190	420
4-1	50	50	0	0	0	0.00	21.5	107	300
4-1	50	50	0	0	0	2.75	20.0	87	345
4-1	50	50	0	0	0	5.00	18.5	126	450
4-1	30	70	0	0	0	0.00	20.5	14	285
4-1	30	70	0	0	0	2.75	19.0	18	420
4-1	30	70	0	0	0	5.00	16.5	38	450
1-3	100	0	0	0	0	0.00	26.0	110	210
1-3	100	0	0	0	0	2.75	25.5	147	315
1-3	100	0	0	0	0	5.00	24.0	171	360
1-3	75	25	0	0	0	0.00	24.5	171	375
1-3	75	25	0	0	0	2.75	23.5	214	510
1-3	75	25	0	0	0	5.00	23.0	238	555
1-3	50	50	0	0	0	0.00	21.5	142	435
1-3	50	50	0	0	0	2.75	21.5	65	495
1-3	50	50	0	0	0	5.00	21.0	73	510
1-3	30	70	0	0	0	0.00	20.0	49	525
1-3	30	70	0	0	0	2.75	20.0	17	135
1-3	30	70	0	0	0	5.00	20.0	12	90

The effect of gypsum addition on the strength gain of the two combinations can be seen below in Figures 4.27 and 4.28. For Combination 4-1, the strengths after one day were slightly increased with increased gypsum addition, except for the 70 percent fly ash mixtures at 56 days. Here, the mixture with zero percent gypsum was greater than the 2 percent gypsum mixture and very close to the 4 percent gypsum mixture. Similar trends were seen for the Combination 1-3 mixtures, but with a significant difference in the 70 percent fly ash mixtures at early ages. As can be seen in the figure below, the 70 percent fly ash mixture with no gypsum experiences very little strength gain through seven days.

The strength gain curve was restored with the addition of 2 percent gypsum and showed further increases in early strengths with the addition of 4 percent gypsum. This indicates that the gypsum addition corrected the sulfate imbalance of this system.

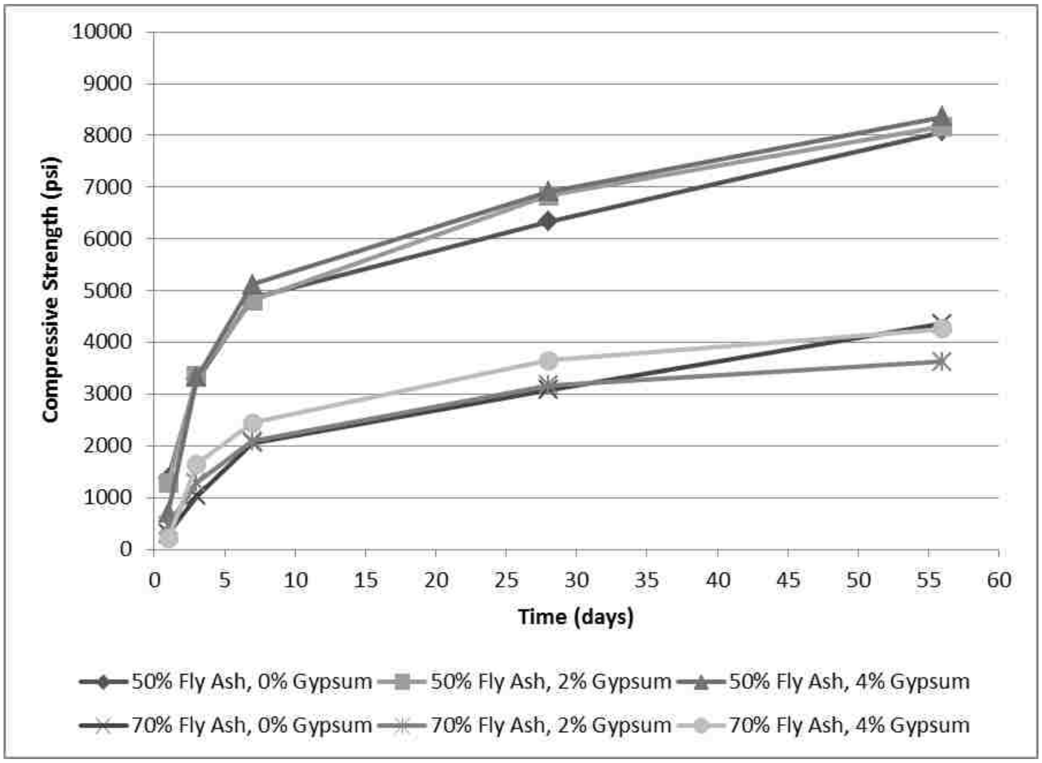

Figure 4.27. Effect of Gypsum Addition on Strength Gain for Combination 4-1

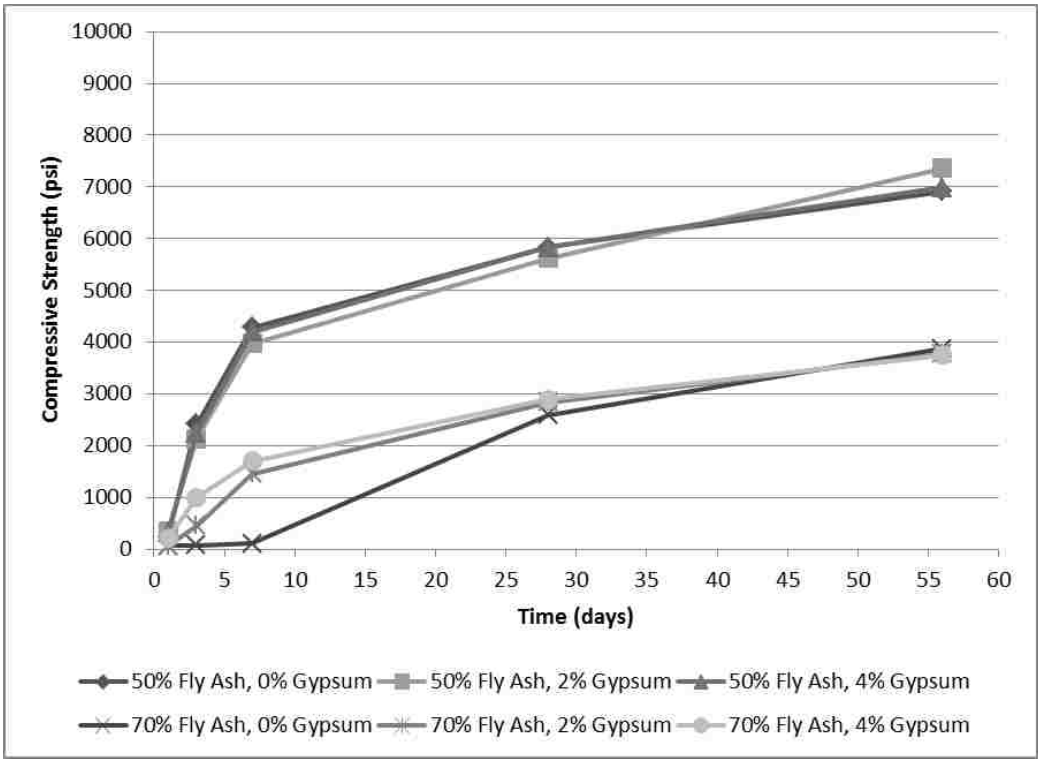

Figure 4.28. Effect of Gypsum Addition on Strength Gain for Combination 1-3

The calorimetry results for the mixtures containing additional gypsum are shown in Table 4.39, along with corresponding mixtures without additional gypsum. Plots of the curves can be found in Appendix D. The curves shapes were not significantly affected by the addition of gypsum, except for Combination 1-3 with 70 percent fly ash. Here, the changes in curve shape with increased gypsum additions may be indicative of less severe sulfate depletion. An asterisk was placed next to the letter C for Combination 1-3 with 50 percent fly ash and 4 percent gypsum. This is because the curve shape for the mixture was similar to Type C except that the small bump occurred after the curve had reached the peak temperature. According to ASTM C 1679, this indicates that sulfate depletion occurred at a later time than it did for the zero and two percent gypsum mixtures. For the

Combination 4-1 mixtures, the predicted final set time increased with increasing gypsum levels. For Combination 1-3, with increasing gypsum levels, the predicted final set time for the 50 percent fly ash mixture decreased with 2 percent gypsum and then increased with 4 percent gypsum. The predicted final set time for the 70 percent fly ash mixture increased with 2 percent gypsum and then decreased with 4 percent gypsum. Figure 4.29 shows a series of thermal curves with increasing gypsum additions. As can be seen, the overall curve shape is not significantly changed, but the positions of the curves are slightly delayed.

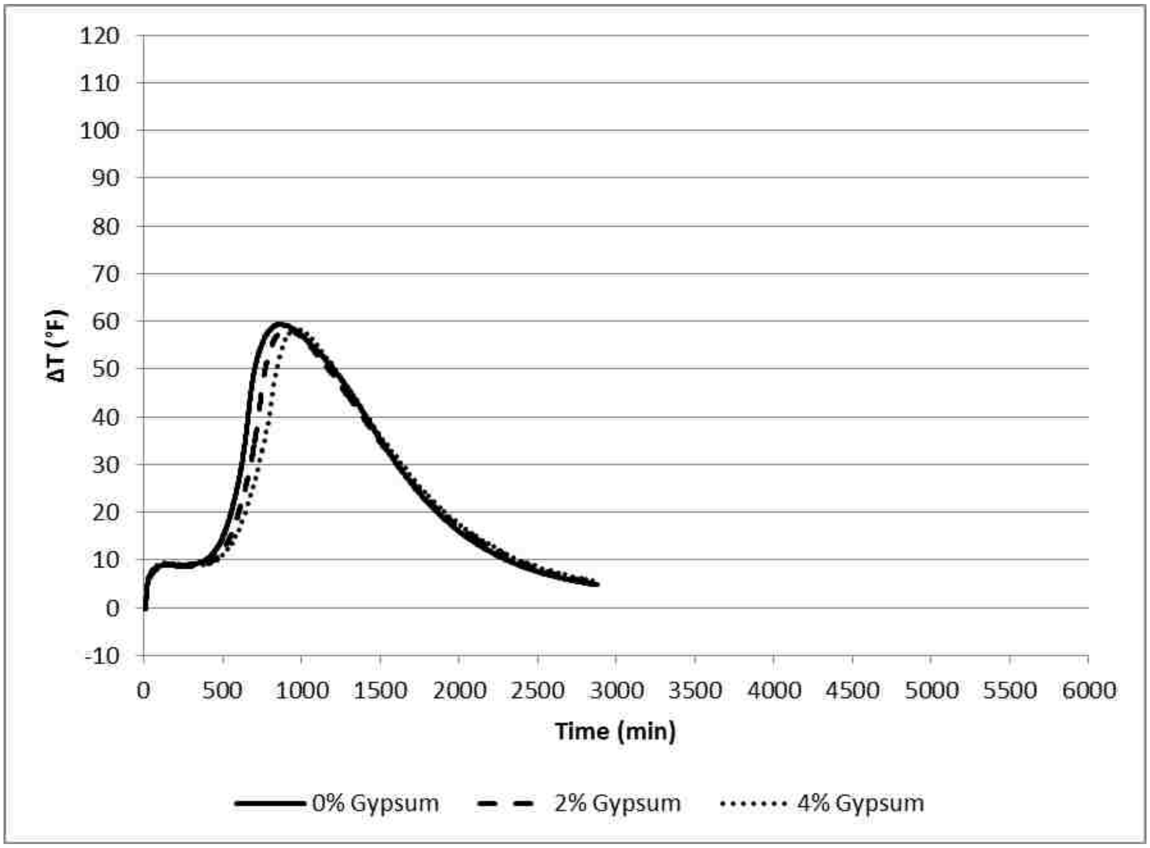

Figure 4.29. Series of Thermal Curves Showing the Effect of Gypsum Addition

Table 4.39. Calorimetry Results for Mixtures with Increasing Gypsum Additions

Combination	**Nominal Proportions**						**Curve Type**	**ΔT_{max} (°F)**	**Time at ΔT_{max} (min)**	**M (°F)**	**Setting Time Predictions**			
											Percentage Method		**Derivatives**	
	Cement (%)	**Fly Ash (%)**	**Gypsum (%)**	**Lime (%)**	**RSC (%)**	**WR (fl.oz./cwt)**					**Initial Set (min)**	**Final Set (min)**	**Initial Set (min)**	**Final Set (min)**
4-1	50	50	0	0	0	2.75	A	59.37	846	50.66	543	639	642	663
4-1	50	50	2	0	0	2.75	A	58.36	908	49.79	588	697	713	736
4-1	50	50	4	0	0	2.75	A	58.34	962	49.42	630	756	788	813
4-1	30	70	0	0	0	2.75	B	28.98	964	20.25	680	796	833	851
4-1	30	70	2	0	0	2.75	B	33.32	995	25.76	684	812	852	872
4-1	30	70	4	0	0	2.75	B	34.39	1148	27.14	787	947	1015	1034
1-3	50	50	0	0	0	2.75	C	34.69	1245	23.07	493	778	335	498
1-3	50	50	2	0	0	2.75	C	33.35	1130	22.69	590	686	672	704
1-3	50	50	4	0	0	2.75	C*	39.27	993	28.70	644	756	777	802
1-3	30	70	0	0	0	2.75	F	19.85	92	12.13	27	36	32	36
1-3	30	70	2	0	0	2.75	G	18.41	209	10.76	26	44	55	56
1-3	30	70	4	0	0	2.75	B	15.62	126	7.52	25	37	50	51

The miniature slump testing results for mixtures with added gypsum are shown in Table 4.40, below. Plots of these results can be found in Appendix E. These results show that for both combinations the addition of gypsum had little effect on the flow of the paste with 50 percent fly ash. With 70 percent fly ash, Combination 4-1 was not significantly affect by the 2 percent addition of gypsum, but maintained greater flow over time with 4 percent gypsum addition. For Combination 1-3 with 70 percent fly ash, the addition of gypsum appeared to have little effect at early ages. Beyond fifteen minutes, the miniature slump test was not able to be performed on this mixture without the addition of gypsum. This indicates that the paste stiffened less over time with the gypsum additions. All of the mixtures in the table below had early stiffening indices which were less than the 0.85 criteria. This indicates that all of the mixtures had early stiffening tendencies, though these were generally lessened with the addition of gypsum.

The Vicat setting time results are shown below in Table 4.41. For Combination 4-1, at both fly ash replacement levels, the 2 percent gypsum addition increased initial set. The addition of 4 percent gypsum resulted in an initial set time less than at 2 percent gypsum but greater than at zero percent gypsum. For Combination 1-3, both gypsum additions increased initial set time for the 50 percent fly ash mixtures. The 70 percent fly ash mixture had an initial set time decreased by two minutes with the 2 percent addition, but increased with the 4 percent addition. The addition of gypsum increased final set times, except for Combination 4-1 with 70 percent fly ash. The final set time for this mixture decreased by 15 minutes with the addition of 2 percent gypsum, but increased with the 4 percent addition. The water required for normal consistency was not affected by more than 0.5 percent with the addition of gypsum.

Table 4.40. Miniature Slump Results for Mixtures with Increasing Gypsum Additions

Combination	**Nominal Proportions**						**Miniature Slump Area (in^2)**					**Early Stiffening Index (30-min/5-min)**
	Cement (%)	**Fly Ash (%)**	**Gypsum (%)**	**Lime (%)**	**RSC (%)**	**WR (fl.oz./cwt)**	**2-min Test**	**5-min Test**	**15-min Test**	**30-min Test**	**45-min Test**	
4-1	50	50	0	0	0	2.75	21.1	18.0	16.4	13.7	12.0	0.76
4-1	50	50	2	0	0	2.75	20.2	19.6	15.5	13.9	11.8	0.71
4-1	50	50	4	0	0	2.75	20.1	18.3	15.0	13.2	12.3	0.72
4-1	30	70	0	0	0	2.75	24.4	20.1	12.3	9.6	8.9	0.48
4-1	30	70	2	0	0	2.75	24.0	20.1	12.2	9.3	8.7	0.46
4-1	30	70	4	0	0	2.75	24.2	21.1	15.2	12.8	11.6	0.61
1-3	50	50	0	0	0	2.75	10.8	6.7	4.4	3.2	3.4	0.47
1-3	50	50	2	0	0	2.75	9.8	7.6	4.8	4.0	4.0	0.53
1-3	50	50	4	0	0	2.75	10.4	7.1	4.7	4.0	3.6	0.56
1-3	30	70	0	0	0	2.75	12.2	6.2	2.8	-----	-----	-----
1-3	30	70	2	0	0	2.75	12.8	6.0	3.2	2.3	2.4	0.39
1-3	30	70	4	0	0	2.75	14.5	6.0	3.1	2.5	2.3	0.42

Table 4.41. Vicat Results for Mixtures with Increasing Gypsum Additions

Combination	Nominal Proportions						Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)		Initial Set (min)	Final Set (min)
4-1	50	50	0	0	0	2.75	20.0	87	345
4-1	50	50	2	0	0	2.75	20.0	136	405
4-1	50	50	4	0	0	2.75	20.0	123	540
4-1	30	70	0	0	0	2.75	19.0	18	420
4-1	30	70	2	0	0	2.75	19.0	48	405
4-1	30	70	4	0	0	2.75	18.5	39	450
1-3	50	50	0	0	0	2.75	21.5	65	495
1-3	50	50	2	0	0	2.75	21.0	77	570
1-3	50	50	4	0	0	2.75	21.5	83	675
1-3	30	70	0	0	0	2.75	20.0	17	135
1-3	30	70	2	0	0	2.75	20.5	15	240
1-3	30	70	4	0	0	2.75	20.5	24	300

4.2.4. Effects of Calcium Hydroxide-Gypsum Addition. The effects of the addition of calcium hydroxide were evaluated for both combinations at the 50 and 70 percent fly ash replacement levels. The two levels of calcium hydroxide addition were five and 10 percent, nominally.

The effects of calcium hydroxide addition on the strength gain of both combinations can be seen below in Figures 4.30 and 4.31. These mixtures all include a four percent nominal addition of gypsum. Combination 4-1 mixtures generally showed decreasing strengths with increasing calcium hydroxide additions, except at one day where slightly higher strengths were achieved. For Combination 1-3 with 50 percent fly ash, the addition of lime slightly increased early strengths, though at 56 days the addition of lime lead to decreased strengths. With 70 percent fly ash replacement, the addition of calcium hydroxide decreased strengths at all ages, except at one day, where slight increases in strength were obtained. The increases in early strengths and decreased later age strengths agree with the findings of Bentz (2010) on calcium hydroxide additions.

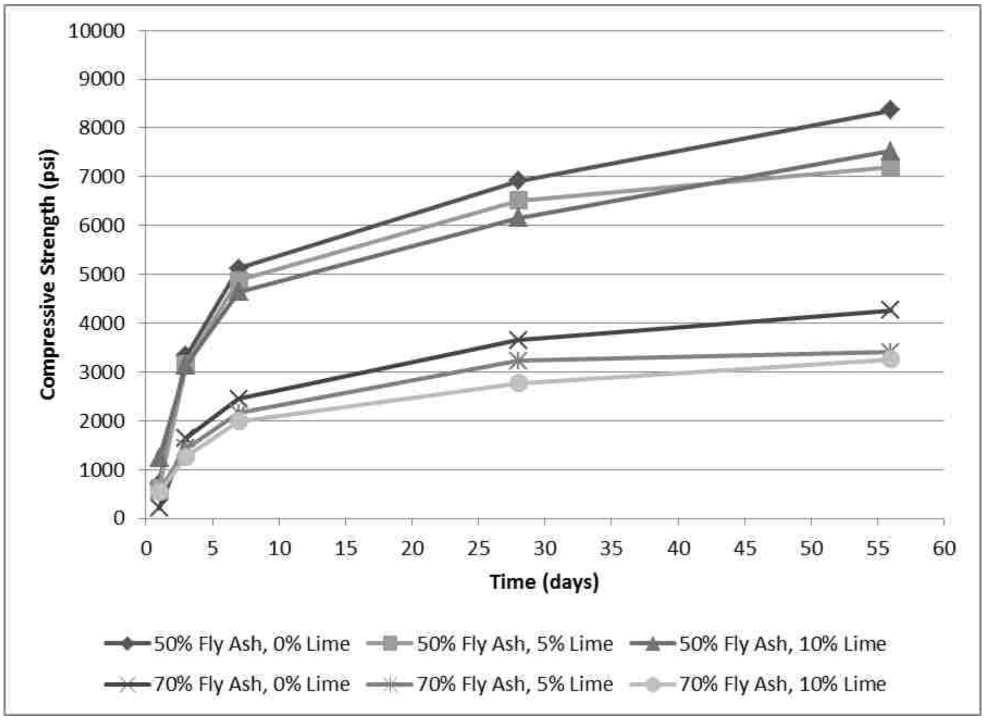

Figure 4.30. Effect of Lime on Combination 4-1 Mixtures with Four Percent Gypsum

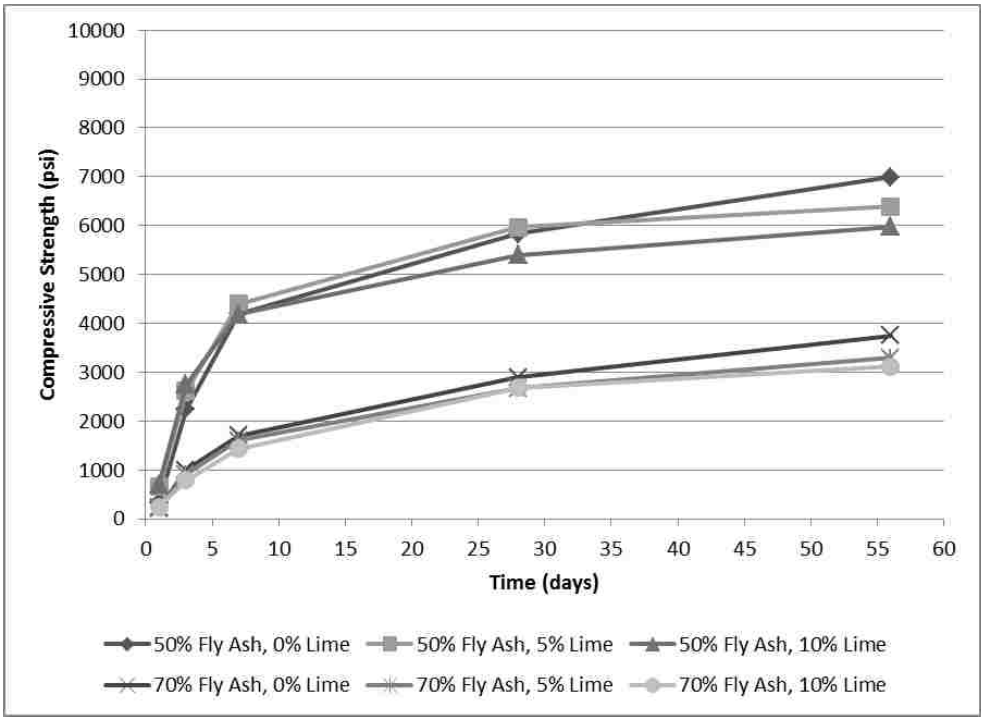

Figure 4.31. Effect of Lime on Combination 1-3 Mixtures with Four Percent Gypsum

The results of the semi-adiabatic calorimetry testing are shown below in Table 4.42 for mixtures with calcium hydroxide and gypsum. The thermal curves for these mixtures can be found in Appendix D. These mixtures all include a nominal four percent addition of gypsum. The curve shapes were not affected by the addition of calcium hydroxide, expect for Combination 1-3 with 50 percent fly ash. Without calcium hydroxide this mixture had a Type C curve with sulfate depletion occurring after the main peak. With both calcium hydroxide additions, this mixture had Type A curves, which are indicative of a normally hydrating mixture. This indicates that the increase in available calcium may have accelerated the silicate hydration. The main hydration response rise (M) changed by less than two degrees for all mixtures with the addition of calcium hydroxide, indicating that the calcium hydroxide had little effect on the amount of heat produced by the system. The predicted final set time by the Percentage Method generally decreased for all mixtures as lime was added to the system, indicating that hydration was accelerated. A typical series of thermal curves with increasing calcium hydroxide additions is shown in Figure 4.32, below. This example shows that the curve shape and magnitude of the main peak are relatively unchanged, while the position of the curve is shifted to earlier times with calcium hydroxide addition.

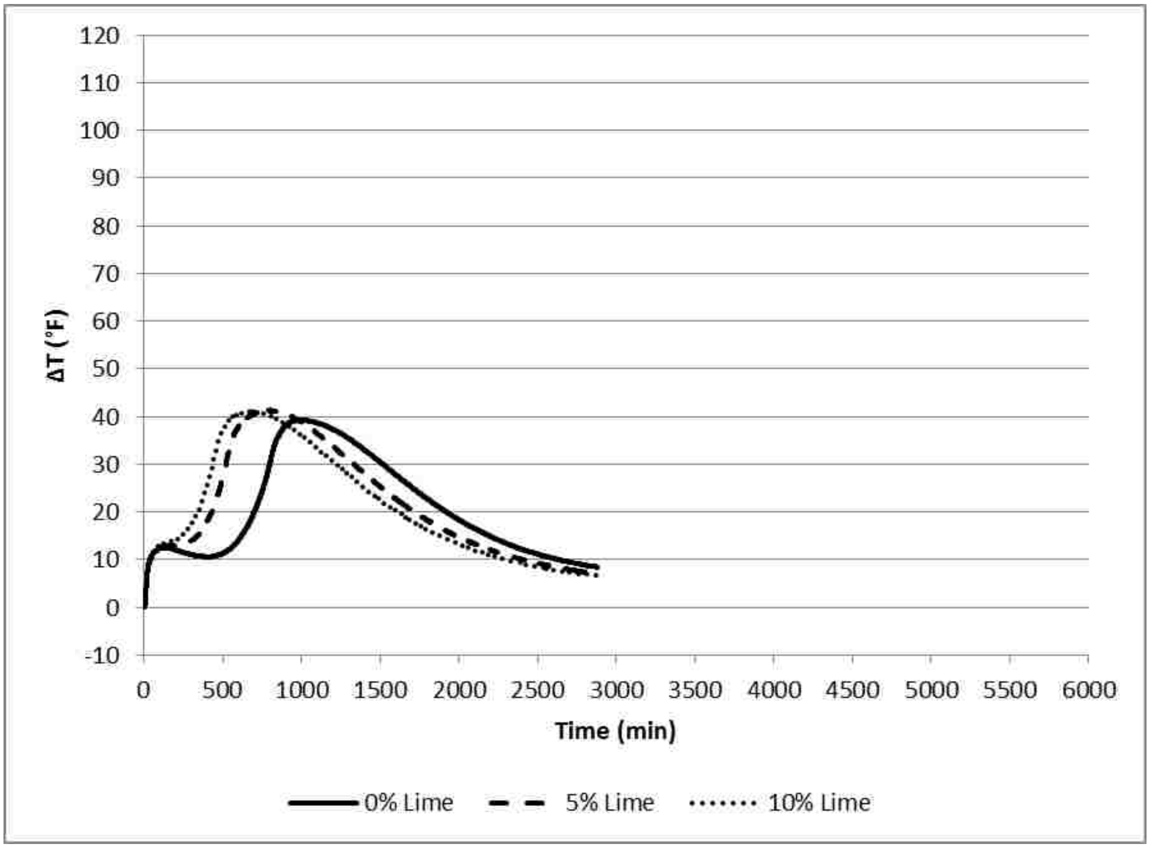

Figure 4.32. Series of Thermal Curves Showing the Effect of Calcium Hydroxide Addition

The miniature slump results for the mixtures containing calcium hydroxide and gypsum are shown, below, in Table 4.43. Plots of these results are given in Appendix E. For all mixtures at all test times, the miniature slump area decreased with increasing calcium hydroxide addition, which may have been caused by an increased water demand from the addition. The change in pat areas over time was similar for all calcium hydroxide addition levels for all mixtures, including those with no calcium hydroxide. For Combination 1-3 with 70 percent fly ash, the mixture with 10 percent calcium hydroxide addition was too stiff to be tested after 15 minutes.

Table 4.42. Calorimetry Results for Mixtures with Increasing Calcium Hydroxide Additions and Four Percent Gypsum

Combination	**Nominal Proportions**						**Curve Type**	**ΔT_{max} (°F)**	**Time at ΔT_{max} (min)**	**M (°F)**	**Setting Time Predictions**			
											Percentage Method		**Derivatives**	
	Cement (%)	**Fly Ash (%)**	**Gypsum (%)**	**Lime (%)**	**RSC (%)**	**WR (fl.oz./cwt)**					**Initial Set (min)**	**Final Set (min)**	**Initial Set (min)**	**Final Set (min)**
4-1	50	50	4	0	0	2.75	A	58.34	962	49.42	630	756	788	813
4-1	50	50	4	5	0	2.75	A	56.58	885	48.06	534	678	723	745
4-1	50	50	4	10	0	2.75	A	59.37	631	49.42	325	444	478	494
4-1	30	70	4	0	0	2.75	B	34.39	1148	27.14	787	947	1015	1034
4-1	30	70	4	5	0	2.75	B	37.37	720	28.69	394	547	610	627
4-1	30	70	4	10	0	2.75	B	36.38	613	27.54	286	441	514	527
1-3	50	50	4	0	0	2.75	C*	39.27	993	28.70	644	756	777	802
1-3	50	50	4	5	0	2.75	A	41.25	792	28.62	406	497	496	523
1-3	50	50	4	10	0	2.75	A	41.02	702	28.17	317	414	420	444
1-3	30	70	4	0	0	2.75	B	15.62	126	7.52	25	37	50	51
1-3	30	70	4	5	0	2.75	B	21.69	620	6.55	439	508	520	541
1-3	30	70	4	10	0	2.75	B	23.83	483	7.29	289	372	191	405

Table 4.43. Miniature Slump Results for Mixtures with Increasing Lime Addition and Four Percent Gypsum

Combination	Nominal Proportions						Miniature Slump Area (in^2)					Early Stiffening Index
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	(30-min/5-min)
4-1	50	50	4	0	0	2.75	20.1	18.3	15.0	13.2	12.3	0.72
4-1	50	50	4	5	0	2.75	15.5	13.8	13.1	11.5	10.6	0.84
4-1	50	50	4	10	0	2.75	12.2	10.6	8.5	6.5	5.6	0.61
4-1	30	70	4	0	0	2.75	24.2	21.1	15.2	12.8	11.6	0.61
4-1	30	70	4	5	0	2.75	16.5	14.4	10.2	7.6	6.8	0.53
4-1	30	70	4	10	0	2.75	12.2	9.0	6.9	5.5	4.9	0.62
1-3	50	50	4	0	0	2.75	10.4	7.1	4.7	4.0	3.6	0.56
1-3	50	50	4	5	0	2.75	7.6	4.1	2.8	2.4	2.3	0.59
1-3	50	50	4	10	0	2.75	6.8	3.7	2.4	2.2	2.2	0.59
1-3	30	70	4	0	0	2.75	14.5	6.0	3.1	2.5	2.3	0.42
1-3	30	70	4	5	0	2.75	9.8	4.4	2.3	2.0	2.1	0.45
1-3	30	70	4	10	0	2.75	6.4	3.0	2.0	-----	-----	-----

The Vicat setting time results for mixtures with increasing calcium hydroxide additions are shown below in Table 4.44. The initial set time generally decreased with increased calcium hydroxide content, except for Combination 4-1 with 70 percent fly ash, which increased with increasing calcium hydroxide content. Also, the initial set time for Combination 1-3 with 70 percent fly ash increased by one minute with the addition of five percent calcium hydroxide. Final set time also generally decreased with additional calcium hydroxide, except for Combination 4-1 with 70 percent fly ash which had the same final set time for both addition levels. The general decrease in setting times with increasing calcium hydroxide contents indicates that the hydration reactions are being accelerated. For all mixtures, an increase in calcium hydroxide content led to an increase in the water required for normal consistency. This correlates with the decreased pat areas of the miniature slump test discussed previously, which indicated that the addition of the calcium hydroxide increased the water demand of the system.

Table 4.44. Vicat Results for Mixtures with Increasing Lime Additions

Combination	Nominal Proportions						Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)		Initial Set (min)	Final Set (min)
4-1	50	50	4	0	0	2.75	20.0	123	540
4-1	50	50	4	5	0	2.75	21.0	111	360
4-1	50	50	4	10	0	2.75	21.5	101	315
4-1	30	70	4	0	0	2.75	18.5	39	450
4-1	30	70	4	5	0	2.75	20.5	80	345
4-1	30	70	4	10	0	2.75	21.0	92	345
1-3	50	50	4	0	0	2.75	21.5	83	675
1-3	50	50	4	5	0	2.75	22.5	63	465
1-3	50	50	4	10	0	2.75	23.0	46	360
1-3	30	70	4	0	0	2.75	20.5	24	300
1-3	30	70	4	5	0	2.75	21.5	25	285
1-3	30	70	4	10	0	2.75	23.0	14	195

4.2.5. Effects of Rapid Set Cement-Gypsum Addition. The effects of the addition of rapid set cement (RSC) were evaluated for both combinations at the 50 and 70 percent fly ash replacement levels. The two levels of rapid set cement addition were nominally 10 and 20 percent.

The results of the cube compressive strength testing for Combination 4-1 with rapid set cement are shown below in Figure 4.33. The results of the cube compressive strength testing for Combination 1-3 with rapid set cement are shown below in Figure 4.34. All of these mixtures include a nominal four percent gypsum addition. For Combination 4-1 with 50 percent fly ash, an increase in RSC content generally led to an increase in strength, except at 56 days where RSC addition resulted in decreased strengths. With 70 percent fly ash, this combination had increased strengths at all ages with increased RSC additions. For Combination 1-3, increasing RSC additions generally led to increased strengths at all ages. An exception to this is the 70 percent fly ash mixture with 20 percent RSC, which gained very little strength from one to three days and had a lower compressive strength than the 0 and 10 percent RSC mixtures at three days.

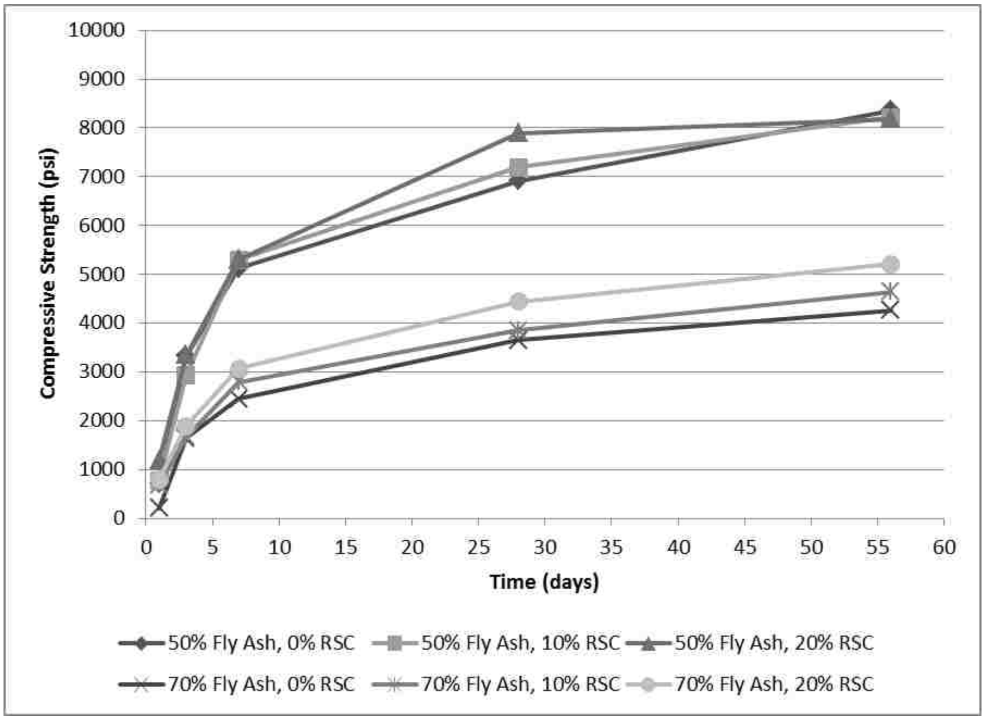

Figure 4.33. Effect of RSC on Combination 4-1 Mixtures with Four Percent Gypsum

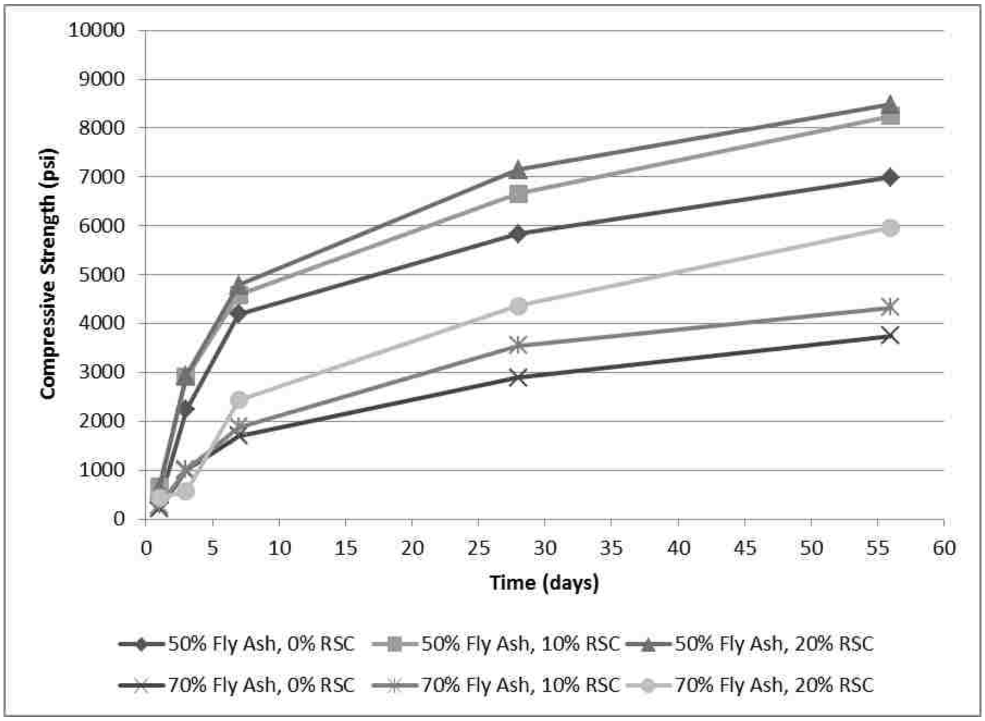

Figure 4.34. Effect of RSC on Combination 1-3 Mixtures with Four Percent Gypsum

The semi-adiabatic calorimetry results for mixtures containing RSC are shown in Table 4.45, below. These mixtures all contain a nominal four percent gypsum addition. Plots of the thermal curves for these mixtures can be found in Appendix D. For Combination 4-1 with 50 percent fly ash, the overall curve shape did not change with the addition of RSC. For the other mixtures, the addition of RSC resulted in changes in curve shape. These changes in shape with increasing RSC contents may indicate increasingly severe sulfate imbalances. This can be seen as the sulfate depletion peak occurs earlier and the silicate peak occurs later, relative to each other. For both combinations with 50 percent fly ash, the addition of RSC decreased the main hydration response rise. With 70 percent fly ash, the addition of RSC increased the main hydration response rise, except for Combination 4-1 with 10 percent RSC, which decreased. For both combinations, increases in RSC generally led to a decrease in the predicted final set time by the Percentage Method. An exception to this was Combination 1-3 with 70 percent fly ash, which had increased predicted final set times for both mixtures containing RSC, when compared to the mixture with no RSC. Figure 4.35, below, shows the thermal curves for a 70 percent fly ash mixture with increasing RSC contents. As can be seen, the curve shape is changed, the peak height is increased, and the peak occurs at earlier times.

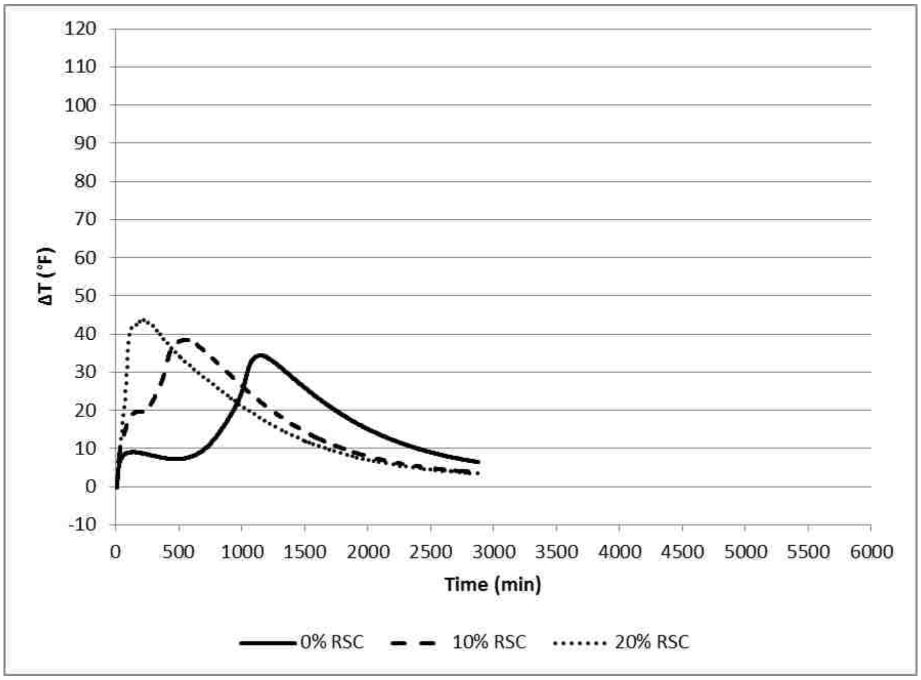

Figure 4.35. Series of Thermal Curves Showing the Effect of RSC Addition

The miniature slump results for mixtures with increasing RSC additions are shown below in Table 4.46. Plots of these results can be found in Appendix E. These mixtures all contain a nominal four percent gypsum addition. The addition of RSC gave results similar to those seen with the addition of calcium hydroxide. However, the cause here may be the accelerated rates of hydration for these systems. For all mixtures, increasing RSC contents led to decreased pat areas at all times. Also, the change in pat areas over time was similar to those for the corresponding mixtures which did not contain RSC. The miniature slump test could not be performed for Combination 1-3 with 70 percent fly ash and 20 percent RSC after 15 minutes due to the stiffness of the paste. With increasing RSC additions, the early stiffening indices decreased for all mixtures, indicating that these mixtures have increased early stiffening tendencies. Also, the early stiffening indices for all mixtures were below 0.85.

Table 4.45. Calorimetry Results for Mixtures with Increasing RSC Additions and Four Percent Gypsum

Combination	Nominal Proportions						Curve Type	ΔT_{max} (°F)	Time at ΔT_{max} (min)	M (°F)	Setting Time Predictions			
											Percentage Method		Derivatives	
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)					Initial Set (min)	Final Set (min)	Initial Set (min)	Final Set (min)
4-1	50	50	4	0	0	2.75	A	58.34	962	49.42	630	756	788	813
4-1	50	50	4	0	10	2.75	A	54.61	726	37.64	433	534	556	576
4-1	50	50	4	0	20	2.75	A	54.13	520	29.46	251	318	313	330
4-1	30	70	4	0	0	2.75	B	34.39	1148	27.14	787	947	1015	1034
4-1	30	70	4	0	10	2.75	F	38.50	544	19.25	303	378	392	405
4-1	30	70	4	0	20	2.75	F	43.67	210	33.44	56	81	78	87
1-3	50	50	4	0	0	2.75	C*	39.27	993	28.70	644	756	777	802
1-3	50	50	4	0	10	2.75	C	42.30	852	23.98	394	473	411	440
1-3	50	50	4	0	20	2.75	D	32.86	171	22.63	55	100	111	119
1-3	30	70	4	0	0	2.75	B	15.62	126	7.52	25	37	50	51
1-3	30	70	4	0	10	2.75	G	30.32	162	18.51	50	84	42	102
1-3	30	70	4	0	20	2.75	F	38.42	149	30.08	39	71	72	78

Table 4.46. Miniature Slump Results for Mixtures with Increasing RSC Addition and Four Percent Gypsum

Combination	Nominal Proportions						Miniature Slump Area (in^2)					Early Stiffening Index (30-min/5-min)
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	2-min Test	5-min Test	15-min Test	30-min Test	45-min Test	
4-1	50	50	4	0	0	2.75	20.1	18.3	15.0	13.2	12.3	0.72
4-1	50	50	4	0	10	2.75	15.1	14.5	11.6	8.5	7.1	0.59
4-1	50	50	4	0	20	2.75	11.9	9.6	7.3	4.0	3.1	0.42
4-1	30	70	4	0	0	2.75	24.2	21.1	15.2	12.8	11.6	0.61
4-1	30	70	4	0	10	2.75	17.0	14.0	6.9	4.0	2.9	0.29
4-1	30	70	4	0	20	2.75	14.9	13.0	6.0	2.6	2.1	0.20
1-3	50	50	4	0	0	2.75	10.4	7.1	4.7	4.0	3.6	0.56
1-3	50	50	4	0	10	2.75	8.3	5.9	3.3	2.5	2.2	0.42
1-3	50	50	4	0	20	2.75	7.9	5.8	3.0	2.1	2.1	0.37
1-3	30	70	4	0	0	2.75	14.5	6.0	3.1	2.5	2.3	0.42
1-3	30	70	4	0	10	2.75	9.8	5.4	2.5	2.1	2.0	0.38
1-3	30	70	4	0	20	2.75	9.8	6.0	2.4	-----	-----	-----

Table 4.47, below, summarizes the results of the Vicat setting time testing for mixtures containing RSC. As expected, the initial and final set times for all mixtures decreased with increasing RSC additions. Also, an increase in RSC content led to an increase in the water required to achieve normal consistency.

Table 4.47. Vicat Results for Mixtures with Increasing RSC Additions

Combination	Nominal Proportions						Water for Normal Consistency (0.5%)	Vicat Results	
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)		Initial Set (min)	Final Set (min)
4-1	50	50	4	0	0	2.75	20.0	123	540
4-1	50	50	4	0	10	2.75	20.5	15	360
4-1	50	50	4	0	20	2.75	21.0	13	180
4-1	30	70	4	0	0	2.75	18.5	39	450
4-1	30	70	4	0	10	2.75	19.0	12	135
4-1	30	70	4	0	20	2.75	20.0	12	90
1-3	50	50	4	0	0	2.75	21.5	83	675
1-3	50	50	4	0	10	2.75	22.0	44	450
1-3	50	50	4	0	20	2.75	22.5	31	165
1-3	30	70	4	0	0	2.75	20.5	24	300
1-3	30	70	4	0	10	2.75	21.0	12	120
1-3	30	70	4	0	20	2.75	22.0	12	75

4.3 CORRELATIONS

Sandberg and Liberman (2007) evaluated the use of thermal curves from semi-adiabatic calorimetry to predict initial and final setting times as determined by ASTM C 403. Using the Derivatives and Fractions (or Percentage) Methods, described previously in the Laboratory Investigation, they were able to find a strong correlation between the results of the two methods. Cost (2009) also discusses the used of semi-adiabatic calorimetry results for determining predicted set times, though he emphasizes their use for comparative, rather than quantitative, purposes. It should be noted that in both cases, the researchers were comparing the results of concrete testing for both the semi-adiabatic and setting time tests.

In this study, correlations between predicted set times, as described by Sandberg and Liberman, and Vicat setting times, according to ASTM C 191, were evaluated. For the Percentage Method, 20 percent of the main hydration response was taken as initial set and 50 percent of the main hydration response was taken as final set. Linear correlations were first evaluated for the results of all mixtures from both the Screening and Main Studies. This involved the initial and final set times, by each prediction method, being correlated with the Vicat initial and final set times, respectively and individually. The best correlation was found between the Vicat final setting time and the predicted final set by the Percentage Method. This correlation is shown below in Figure 4.36.

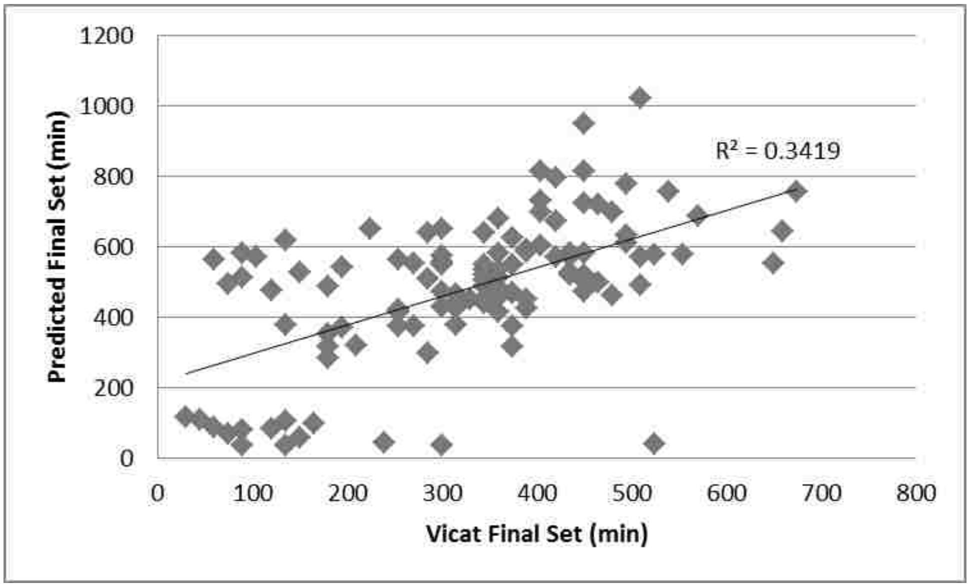

Figure 4.36. Correlation of Percentage Method Final Set Times for All Mixtures

It was thought that, because many of the mixtures were found to be affected by sulfate imbalances, a better correlation would exist for those mixtures which showed hydration characteristics typical of a portland cement. Therefore, the correlation was evaluated only for mixtures with Type A thermal curve shapes, as determined from the semi-adiabatic calorimetry testing. The results of this evaluation are shown below in Figure 4.37.

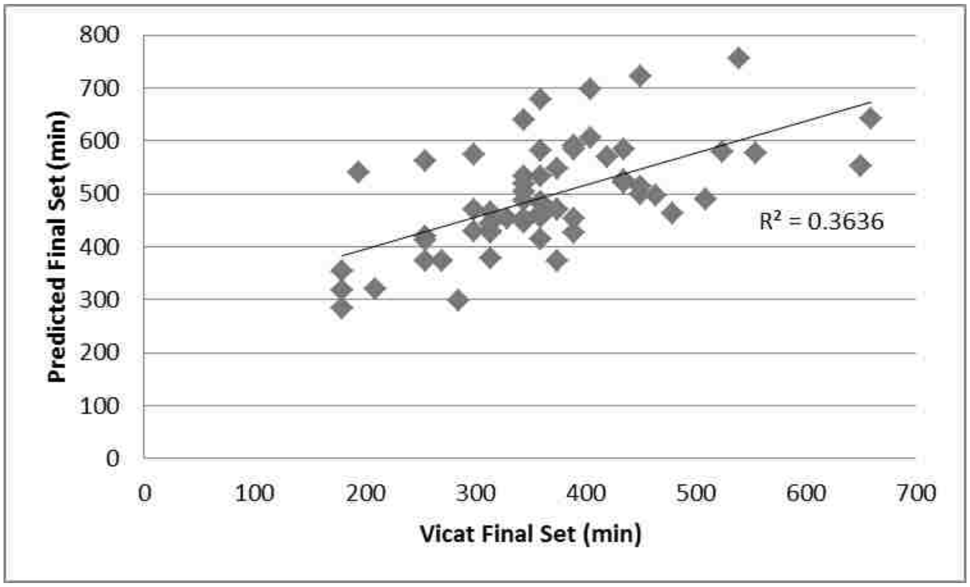

Figure 4.37. Correlation of Percentage Method Final Set Times for Type A Mixtures

As can be seen from the results above, the correlation between the two methods of evaluating setting times is poor with R-squared values less than 0.4. This may be the result of various factors including differences in water-cementitious materials ratios and differences in the curing conditions of the pastes for each test method. The differences in the w/cm occur because all of the paste mixtures used for the calorimetry testing were mixed with a w/cm of 0.40, while the paste used in the Vicat procedure was prepared at a water content that resulted in a paste with normal consistency, according to ASTM C 187. This resulted in different water-cementitious materials ratios for each paste mixture used in the Vicat procedure. The differences in curing conditions occur because the paste used for the calorimetry testing was sealed in plastic cylinders and placed in the calorimeter, while the paste in the Vicat procedure was placed in the moist cure room for the duration of the test. This resulted in differences in the temperature and relative humidity at which the pastes for the two procedures were hydrating.

5. SUMMARY AND CONCLUSIONS

5.1 SUMMARY

As part of a larger study on high volume fly ash (HVFA) concrete, paste mixtures were tested to evaluate the effects of Class C fly ash on cementitious systems and to determine possible solutions for common problems associated with mixtures high in Class C fly ash content. These problems include extreme delays in setting and slow strength development.

The first part of the study, the Screening Study, evaluated five Type I or Type I/II portland cements in combination with five Class C fly ashes. The materials were chosen to be representative of those commonly used in the state of Missouri. The effects of each fly ash were evaluated at replacement levels of 0, 25, 50, and 70 percent by mass for each of the cements. Testing in the Screening Study included cube compressive strength at one day, cube compressive strength at 28 days, semi-adiabatic calorimetry, miniature slump, and Vicat setting time.

The second part of the study, the Main Study, evaluated the use of powder additions for correcting the negative effects seen with the use of high amounts of Class C fly ash replacement. Here, the most and least reactive cement-fly ash combinations from the Screening Study were used for further evaluation. The powder additions were each evaluated at two addition levels for mixtures with 50 and 70 percent fly ash and included gypsum, calcium hydroxide, and rapid set cement. The effects of a water reducer were also evaluated for mixtures with 0, 25, 50, and 70 percent fly ash. Testing in the Main Study included cube compressive strength, semi-adiabatic calorimetry, miniature slump, and Vicat setting time. Compressive strength testing was performed at 1, 3, 7, 28, and 56 days.

5.2 CONCLUSIONS

From the results of the Screening Study, it was apparent that the replacement of portland cement with Class C fly ash had varied results on the properties of the paste mixtures. Generally, increasing fly ash contents led to decreased strengths at one and 28 days. The calorimetry results generally showed that the peak temperature was decreased and the silicate hydration was delayed by increasing the fly ash content. However, it was also seen that with 50 and 70 percent replacements with fly ash, the hydration curve was severely affected. The miniature slump results illustrated that as fly ash contents increased, the fluidity of the paste increased at very early ages, though it was accompanied by a more severe loss of fluidity over time, which may have been the result of rapid aluminate hydration, due to a sulfate imbalance. From the results of the Vicat setting time tests, it was observed that, up to a point, increasing fly ash contents delayed setting times, after which setting times were significantly shortened. From review of the literature and previous research, it was determined that many of the inconsistencies observed in the results of the Screening Study could be attributed to sulfate imbalances in the cementitious systems. This would explain the significantly changed hydration curves, severe fluidity loss, and accelerated setting times experienced by many of the 50 and 70 percent fly ash mixtures.

The results of the Main Study showed the effects of powder additions and a water reducer on the paste mixtures. Generally, the addition of the water reducer decreased the one day strengths of the mixtures containing fly ash, showed similar or increased strengths at 56 days, had little effect on the shapes of the thermal curves, led to delays in the main hydration curve, and increased fluidity of the paste at all times. The addition of gypsum was found to at least partially correct the sulfate imbalances experienced by some of the mixtures. It was seen that the addition of gypsum significantly improved the strength gain characteristics of the Combination 1-3 mixture with 70 percent fly ash at early ages. Also, some of the thermal curves indicated that the sulfate depletion point was being delayed and suppressed or that silicate hydration was accelerated by increasing gypsum contents. The calcium hydroxide showed improvements in one day strengths and appeared to partially mitigate some problems seen in the thermal curves. However, strengths past one day were found to decrease with increased lime contents. Bentz (2010) found similar effects from the use of calcium hydroxide and suggested that other sources of calcium ions be investigated. The use of rapid set cement generally increased compressive strengths at all ages and accelerated the occurrence of the silicate hydration peak. However, some of the thermal curves indicated that the rapid set cement might have worsened any sulfate imbalance in the system. The changes in miniature slump and Vicat setting time results were similar for both the use of calcium hydroxide and rapid set cement. The miniature slump results were shown to decrease at all ages for increased contents of both powders. However, the loss of fluidity over time was not significantly affected. The Vicat setting times were generally found to decrease with both powders, indicating that the hydration reactions were accelerated. As with the results of the

Screening Study, many of the inconsistencies experienced in the results of the Main Study can be explained by sulfate imbalances. Though gypsum was added as a source of additional sulfate, this may not have been sufficient for the increased aluminate levels of the mixtures with 50 or 70 percent fly ash. It should also be noted that this sulfate imbalance would adversely affect the hydration of the silicates by decreasing the amounts of available sulfate and calcium.

5.3 FUTURE RESEARCH

As an extension of the study presented here, further testing should be performed on the materials to more fully characterize the portland cements, fly ashes, and powder additions which were utilized. This would provide further insight into the test results that have been presented, because it is known, for example, that the mineralogical characteristics of a fly ash plays an important role in the reactivity of the material. Also, more information about the particle size distributions of the materials would assist in determining what effect they may have on the fluidity of the paste mixtures.

Bentz (2010) suggested that a source of calcium, other than calcium hydroxide, should be explored to ensure sufficient calcium is available for hydration of the silicates without adversely affecting compressive strengths at later ages. Also, the addition of another sulfate source, such as hemihydrate, should be investigated which would go into solution more quickly to control the increased aluminate reactions of the HVFA mixtures.

A standardized mixing procedure, which allowed early data collection for calorimetric or rheological testing, would allow better interlaboratory comparison of the results from paste studies. Many researchers have utilized procedures that achieve sufficient mixing in under 2 minutes with handheld mixers or high-shear blenders. This has been done to characterize paste mixtures at ages earlier than would be allowed using the mixing procedure outlined in ASTM C 305.

APPENDIX A

TESTING PROCEDURES

Compressive Strength of Cement Cubes
(ASTM C 109 and ASTM C 305)
(Revised 6-19-2012)

Equipment

1. Black and Decker 250-Watt Hand Mixer (Model MX217) with egg beater paddles
2. 20-quart Hobart mixing bowl
3. Plastic ladle
4. Hamilton 1-mL Adjustable Volume SoftGrip Pipette, (readable to 0.01 mL)
5. 3-quart or larger white plastic bowl with spout
6. Metal spoon
7. Small stainless steel spatula
8. Form oil and brush
9. 2” cube molds, tamper, and trowel
10. Analog thermometer with 5-inch probe
11. Sandpaper (Grit #60)
12. Digital calipers
13. Spherically seated circular upper bearing block with a diameter of 3.5 inches
14. Square lower bearing block with a diagonal of 3.5 inches
15. Sper Scientific Humidity/Temperature Monitor (Model 800016)
16. 4x8 in. plastic cylinder mold with lid
17. 12-kg Denver Instrument balance

Procedure

1. Apply a coating of vacuum grease to seal the surfaces where the halves of the mold join. Tighten the halves together and remove any extruded grease with a cloth.
2. Apply a small amount of vacuum grease to the surfaces of the mold that will be in contact with the base plate. Clamp the mold down to the base plate and wipe/scrape away any excess sealant, especially in the corners to avoid rounded cube edges
3. Apply a thin, even coating of form oil to the interior faces of the mold using a brush and wipe off any excess oil.
4. Verify that the air temperature is 23.0±3.0°C (68.0-78.8°F), mixing water temperature is 23.0±2°C (69.8-77.0°F), and that the relative humidity of the air is not less than 50%. Record these parameters.
5. Using the predetermined mix design, mix the paste using the following procedure:
    a. To blend the dry constituents of the mix: Place about 1000 grams of the dry materials into a 4”x8” cylinder mold in the same proportions to be used in the paste mixture, hold the cylinder horizontally with one hand on each end of the cylinder, and then shake the cylinder 25 cycles using a 6” throw.
    b. To dissolve admixtures into the mix water: Place all of the deionized water into the plastic bowl, use the 1-mL syringe to add the desired amount of admixture to the water, and use the small spatula to gently stir the water until all of the admixture is dissolved.
    c. Add the premixed cementitious materials to the mixing bowl, forming a donut shape.
    d. Add all of the mix water to the mixing bowl, start the timer, and record the time (Start Time).
    e. Wait 10 seconds to allow the cement to absorb the water.
    f. Mix at Speed 2 (440 RPM) for 20 seconds. Rotate the bowl 90° every 5 seconds.

   g. Mix at Speed 6 (670 RPM) for 60 seconds. Rotate the bowl 90° every 15 seconds and occasionally run the mixing paddles along the side of the bowl.
   h. At the end of the initial mixing, record the temperature of the paste.
   i. At 4 minutes, remix the paste at Speed 2 for 30 seconds.
   j. At 13 minutes, remix the paste at Speed 2 for 30 seconds.
6. Molding the specimens must begin within 2 minutes and 30 seconds after completion of mixing or remixing.
7. Place a layer of paste in each of the cube compartments of 1 inch (about half the depth of the mold).
8. Tamp the paste in each compartment 32 times in about 10 seconds, in 4 rounds. Each round consists of 8 adjoining strokes and should be at right angles to the other rounds. The tamping pressure should be just enough to ensure uniform filling of the mold.
9. Fill the remaining portion of the molds and repeat the tamping procedure used on the first layer. Bring in paste that is forced out onto the tops of the molds during tamping.
10. Draw the flat side of the trowel, with the leading edge slightly raised, once across the top of each cube at right angles to the length of mold.
11. Draw the flat side of the trowel, with the leading edge slightly raised, lightly once along the length of the mold.
12. Using the straight edge of the trowel, held perpendicular to the surface of the mold andwith a sawing motion along the length of the mold, cut the paste flush with the mold.
13. Immediately, place the specimens in the moist cure room. Protect the specimens from dripping water by using an arched sheet of thin plastic to cover the molds.
14. In the case of specimens to be tested for 1-day strengths, remove the specimens from the molds after 24 hours and proceed to step 15. For all other cases, remove the specimens from the molds after 72 hours, label each specimen with the Mix ID and age of testing using a China marker,

and place them in buckets of water saturated with hydrated lime (not aglime) in the moist cure room until they are needed for testing. Then proceed to step 15. Specimen age at the time of testing and at mold removal times shall be within the tolerances given below in Table 1. Cubes tested at 56 days shall have the same age tolerance as cubes tested at 28 days.

Table 1: Specimen age tolerances

Test Age	**Permissible Tolerance**
24 hours	± ½ hour
3 days	± 1 hour
7 days	± 3 hours
28 days	± 12 hours

15. Transport specimens from the moist room in a saturated towel and keep the specimens covered with the saturated towel until the time of testing.
16. Use a damp towel to wipe the specimens to a surface-dry condition, and remove any loose particles.
17. Secure the sandpaper on a flat surface and lightly sand each face of the specimens to provide plane loading surfaces and remove any fins from the edges of the specimens.
18. Use a straightedge to check that the faces are plane.
19. Use electronic calipers to measure the width, depth, and height of the specimens. The width and depth will be used to find the area of the specimen face perpendicular to the direction of loading. Measurements should be made across the middle of the specimen.
20. Verify that the spherically seated block is free to tilt.
21. Place a specimen in the testing machine below the center of the upper bearing block. The specimen should be turned on its side, so that the load is applied to molded faces.

22. Bring the block into uniform contact with the surface of the specimen.
23. Apply the load to the specimen at a rate of 200 lb/s. This rate should be obtained during the first half of the anticipated maximum load and no adjustment should be made during the latter half.
24. Record the total maximum load and calculate the compressive strength as follows:

$$f_m = P/A$$

where:

f_m = compressive strength (psi)

P = total maximum load (lbf)

A = area of loaded surface (in^2)

Cube Compressive Strength Data Sheet

High Volume Fly Ash Cement Paste Study

Date:_______________

Technician:_______________

Mix ID:____

Cement:__________% Fly Ash:__________% Gypsum:__________%

CH:__________% RS Cem:__________% Admix:__________ w/cm:______________

Cement Source:______________________________ Fly Ash Source:______________________________

Start Time:______________ Moist Room Time:____________________

Age (days)	Specimen Number	Molding		1-Day Removal from Mold		3-Day Removal from Mold		Testing Date/Time		Width (in)	Length (in)	Height (in)	Maximum Load (lbs)	Compressive Strength (psi)	Average Compressive Strength (psi)
		Date	Time	Date	Time	Date	Time	Date	Time						
1	1					☒	☒								
	2					☒	☒								
	3					☒	☒								
3	1			☒	☒										
	2			☒	☒										
	3			☒	☒										
7	1			☒	☒										
	2			☒	☒										
	3			☒	☒										
28	1			☒	☒										
	2			☒	☒										
	3			☒	☒										
56	1			☒	☒										
	2			☒	☒										
	3			☒	☒										

Notes/Deviations:____

____

Using the F-Cal 4000 & CalCommander Software for Testing Cement Paste

(Calmetrix F-Cal 4000/8000 User Manual, CalCommander Software v1.3 User Manual, and ASTM C 305)

(Revised 6-19-2012)

Equipment and Materials

18. F-Cal 4000, USB cable, and CalCommander Software v1.3.
19. Black and Decker 250-Watt Hand Mixer (Model MX217) with egg beater paddles
20. 20-quart Hobart mixing bowl
21. Plastic ladle
22. Hamilton 1-mL Adjustable Volume SoftGrip Pipette (readable to 0.01 mL)
23. 3-quart or larger white plastic bowl with spout
24. Metal spoon
25. Small stainless steel spatula
26. Four, clean 4”x8” plastic cylinder molds and caps per mix
27. Sper Scientific Humidity/Temperature Monitor (Model 800016)
28. Analog thermometer with 5-inch probe
29. High silica sand obtained from U.S. Silica, Pacific, MO
30. 12-kg Denver Instrument balance
31. Space heater
32. Microsoft Excel and TableCurve 2D software

Procedure

1. At least 1 hour before inserting the first specimen: connect the F-Cal to the computer using the USB cable, open the CalCommander program, click on the “F-Cal Logger” tab at the top of the window, and click on “Start Logging” at the right side of the window.

2. To enter information about the mix: click “Read Configuration from Logger”, click on the tab in the bottom portion of the window which corresponds to the slot in which the specimen will be placed in the F-Cal; enter the Mix ID, Water/Cement Ratio, Cement Source, Cement Content (lbs/cy), and any SCMs (Type, Percent, and Source); and click “Update Configuration File” on the right side of the window. Also, make sure the Sensor Enabled box is checked.
3. Prepare a clean mold with a 1250 gram inert specimen. The inert specimen consists of high silica sand and deionized water. The proportion of water to oven-dried sand should reflect the proportion of water to cementitious materials used in the mixture being tested.
4. Verify that the air temperature is 23.0±3.0°C (68.0-78.8°F), mixing water temperature is 23.0±2°C (69.8-77.0°F), and that the relative humidity of the air is not less than 50%. Record these parameters.
5. To blend the dry constituents of the mix: Place about 1000 grams of the dry materials into a 4”x8” cylinder mold in the same proportions to be used in the paste mixture, hold the cylinder horizontally with one hand on each end of the cylinder, and then shake the cylinder 25 cycles using a 6” throw.
6. To dissolve admixtures into the mix water: Place all of the deionized water into the plastic bowl, use the 1-mL syringe to add the desired amount of admixture to the water, and use the small spatula to gently stir the water until all of the admixture is dissolved.
7. Add the pre-mixed cementitious materials to the mixing bowl, forming a donut shape.
8. Add all of the mix water to the mixing bowl, start the timer, and record the time (Start Time).
9. Wait 10 seconds to allow the cement to absorb the water.
10. Mix at Speed 2 (440 RPM) for 20 seconds. Rotate the bowl 90° every 5 seconds.

11. Mix at Speed 6 (670 RPM) for 60 seconds. Rotate the bowl 90° every 15 seconds and occasionally run the mixing paddles along the side of the bowl.
12. At the end of the initial mixing, record the temperature of the paste.
13. At 4 minutes, remix the paste at Speed 2 for 30 seconds.
14. After remixing, pour 1250 grams of paste into each of the three remaining 4”x8” cylinder molds. Tap each cylinder with an open hand 10 times to remove entrapped air.
15. Quickly cap the molds, ensure that the outsides of the molds are clear of paste or other debris, and place the molds into the appropriate slots in the F-Cal (including the mold with the control sand). This should be done within 10 minutes after the Start Time.
16. Enter the “Mix Date/Time” (noted in step #8) and “Mix Temperature” (noted in step #12) into the software under the mix information tabs and click “Update Configuration File”.
17. Disconnect the USB cable from the computer and F-Cal, close and latch the F-Cal lid, and leave the specimens for at least 48 hours. Note: shorter logging times may be used depending on the amount of information desired and prior knowledge of the materials being tested. (CAUTION: DO NOT MOVE THE F-CAL WHILE TESTING IS IN PROGRESS)
18. After 48 hours, open the F-Cal lid, reconnect the USB cable, open the CalCommander software, click the “F-Cal Logger” tab, and click “Read Data from Logger” at the right side of the window. If it is decided that logging should cease, click “Stop Logging”.
19. Save the log data by clicking “Read Data from Logger” and then selecting “Save Log Data to File”.
20. Remove the specimens from the F-Cal.

21. To export data: click on “F-Cal Reports” at the top of the CalCommander software window, click “Add Logs” in the bottom right corner of the screen, select the appropriate file(s), select “Accept” in the “Add F-Cal/AdiaCal Logs” window, select the tab corresponding to the channel from which data is needed, click on “Save Selected Log as Text File” in the bottom right corner of the screen, input desired file name, and click “Save”.
22. To import data into Microsoft Excel: Open Microsoft Excel, select “Data” at the top of the screen, go to “Import External Data”, click “Import Data...”, double-click on the desired text file, click the “Next >” button two times in the “Text Import Wizard” window, click “Finish”, and then select “OK” in the “Import Data” window.
23. Record the Signal-to-Noise Ratio for each specimen. The Signal is the difference between the highest and lowest temperatures recorded for the sample being tested. The Noise is the difference between the highest and lowest temperatures recorded for the inert specimen. To calculate the Signal-to-Noise Ratios:
    a. Import the data for each specimen into Excel.
    b. Determine the difference between the time logging began and the time water was added to the cementitious materials (Start Time). This will be used to determine the log time that corresponds to the Start Time.
    c. For each specimen log, find the maximum temperature by using the MAX function for the range of specimen temperatures starting with the log time that corresponds to the Start Time and ending at the end of the logging period. To find the minimum temperature, follow a similar procedure using the MIN function for the same range.
    d. Calculate the Signal for each specimen by subtracting the minimum specimen temperature from the maximum specimen temperature.
    e. Calculate the Noise by subtracting the minimum temperature of the inert specimen from the maximum temperature of the inert specimen.
    f. Divide the Signal for each specimen by the Noise to determine the Signal-to-Noise ratio for each specimen.

24. To estimate set times using the Percentage Method:
    a. Import the data for each specimen into Excel.
    b. Determine the difference between the time logging began and the time water was added to the cementitious materials (Start Time). This will be used to determine the log time that corresponds to the Start Time.
    c. Remove all log data prior to the log time corresponding to the Start Time.
    d. Find the average temperature log for the specimens by averaging the temperatures of the three specimens at every minute for the duration of the logging.
    e. Subtract the inert specimen temperature log from the average temperature log to determine the corrected average temperature log.
    f. Plot the corrected average hydration curve by plotting the corrected average temperatures against time.
    g. Visually examine the curve to determine a time window that encompasses the dormant period and the peak of the hydration curve. There will be an initial rise in the temperature near time zero that indicates the initial rise in temperature of the thermistors from the ambient temperature to the specimen temperature. This area should not be considered to be part of the dormant period.
    h. Use the MAX and MIN functions, within the time range chosen above, to determine the maximum and minimum temperatures (ΔT_{max} and ΔT_{min}) of the hydration curve.
    i. Using the values from Step 25.h., calculate the main hydration response rise ($M = \Delta T_{max} - \Delta T_{min}$), twenty percent of the main hydration response rise ($M_{20\%} = 0.2M$), and fifty percent of the main hydration response rise ($M_{50\%} = 0.5M$).
    j. Initial Set is taken as the time when 20% of the main hydration response rise ($M_{20\%}+\Delta T_{min}$) occurs.
    k. Final Set is taken as the time when 50% of the main hydration response rise ($M_{50\%}+\Delta T_{min}$) occurs.

25. To estimate set times using the Derivatives Method:

    a. Copy and paste the time log and corrected average temperature log from Step 25, above, into a new Excel file.

    b. In TableCurve 2D, click “Import” in the upper left corner of the window and “Open” the Excel file.

    c. In the “Select Columns for X-Y Data Table” window, select “(1)Sheet1!A” for the X Column, select “(1)Sheet1!B” for the Y Column, and then select “OK”.

    d. In the “Data Description and Variable Names” window, enter a title for the plot, enter titles for the axes, and select “OK”.

    e. Select “Data” at the top of the window, choose “Section Data...”, select a time range from the dormant period to the peak of the main hydration curve, click the green checkmark box in the upper left corner, and select “Yes” in the “Update Data Table” window.

    f. Select “Process” at the top of the window, choose “Curve-Fit All Equations”, and select “Graph Start” after fitting has ceased. The curve-fit automatically applied has the highest R-squared value and should not be changed.

    g. On the left side of the screen, select “Numeric”. Look toward the bottom of the “Numeric Summary” screen to find the “1st Deriv max” and the “2nd Deriv max” with corresponding X-Values.

    h. The time for Initial Set is the x-value corresponding to the maximum second derivative (2nd Deriv max).

    i. The time for Final Set is the x-value corresponding to the maximum first derivative (1st Deriv max).

Calorimeter Data Sheet

High Volume Fly Ash Cement Paste Study

Date: ____________

Technician: ____________

Mix ID: ____________

Cement: ______% Fly Ash: ______% Gypsum: ______%

CH: ______% RS Cem: ______% Admix: ______ w/cm: ______

Cement Source: ____________ Fly Ash Source: ____________

Thermal Measurement Equip.: ____________ Specimen Containers: ____________

Material Type: ____________

Inert Specimen Preparation	
Total Design Mass, $m_{i,T}$ (g):	
Proportion of Water to Sand, w/s [=w/cm]:	
Design Mass of Sand, $m_{i,S}$ (g) [=($m_{i,T}$)/(1+w/s)]:	
Design Mass of Water, $m_{i,W}$ (g) [=$m_{i,T}$ - $m_{i,S}$]:	
Actual Mass of Sand (g):	
Actual Mass of Water (g):	
Total Actual Mass of Inert Specimen (g):	

Mixing and Sample Preparation	
Air Temperature (°F):	
Water Temperature (°F):	
Relative Humidity (%):	
Start Time:	
Admix Addition Time:	
Paste Temp. at End of Mixing (°F):	
Sample 1 Mass (g):	
Sample 2 Mass (g):	
Sample 3 Mass (g):	

Signal-to-Noise Ratios (Raw Data)	
Inert Specimen	
Max. Temperature of Inert Specimen, $T_{i,max}$ (°F):	
Min. Temperature of Inert Specimen, $T_{i,min}$ (°F):	
Sample 1	
Max. Temperature of Sample, $T_{s,max}$ (°F):	
Min. Temperature of Sample, $T_{s,min}$ (°F):	
Signal-to-Noise Ratio [=($T_{s,max}$-$T_{s,min}$)/($T_{i,max}$-$T_{i,min}$)]:	
Sample 2	
Max. Temperature of Sample, $T_{s,max}$ (°F):	
Min. Temperature of Sample, $T_{s,min}$ (°F):	
Signal-to-Noise Ratio [=($T_{s,max}$-$T_{s,min}$)/($T_{i,max}$-$T_{i,min}$)]:	
Sample 3	
Max. Temperature of Sample, $T_{s,max}$ (°F):	
Min. Temperature of Sample, $T_{s,min}$ (°F):	
Signal-to-Noise Ratio [=($T_{s,max}$-$T_{s,min}$)/($T_{i,max}$-$T_{i,min}$)]:	

Thermal Setting Times (Corrected Average Data)	
Percentage Method	
Max. Temp. of Main Hydration Curve, ΔT_{max} (°F):	
Time when ΔT_{max} Occurs (min):	
Min. Temp. During Dormant Period, ΔT_{min} (°F):	
Main Hydration Response Rise, M (°F) [=ΔT_{max} - ΔT_{min}]:	
20% of Main Hydration Response Rise, $M_{20\%}$ (°F) [=0.2M]:	
$M_{20\%}+\Delta T_{min}$ (°F):	
Initial Set (min) [=Time when $M_{20\%}+\Delta T_{min}$ First Occurs]:	
50% of Main Hydration Response Rise, $M_{50\%}$ (°F) [=0.5M]:	
$M_{50\%}+\Delta T_{min}$ (°F):	
Final Set (min) [=Time when $M_{50\%}+\Delta T_{min}$ First Occurs]:	
Derivatives Method	
Maximum 2nd Derivative (from Tablecurve):	
Initial Set (min) [=Time when Max. 2nd Derivative Occurs]:	
Maximum 1st Derivative (from Tablecurve):	
Final Set (min) [=Time when Max. 1st Derivative Occurs]:	

Notes/Deviations: ____________

Miniature Slump Cone
(Kantro (1980) and Bhattacharja & Tang (2001))
(Revised 6-19-2012)

Equipment

1. Black and Decker 250-Watt Hand Mixer (Model MX217) with egg beater paddles

2. 20-quart Hobart mixing bowl
3. Plastic ladle
4. Hamilton 1-mL Adjustable Volume SoftGrip Pipette, (readable to 0.01 mL)
5. 3-quart or larger white plastic bowl with spout
6. Metal spoon
7. Analog thermometer with 5-inch probe
8. Stopwatch
9. Small stainless steel spatula (0.625 in. wide and 4 in. long)

10. 2 mini-slump cones

11. Lucite sheet (0.2 inches thick). Label the area of the sheet where each test will be performed with the time the cone will be lifted (2, 5, 15, 30, 45 minutes)
12. Plastic wrap
13. 5 thin plastic discs (2 in. diameter) cut from Zip-lock bags
14. 12-kg Denver Instrument balance
15. Sper Scientific Humidity/Temperature Monitor (Model 800016)

Procedure

1. Place the 5 plastic discs on the board 8 inches apart on center and at least 3 inches away from any edge of the board.
2. Place each of the two mini-slump cones on a plastic disc.
3. Verify that the air temperature is 23.0±3.0°C (68.0-78.8°F), mixing water temperature is 23.0±2°C (69.8-77.0°F), and that the relative humidity of the air is not less than 50%. Record these parameters.
4. To blend the dry constituents of the mix: Place about 1000 grams of the dry materials into a plastic 4”x8” cylinder mold in the same proportions to be used in the paste mixture, hold the cylinder horizontally with one hand on each end of the cylinder, and then shake the cylinder 25 cycles using a 6” throw.

5. To dissolve admixtures into the mix water: Place all of the deionized water into the plastic bowl, use the 1-mL syringe to add the desired amount of admixture to the water, and use the small spatula to gently stir the water until all of the admixture is dissolved.
6. Add all cementitious materials to the mixing bowl, forming a donut shape.
7. Add all of the water to the mixing bowl, start the timer, and record the time (Start Time).
8. Wait 10 seconds to allow the cement to absorb the water.
9. Mix at Speed 2 (440 RPM) for 20 seconds. Rotate the bowl 90° every 5 seconds.
10. Mix at Speed 6 (670 RPM) for 60 seconds. Rotate the bowl 90° every 15 seconds and occasionally run the mixing paddles along the side of the bowl.
11. Record the temperature of the paste.
12. At the completion of mixing (1.5 minutes after the Start Time), fill the first mini-slump cone until a slight hump is formed above the top of the cone.
13. Use the spatula with a rodding motion at a slight angle to remove entrapped air. The paste should be “rodded” 5 to 10 times.
14. If the paste is depressed below the top of the cone after removing the entrapped air, use paste spilled on the rim to fill the cone.
15. Use the spatula to strike off the top surface of the cone.
16. At 2 minutes after the Start Time, lift the cone within a few tenths of a second. The lifting motion should be rapid enough for the bottom of the cone to be free of the flowing paste, but slow enough to avoid imparting an upward momentum to the paste as it is flowing from the cone.
17. At 4 minutes after the Start Time, remix the paste remaining in the bowl at Speed 2 for 30 seconds.
18. Pour the paste into the second cone and remove entrapped air with the same procedure used above.
19. At 5 minutes after the Start Time, lift the cone.
20. Cover the remaining paste in the mixing bowl using plastic wrap.

21. At 13 minutes after the Start Time, uncover the paste and remix the paste at Speed 2 for 30 seconds.
22. Pour the paste into a clean, dry cone and remove entrapped air with the same procedure used above.
23. At 15 minutes after the Start Time, lift the cone.
24. Repeat the procedure in Steps 21-23 for slumps at 30 and 45 minutes after the Start Time. See the table, below, which summarizes the mixing, pausing, and testing times
25. At 1 hour after the Start Time, measure and record the diameter of each of the paste pats 4 times using digital calipers. The measurements should each be rotated 45°.
26. Calculate the average diameter of each pat and use the average diameter to calculate the area of the pat. Record this area in square inches.

Elapsed Time (mm:ss)	Action
0:00	Add water to mixing bowl with cementitious materials Record Time (Start Time)
0:10	Start mixing at Speed 2
0:30	Start mixing at Speed 6
1:30	Stop Mixing Record Temperature of Paste Prepare mini-slump test
2:00	Lift mini-slump cone
4:00	Remix paste at Speed 2
4:30	Prepare mini-slump test
5:00	Lift mini-slump cone
13:00	Remix paste at Speed 2
13:30	Prepare mini-slump test
15:00	Lift mini-slump cone
28:00	Remix paste at Speed 2
28:30	Prepare mini-slump test
30:00	Lift mini-slump cone
43:00	Remix paste at Speed 2
43:30	Prepare mini-slump test
45:00	Lift mini-slump cone
60:00	Measure and record mini-slump diameters

Miniature Slump Data Sheet

High Volume Fly Ash Cement Paste Study

Date: ____________

Technician: ____________

Mix ID: ____

Cement: ________ %   **Fly Ash:** ________ %   **Gypsum:** ________ %

CH: ________ %   **RS Cem:** ________ %   **Admix:** ________   **w/cm:** ________

Cement Source: ________________________   **Fly Ash Source:** ________________________

Air Temperature (°F): ________   **Water Temperature (°F):** ________   **Relative Humidity (%):** ________

Start Time: ________   **Paste Temperature at Completion of Mixing (°F):** ________

Test Time (min)	Diameter Measurements (in)				Average Diameter (in)	Area (in^2)
2						
5						
15						
30						
45						

Notes/Deviations: ____

____

____

Time of Setting by Vicat Needle
(ASTM C 187, ASTM C 191, and ASTM C 305)
(Revised 6-19-2012)

Equipment

33. 5-quart Hobart mixer (Model N50), bowl, and paddle
34. Bowl scraper with semi-rigid rubber blade
35. Rubber gloves
36. Vicat Apparatus, glass plate, and conical ring
37. Flat trowel
38. Stopwatch
39. Analog thermometer with 5-inch probe
40. 12-kg Denver Instrument balance
41. Sper Scientific Humidity/Temperature Monitor (Model 800016)

Procedure

A. Mixing

26. Verify that the air temperature is 23.0±3.0°C (68.0-78.8°F), mixing water temperature is 23.0±2°C (69.8-77.0°F), and that the relative humidity of the air is not less than 50%. Record these parameters.
27. Obtain 650 grams of the cementitious materials and the desired amount of deionized water to be used. (To blend the dry constituents of the mix: Place about 1000 grams of the dry materials into a 4”x8” cylinder mold in the same proportions to be used in the paste mixture, hold the cylinder horizontally with one hand on each end of the cylinder, and then shake the cylinder 25 cycles using a 6” throw.)
28. Wet the paddle and the inside of the mixing bowl.
29. Place all of the mixing water in the bowl. (To dissolve admixtures into the mix water: Place all of the deionized water into the plastic bowl, use the 1-mL syringe to add the desired amount of admixture to the water, and use

the small spatula to gently stir the water until all of the admixture is dissolved.)

30. Add the cementitious materials to the water and wait 30 seconds for the absorption of water. While waiting, make note of the time the cement was added (Start Time), attach the bowl and paddle in the Hobart mixer, secure the latches on the bowl, and then turn the lever on the right side of the mixer counter-clockwise to lift the bowl into the mixing position.
31. On the left side of the mixer, set the speed to 1.
32. Start the mixer and mix at slow speed for 30 seconds.
33. Stop the mixer for 15 seconds and use the bowl scraper to scrape paste from the sides of the bowl down into the batch.
34. Set the mixing speed to setting 2.
35. Start the mixer and mix at medium speed for 60 seconds.
36. Stop the mixer and remove the paddle.

B. Normal Consistency

37. Put on rubber gloves and immediately form a portion of the cement paste into a ball and toss the ball from one hand to the other six times (hands should be about 6 inches apart).
38. Place the ball in the palm of one hand and press the ball into the larger end of the ring until the ring is filled with paste.
39. Use a single sweeping motion of the palm of the hand to remove excess paste at the larger end of the ring and place the large end of the ring onto the plate.
40. Remove excess paste at the top (smaller end) of the ring using a single oblique stroke of the trowel held at a slight angle with the top of the ring. If necessary, smooth the top with no more than two light touches of the pointed end of the trowel.
41. Center the paste under the **10 mm** end of the rod, bring the end of the rod into contact with the surface of the paste, and tighten the set-screw.

42. Set the indicator to zero and release the rod quickly. This must be done within 30 seconds after mixing is completed.
43. After 30 seconds, read and record the depth of penetration. If this depth is 10±1 mm continue to step 19. If the depth is outside of this range, repeat steps 2-18, with fresh cement and a different percentage of water, until a depth of 10±1 mm is obtained.
44. Calculate the amount of water required to the nearest 0.1% and record it to the nearest 0.5% of the weight of the dry cement.

C. Setting Time

45. Using 650 grams of the cementitious materials and the percentage of water determined in step 19, repeat steps 3-15 and then continue with step 21. (Note: The paste remaining from the normal consistency test may also be used.)
46. Place the specimen in the moist room and do not disturb it for 30 minutes. Protect the specimen from dripping water by using an arched sheet of thin plastic to cover the specimen.
47. After the 30 minutes and at 15 minute intervals thereafter until a penetration of 25 mm or less is obtained, determine the penetration using the following procedure:
    a. Lower the **1 mm** diameter needle until it rests on the surface of the paste.
    b. Tighten the setscrew to secure the rod and set the indicator to zero at the top of the scale.
    c. Release the setscrew quickly and let the needle settle for 30 seconds.
    d. At the end of the 30 seconds, take the penetration reading. (Note: Each penetration test should be at least 5 mm from any previous test and at least 10 mm away from the edge of the specimen)

48. Interpolate to determine the time when a penetration of 25 mm would be obtained. This elapsed time is the Vicat initial time of setting. Calculate the initial set time, in minutes, as follows:

Initial Set Time = [(H-E)x(C-25)/(C-D)]+E

where: H = time of first penetration less than 25 mm (min)
E = time of last penetration greater than 25 mm (min)
C = penetration reading at time E (mm)
D = penetration reading at time H (mm)

49. Repeat the procedure described in steps 22a-22d, at 15 minute intervals, until the needle does not leave a complete circular impression. This elapsed time is the Vicat final time of setting.
50. Within 90 seconds, perform two additional tests on different areas of the specimen to verify the final set time.

Normal Consistency Data Sheet

High Volume Fly Ash Cement Paste Study

Date: ____________________

Technician: ____________________

Mix ID: ____

Cement: __________ % Fly Ash: __________ % Gypsum: __________ %

CH: __________ % RS Cem: __________ % Admix: __________ w/cm: __________

Cement Source: ______________________________ Fly Ash Source: ______________________________

Air Temperature (°F): ______________________ Mixer Type: ______________________________

Water Temperature (°F): ______________________

Relative Humidity (%): ______________________

Trial	Cement Mass (g)	Fly Ash Mass (g)	Water Mass (g)	Penetration (mm)	Start Time
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					

Calculated Required Water for Normal Consistency (0.1%) = ______________

Reported Required Water for Normal Consistency (0.5%) = ______________

Notes/Deviations: ____

____

Vicat Time of Setting (Method A) Data Sheet

High Volume Fly Ash Cement Paste Study

Date:
Technician:

Mix ID:

Cement: % Fly Ash: % Gypsum: %
CH: % RS Cem: % Admix:

w/cm:

Cement Source: Fly Ash Source:

Air Temperature (°F): Start Time:
Water Temperature (°F): Time into Moist Room:
Relative Humidity (%):

Elapsed Time (hh:mm)	Penetration (mm)	Elapsed Time (hh:mm)	Penetration (mm)

Time of Last Penetration > 25 mm, E (min):	
Time of First Penetration < 25 mm, H (min):	
Penetration Reading at Time E, C (min):	
Penetration Reading at Time H, D (min):	
Initial Set Time (min), [=((H-E)x(C-25)/(C-D))+E]:	
Final Set Time (min):	

Notes/ Deviations:

APPENDIX B

OUTLIER ANALYSIS FOR CALORIMETRY DATA

Table B.1. Outlier Analysis of Calorimetry Data for Cement 1 Combinations in the Screening Study

Combination	**Proportions**		**Calorimeter Outlier Analysis**													
	Cement (%)	**Fly Ash (%)**	**$(S/N)_1$**	**$(S/N)_2$**	**$(S/N)_3$**	**Avg.**	**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**$Outlier_{MAX}$?**	**$Outlier_{MIN}$?**	**New Avg.**
Baseline 1	100	0	14.23	14.49	14.46	14.39	0.14	3	14.49	14.23	1.153	0.686	1.147	NO	NO	14.39
1-1	75	25	18.22	19.08	18.33	18.54	0.47	3	19.08	18.22	1.153	1.147	0.687	NO	NO	18.54
1-1	50	50	16.04	16.52	16.06	16.20	0.27	3	16.52	16.04	1.153	1.154	0.616	YES	NO	16.20
1-1	30	70	3.85	3.90	3.83	3.86	0.04	3	3.90	3.83	1.153	1.132	0.763	NO	NO	3.86
1-2	75	25	7.05	7.42	7.22	7.23	0.19	3	7.42	7.05	1.153	1.033	0.963	NO	NO	7.23
1-2	50	50	6.21	6.54	6.35	6.36	0.17	3	6.54	6.21	1.153	1.049	0.942	NO	NO	6.36
1-2	30	70	4.25	4.32	4.20	4.26	0.06	3	4.32	4.20	1.153	1.044	0.949	NO	NO	4.26
1-3	75	25	10.42	10.88	10.66	10.65	0.23	3	10.88	10.42	1.153	0.976	1.022	NO	NO	10.65
1-3	50	50	12.12	12.89	12.73	12.58	0.41	3	12.89	12.12	1.153	0.763	1.132	NO	NO	12.58
1-3	30	70	4.20	4.19	4.18	4.19	0.01	3	4.20	4.18	1.153	0.844	1.104	NO	NO	4.19
1-4	75	25	12.77	13.34	12.84	12.98	0.31	3	13.34	12.77	1.153	1.146	0.693	NO	NO	12.98
1-4	50	50	9.44	10.17	9.77	9.80	0.37	3	10.17	9.44	1.153	1.030	0.967	NO	NO	9.80
1-4	30	70	10.24	10.46	10.52	10.41	0.15	3	10.52	10.24	1.153	0.769	1.131	NO	NO	10.41
1-5	75	25	10.75	11.40	11.08	11.08	0.32	3	11.40	10.75	1.153	0.995	1.004	NO	NO	11.08
1-5	50	50	11.79	12.61	12.14	12.18	0.41	3	12.61	11.79	1.153	1.046	0.946	NO	NO	12.18
1-5	30	70	-----	27.19	-----	27.19	-----	-----	-----	-----	-----	-----	-----	-----	-----	27.19

Table B.2. Outlier Analysis of Calorimetry Data for Cement 2 Combinations in the Screening Study

Combination	**Proportions**		**Calorimeter Outlier Analysis**													
	Cement (%)	**Fly Ash (%)**	**$(S/N)_1$**	**$(S/N)_2$**	**$(S/N)_3$**	**Avg.**	**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**Outlier$_{MAX}$?**	**Outlier$_{MIN}$?**	**New Avg.**
Baseline 2	100	0	14.39	14.53	14.43	14.45	0.07	3	14.53	14.39	1.153	1.097	0.860	NO	NO	14.45
2-1	75	25	13.97	14.45	14.41	14.28	0.26	3	14.45	13.97	1.153	0.637	1.153	NO	NO	14.28
2-1	50	50	13.61	14.10	13.96	13.89	0.25	3	14.10	13.61	1.153	0.846	1.104	NO	NO	13.89
2-1	30	70	14.83	15.17	14.81	14.94	0.20	3	15.17	14.81	1.153	1.153	0.638	NO	NO	14.94
2-2	75	25	11.50	12.08	11.92	11.83	0.30	3	12.08	11.50	1.153	0.827	1.111	NO	NO	11.83
2-2	50	50	7.12	7.43	7.20	7.25	0.16	3	7.43	7.12	1.153	1.127	0.783	NO	NO	7.25
2-2	30	70	9.33	9.52	9.36	9.41	0.10	3	9.52	9.33	1.153	1.145	0.704	NO	NO	9.41
2-3	75	25	14.65	15.21	14.93	14.93	0.28	3	15.21	14.65	1.153	0.998	1.002	NO	NO	14.93
2-3	50	50	15.64	16.23	15.80	15.89	0.31	3	16.23	15.64	1.153	1.114	0.820	NO	NO	15.89
2-3	30	70	15.11	15.83	15.26	15.40	0.38	3	15.83	15.11	1.153	1.133	0.759	NO	NO	15.40
2-4	75	25	12.18	12.69	12.49	12.46	0.26	3	12.69	12.18	1.153	0.924	1.062	NO	NO	12.46
2-4	50	50	12.44	13.10	12.65	12.73	0.34	3	13.10	12.44	1.153	1.098	0.858	NO	NO	12.73
2-4	30	70	5.94	6.13	6.05	6.04	0.09	3	6.13	5.94	1.153	0.949	1.044	NO	NO	6.04
2-5	75	25	12.87	13.33	13.18	13.13	0.24	3	13.33	12.87	1.153	0.853	1.100	NO	NO	13.13
2-5	50	50	10.18	10.70	10.31	10.40	0.27	3	10.70	10.18	1.153	1.125	0.789	NO	NO	10.40
2-5	30	70	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

Table B.3. Outlier Analysis of Calorimetry Data for Cement 3 Combinations in the Screening Study

Combination	**Proportions**		**Calorimeter Outlier Analysis**													
	Cement (%)	**Fly Ash (%)**	**$(S/N)_1$**	**$(S/N)_2$**	**$(S/N)_3$**	**Avg.**	**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**$Outlier_{MAX}$?**	**$Outlier_{MIN}$?**	**New Avg.**
Baseline 3	100	0	13.22	13.48	13.20	13.30	0.15	3	13.48	13.20	1.153	1.152	0.640	NO	NO	13.30
3-1	75	25	13.83	14.27	13.86	13.99	0.25	3	14.27	13.83	1.153	1.152	0.649	NO	NO	13.99
3-1	50	50	12.54	13.38	13.14	13.02	0.43	3	13.38	12.54	1.153	0.831	1.110	NO	NO	13.02
3-1	30	70	10.87	11.14	10.94	10.98	0.14	3	11.14	10.87	1.153	1.109	0.834	NO	NO	10.98
3-2	75	25	14.92	15.43	15.24	15.20	0.26	3	15.43	14.92	1.153	0.908	1.071	NO	NO	15.20
3-2	50	50	14.67	15.45	14.86	14.99	0.41	3	15.45	14.67	1.153	1.125	0.788	NO	NO	14.99
3-2	30	70	1.70	1.70	1.71	1.70	0.01	3	1.71	1.70	1.153	1.125	0.788	NO	NO	1.70
3-3	75	25	15.65	15.95	15.75	15.78	0.16	3	15.95	15.65	1.153	1.093	0.870	NO	NO	15.78
3-3	50	50	12.67	13.39	12.96	13.01	0.36	3	13.39	12.67	1.153	1.055	0.933	NO	NO	13.01
3-3	30	70	7.78	8.03	7.81	7.87	0.13	3	8.03	7.78	1.153	1.146	0.697	NO	NO	7.87
3-4	75	25	12.13	12.49	12.36	12.33	0.18	3	12.49	12.13	1.153	0.899	1.077	NO	NO	12.33
3-4	50	50	10.74	11.44	10.94	11.04	0.36	3	11.44	10.74	1.153	1.110	0.832	NO	NO	11.04
3-4	30	70	8.41	8.46	8.40	8.43	0.03	3	8.46	8.40	1.153	1.146	0.696	NO	NO	8.43
3-5	75	25	15.72	16.14	15.80	15.88	0.23	3	16.14	15.72	1.153	1.137	0.745	NO	NO	15.88
3-5	50	50	9.31	9.89	9.43	9.54	0.31	3	9.89	9.31	1.153	1.130	0.769	NO	NO	9.54
3-5	30	70	8.96	9.10	9.05	9.04	0.07	3	9.10	8.96	1.153	0.865	1.095	NO	NO	9.04

Table B.4. Outlier Analysis of Calorimetry Data for Cement 4 Combinations in the Screening Study

Combination	**Proportions**		**Calorimeter Outlier Analysis**														
	Cement (%)	**Fly Ash (%)**	**$(S/N)_1$**	**$(S/N)_2$**	**$(S/N)_3$**	**Avg.**	**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**Outlier$_{MAX}$?**	**Outlier$_{MIN}$?**	**New Avg.**
Baseline 4	100	0	14.41	14.55	14.47	14.47	0.07	3	14.55	14.41	1.153	1.052	0.938	NO	NO	14.47
4-1	75	25	11.74	12.25	11.87	11.95	0.27	3	12.25	11.74	1.153	1.119	0.806	NO	NO	11.95
4-1	50	50	11.91	12.26	12.04	12.07	0.18	3	12.26	11.91	1.153	1.076	0.901	NO	NO	12.07
4-1	30	70	8.96	9.10	8.23	8.77	0.47	3	9.10	8.23	1.153	0.724	1.141	NO	NO	8.77
4-2	75	25	17.00	17.89	17.42	17.44	0.44	3	17.89	17.00	1.153	1.016	0.984	NO	NO	17.44
4-2	50	50	13.37	13.72	13.58	13.56	0.18	3	13.72	13.37	1.153	0.937	1.053	NO	NO	13.56
4-2	30	70	2.66	2.70	2.65	2.67	0.03	3	2.70	2.65	1.153	1.146	0.696	NO	NO	2.67
4-3	75	25	12.52	12.94	12.89	12.79	0.23	3	12.94	12.52	1.153	0.681	1.148	NO	NO	12.79
4-3	50	50	10.32	10.71	10.50	10.51	0.20	3	10.71	10.32	1.153	1.013	0.987	NO	NO	10.51
4-3	30	70	5.68	6.00	5.81	5.83	0.16	3	6.00	5.68	1.153	1.064	0.921	NO	NO	5.83
4-4	75	25	11.97	12.25	12.06	12.09	0.14	3	12.25	11.97	1.153	1.096	0.863	NO	NO	12.09
4-4	50	50	12.13	13.01	12.63	12.59	0.44	3	13.01	12.13	1.153	0.952	1.042	NO	NO	12.59
4-4	30	70	5.11	5.45	5.32	5.29	0.17	3	5.45	5.11	1.153	0.913	1.069	NO	NO	5.29
4-5	75	25	16.88	17.08	17.11	17.03	0.13	3	17.11	16.88	1.153	0.693	1.146	NO	NO	17.03
4-5	50	50	11.05	11.74	11.51	11.43	0.35	3	11.74	11.05	1.153	0.873	1.091	NO	NO	11.43
4-5	30	70	20.67	21.35	20.57	20.86	0.42	3	21.35	20.57	1.153	1.147	0.690	NO	NO	20.86

Table B.5. Outlier Analysis of Calorimetry Data for Cement 5 Combinations in the Screening Study

Combination	**Proportions**		**Calorimeter Outlier Analysis**													
	Cement (%)	**Fly Ash (%)**	**$(S/N)_1$**	**$(S/N)_2$**	**$(S/N)_3$**	**Avg.**	**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**$Outlier_{MAX}$?**	**$Outlier_{MIN}$?**	**New Avg.**
Baseline 5	100	0	13.92	14.23	14.14	14.10	0.16	3	14.23	13.92	1.153	0.824	1.112	NO	NO	14.10
5-1	75	25	15.14	15.44	15.34	15.31	0.15	3	15.44	15.14	1.153	0.879	1.088	NO	NO	15.31
5-1	50	50	16.22	16.97	16.42	16.54	0.39	3	16.97	16.22	1.153	1.113	0.823	NO	NO	16.54
5-1	30	70	16.21	16.62	16.50	16.44	0.21	3	16.62	16.21	1.153	0.839	1.107	NO	NO	16.44
5-2	75	25	12.66	13.15	12.93	12.91	0.24	3	13.15	12.66	1.153	0.964	1.033	NO	NO	12.91
5-2	50	50	13.16	13.82	13.32	13.43	0.34	3	13.82	13.16	1.153	1.124	0.790	NO	NO	13.43
5-2	30	70	3.15	3.17	3.12	3.14	0.03	3	3.17	3.12	1.153	0.818	1.115	NO	NO	3.14
5-3	75	25	13.41	13.96	13.60	13.66	0.28	3	13.96	13.41	1.153	1.082	0.890	NO	NO	13.66
5-3	50	50	11.31	11.70	11.40	11.47	0.20	3	11.70	11.31	1.153	1.128	0.779	NO	NO	11.47
5-3	30	70	12.09	11.99	11.62	11.90	0.25	3	12.09	11.62	1.153	0.779	1.128	NO	NO	11.90
5-4	75	25	11.10	11.58	11.46	11.38	0.25	3	11.58	11.10	1.153	0.794	1.123	NO	NO	11.38
5-4	50	50	8.13	8.66	8.54	8.44	0.28	3	8.66	8.13	1.153	0.773	1.129	NO	NO	8.44
5-4	30	70	4.14	4.27	4.13	4.18	0.08	3	4.27	4.13	1.153	1.154	0.613	YES	NO	4.18
5-5	75	25	18.10	18.83	18.14	18.36	0.41	3	18.83	18.10	1.153	1.153	0.622	YES	NO	18.36
5-5	50	50	8.32	8.78	8.44	8.51	0.24	3	8.78	8.32	1.153	1.113	0.823	NO	NO	8.51
5-5	30	70	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

Table B.6. Outlier Analysis of Calorimetry Data for Combination 4-1 Mixtures in the Main Study

Combination	**Nominal Proportions**						**Calorimeter Outlier Analysis**														
	Cement (%)	**Fly Ash (%)**	**Gypsum (%)**	**Lime (%)**	**RSC (%)**	**WR (fl.oz./cwt)**	**$(S/N)_1$**	**$(S/N)_2$**	**$(S/N)_3$**	**Avg.**	**σ**	**n**	**Max.**	**Min.**	**t_{CRIT}**	**t_{MAX}**	**t_{MIN}**	**$Outlier_{MAX}$?**	**$Outlier_{MIN}$?**	**New Avg.**
4-1	100	0	0	0	0	0.00	14.41	14.55	14.47	14.47	0.07	3	14.55	14.41	1.153	1.052	0.938	NO	NO	14.47
4-1	100	0	0	0	0	2.75	14.56	15.05	14.83	14.81	0.24	3	15.05	14.56	1.153	0.953	1.041	NO	NO	14.81
4-1	100	0	0	0	0	5.00	17.02	17.48	17.31	17.27	0.23	3	17.48	17.02	1.153	0.911	1.070	NO	NO	17.27
4-1	75	25	0	0	0	0.00	11.74	12.25	11.87	11.95	0.27	3	12.25	11.74	1.153	1.119	0.806	NO	NO	11.95
4-1	75	25	0	0	0	2.75	11.81	12.03	11.85	11.89	0.12	3	12.03	11.81	1.153	1.134	0.754	NO	NO	11.89
4-1	75	25	0	0	0	5.00	12.23	12.61	12.58	12.47	0.21	3	12.61	12.23	1.153	0.634	1.153	NO	NO	12.47
4-1	50	50	0	0	0	0.00	11.91	12.26	12.04	12.07	0.18	3	12.26	11.91	1.153	1.076	0.901	NO	NO	12.07
4-1	50	50	0	0	0	2.75	11.01	11.70	11.31	11.34	0.35	3	11.70	11.01	1.153	1.041	0.954	NO	NO	11.34
4-1	50	50	0	0	0	5.00	10.67	11.10	10.85	10.87	0.22	3	11.10	10.67	1.153	1.056	0.932	NO	NO	10.87
4-1	50	50	2	0	0	2.75	11.63	12.04	11.90	11.86	0.21	3	12.04	11.63	1.153	0.877	1.089	NO	NO	11.86
4-1	50	50	4	0	0	2.75	11.21	11.70	11.47	11.46	0.24	3	11.70	11.21	1.153	0.973	1.025	NO	NO	11.46
4-1	50	50	4	5	0	2.75	8.88	9.15	9.08	9.04	0.14	3	9.15	8.88	1.153	0.793	1.123	NO	NO	9.04
4-1	50	50	4	10	0	2.75	6.44	6.57	6.50	6.50	0.07	3	6.57	6.44	1.153	1.047	0.946	NO	NO	6.50
4-1	50	50	4	0	10	2.75	10.37	10.81	10.57	10.58	0.22	3	10.81	10.37	1.153	1.036	0.960	NO	NO	10.58
4-1	50	50	4	0	20	2.75	17.11	17.67	17.36	17.38	0.28	3	17.67	17.11	1.153	1.032	0.965	NO	NO	17.38
4-1	30	70	0	0	0	0.00	8.96	9.10	8.23	8.77	0.47	3	9.10	8.23	1.153	0.724	1.141	NO	NO	8.77
4-1	30	70	0	0	0	2.75	4.27	4.40	4.32	4.33	0.07	3	4.40	4.27	1.153	1.082	0.890	NO	NO	4.33
4-1	30	70	0	0	0	5.00	9.86	10.00	9.82	9.89	0.10	3	10.00	9.82	1.153	1.129	0.774	NO	NO	9.89
4-1	30	70	2	0	0	2.75	11.75	12.01	11.89	11.88	0.13	3	12.01	11.75	1.153	0.972	1.026	NO	NO	11.88
4-1	30	70	4	0	0	2.75	7.33	7.65	7.43	7.47	0.16	3	7.65	7.33	1.153	1.089	0.877	NO	NO	7.47
4-1	30	70	4	5	0	2.75	16.97	17.51	17.28	17.25	0.27	3	17.51	16.97	1.153	0.951	1.043	NO	NO	17.25
4-1	30	70	4	10	0	2.75	14.12	14.40	14.27	14.26	0.14	3	14.40	14.12	1.153	0.980	1.018	NO	NO	14.26
4-1	30	70	4	0	10	2.75	13.38	13.77	13.64	13.60	0.20	3	13.77	13.38	1.153	0.860	1.097	NO	NO	13.60
4-1	30	70	4	0	20	2.75	12.68	12.95	12.75	12.79	0.14	3	12.95	12.68	1.153	1.121	0.801	NO	NO	12.79

Table B.7. Outlier Analysis of Calorimetry Data for Combination 1-3 Mixtures in the Main Study

Combination	Nominal Proportions						Calorimeter Outlier Analysis													
	Cement (%)	Fly Ash (%)	Gypsum (%)	Lime (%)	RSC (%)	WR (fl.oz./cwt)	$(S/N)_1$	$(S/N)_2$	$(S/N)_3$	Avg.	σ	n	Max.	Min.	t_{CRIT}	t_{MAX}	t_{MIN}	Outlier$_{MAX}$?	Outlier$_{MIN}$?	New Avg.
1-3	100	0	0	0	0	0.00	14.23	14.49	14.46	14.39	0.14	3	14.49	14.23	1.153	0.686	1.147	NO	NO	14.39
1-3	100	0	0	0	0	2.75	8.63	8.85	8.83	8.77	0.12	3	8.85	8.63	1.153	0.666	1.150	NO	NO	8.77
1-3	100	0	0	0	0	5.00	12.91	13.14	13.10	13.05	0.12	3	13.14	12.91	1.153	0.756	1.134	NO	NO	13.05
1-3	75	25	0	0	0	0.00	10.42	10.88	10.66	10.65	0.23	3	10.88	10.42	1.153	0.976	1.022	NO	NO	10.65
1-3	75	25	0	0	0	2.75	7.96	8.46	8.11	8.18	0.25	3	8.46	7.96	1.153	1.109	0.834	NO	NO	8.18
1-3	75	25	0	0	0	5.00	10.15	10.61	10.34	10.37	0.23	3	10.61	10.15	1.153	1.046	0.947	NO	NO	10.37
1-3	50	50	0	0	0	0.00	12.12	12.89	12.73	12.58	0.41	3	12.89	12.12	1.153	0.763	1.132	NO	NO	12.58
1-3	50	50	0	0	0	2.75	11.82	12.54	12.10	12.15	0.36	3	12.54	11.82	1.153	1.063	0.922	NO	NO	12.15
1-3	50	50	0	0	0	5.00	9.24	9.91	9.55	9.57	0.34	3	9.91	9.24	1.153	1.023	0.975	NO	NO	9.57
1-3	50	50	2	0	0	2.75	12.11	12.77	12.47	12.45	0.33	3	12.77	12.11	1.153	0.971	1.026	NO	NO	12.45
1-3	50	50	4	0	0	2.75	7.23	7.57	7.40	7.40	0.17	3	7.57	7.23	1.153	0.998	1.002	NO	NO	7.40
1-3	50	50	4	5	0	2.75	7.28	7.72	7.51	7.50	0.22	3	7.72	7.28	1.153	0.990	1.009	NO	NO	7.50
1-3	50	50	4	10	0	2.75	7.23	7.57	7.38	7.39	0.17	3	7.57	7.23	1.153	1.036	0.960	NO	NO	7.39
1-3	50	50	4	0	10	2.75	8.44	8.99	8.80	8.74	0.28	3	8.99	8.44	1.153	0.878	1.089	NO	NO	8.74
1-3	50	50	4	0	20	2.75	10.57	11.34	11.04	10.99	0.39	3	11.34	10.57	1.153	0.923	1.062	NO	NO	10.99
1-3	30	70	0	0	0	0.00	4.20	4.19	4.18	4.19	0.01	3	4.20	4.18	1.153	0.844	1.104	NO	NO	4.19
1-3	30	70	0	0	0	2.75	9.06	9.07	9.10	9.08	0.02	3	9.10	9.06	1.153	1.129	0.776	NO	NO	9.08
1-3	30	70	0	0	0	5.00	6.51	6.55	6.58	6.55	0.03	3	6.58	6.51	1.153	0.984	1.015	NO	NO	6.55
1-3	30	70	2	0	0	2.75	13.72	14.08	13.77	13.86	0.20	3	14.08	13.72	1.153	1.147	0.688	NO	NO	13.86
1-3	30	70	4	0	0	2.75	10.94	11.41	11.08	11.14	0.24	3	11.41	10.94	1.153	1.102	0.850	NO	NO	11.14
1-3	30	70	4	5	0	2.75	13.27	14.11	13.73	13.70	0.42	3	14.11	13.27	1.153	0.969	1.028	NO	NO	13.70
1-3	30	70	4	10	0	2.75	11.34	11.62	11.42	11.46	0.14	3	11.62	11.34	1.153	1.114	0.821	NO	NO	11.46
1-3	30	70	4	0	10	2.75	9.24	9.32	9.43	9.33	0.10	3	9.43	9.24	1.153	1.031	0.966	NO	NO	9.33
1-3	30	70	4	0	20	2.75	8.69	8.67	8.75	8.70	0.04	3	8.75	8.67	1.153	1.123	0.794	NO	NO	8.70

APPENDIX C

SCREENING STUDY THERMAL CURVES

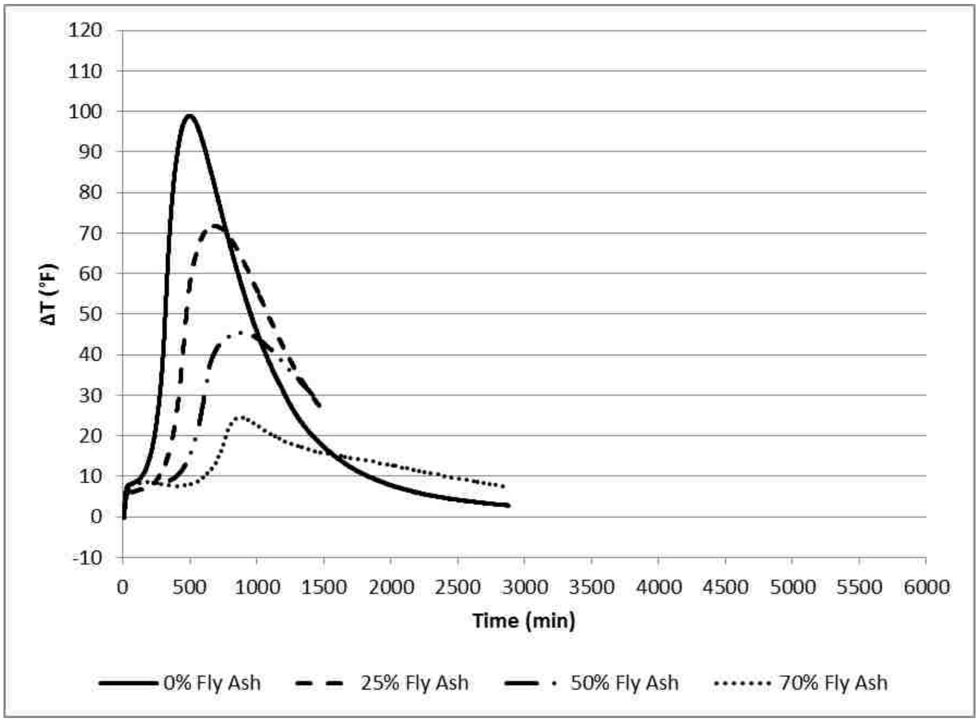

Figure C.1. Thermal Curve Plots for Combination 1-1

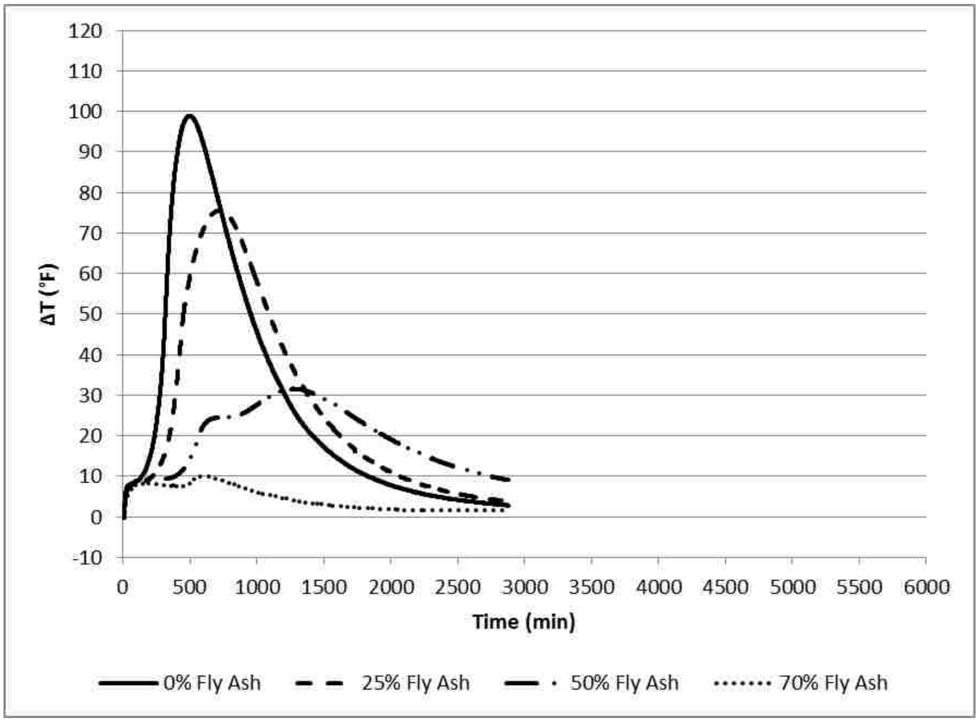

Figure C.2. Thermal Curve Plots for Combination 1-2

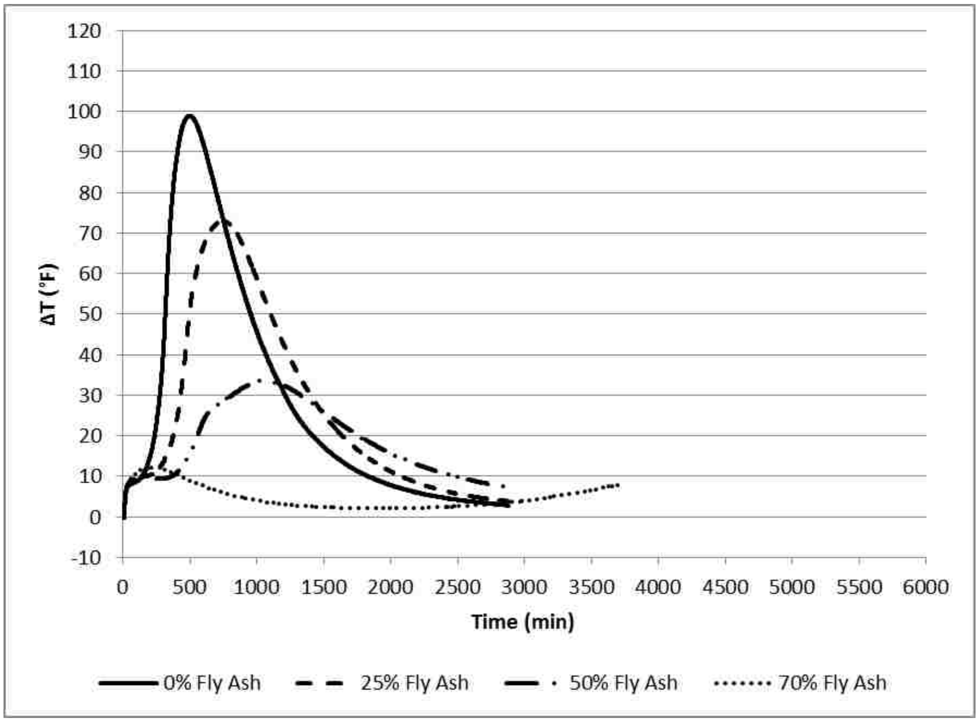

Figure C.3. Thermal Curve Plots for Combination 1-3

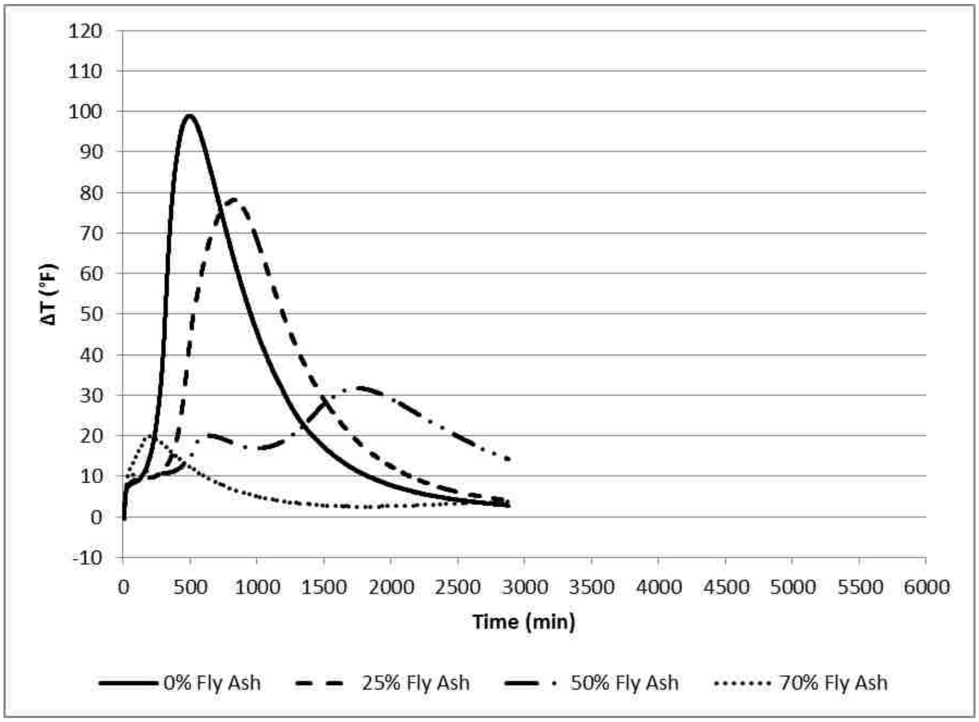

Figure C.4. Thermal Curve Plots for Combination 1-4

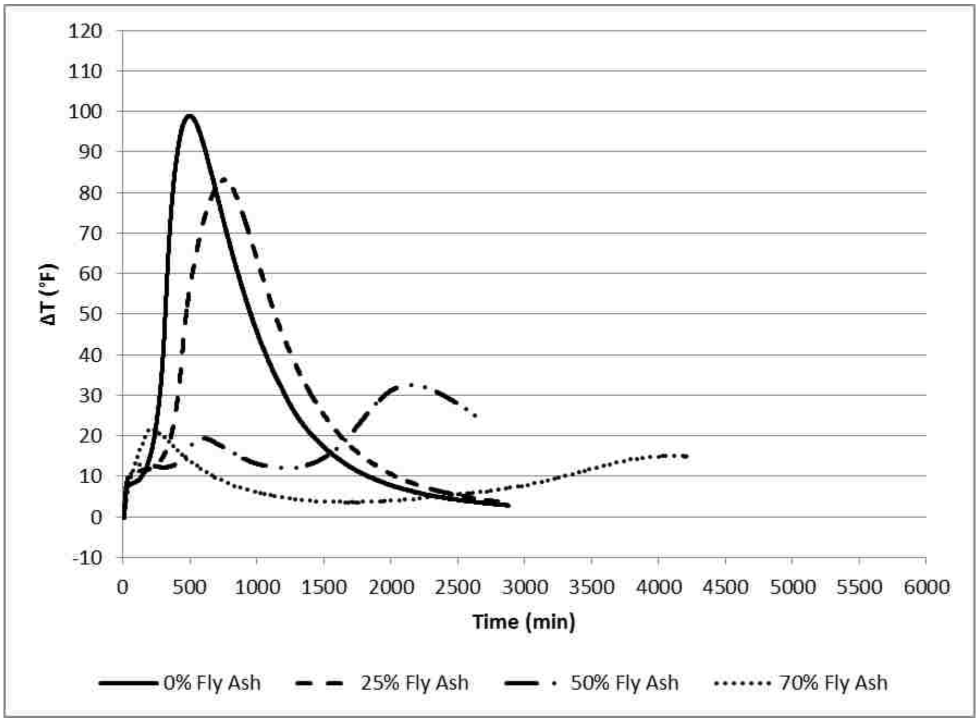

Figure C.5. Thermal Curve Plots for Combination 1-5

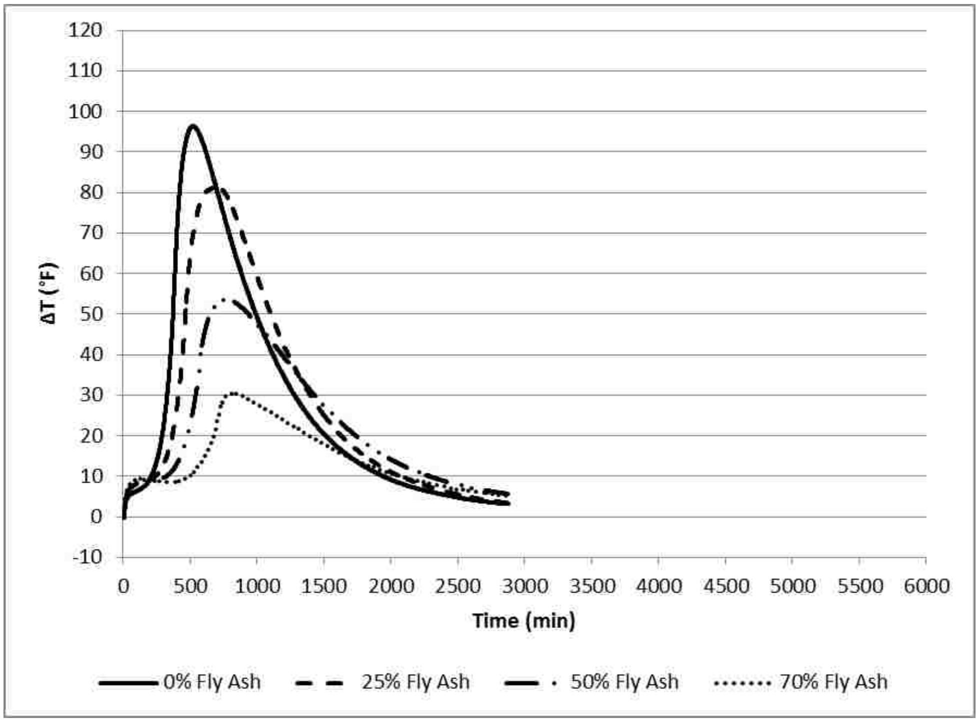

Figure C.6. Thermal Curve Plots for Combination 2-1

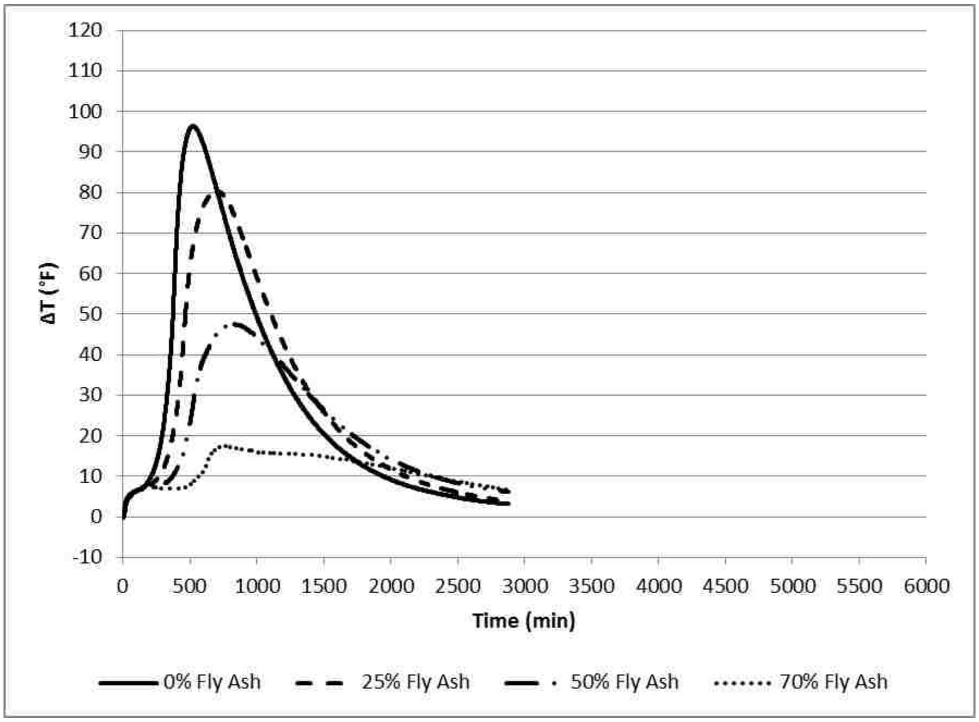

Figure C.7. Thermal Curve Plots for Combination 2-2

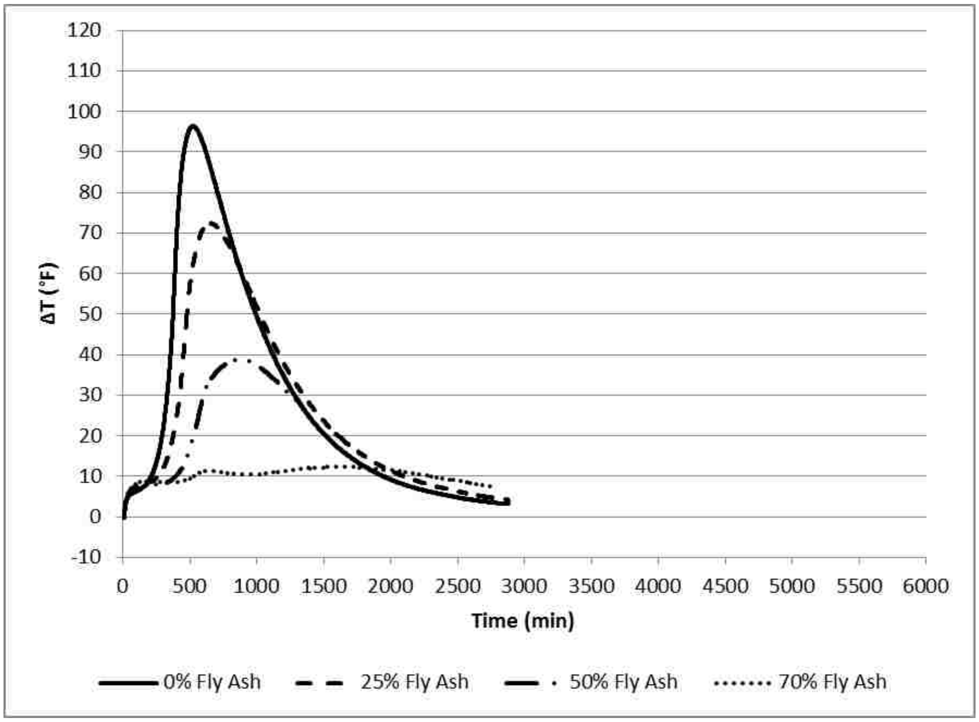

Figure C.8. Thermal Curve Plots for Combination 2-3

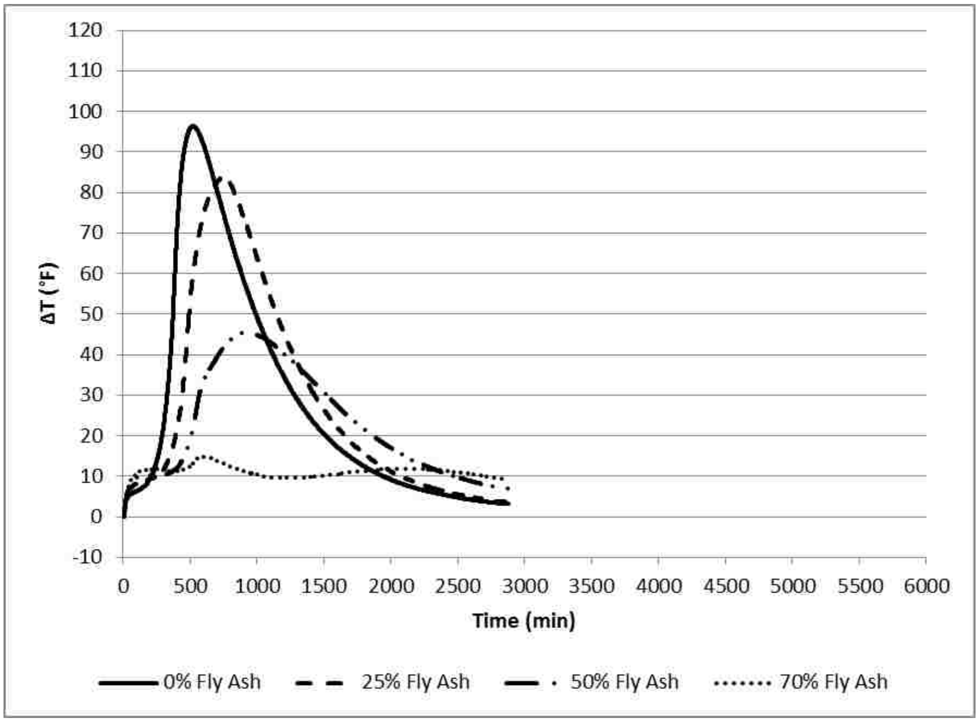

Figure C.9. Thermal Curve Plots for Combination 2-4

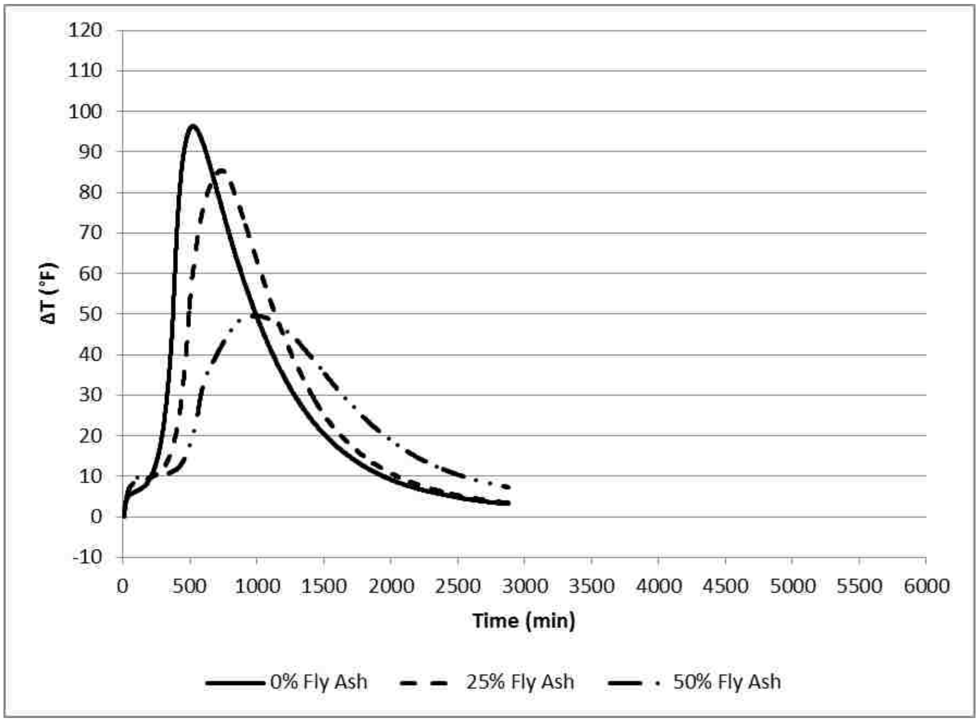

Figure C.10. Thermal Curve Plots for Combination 2-5

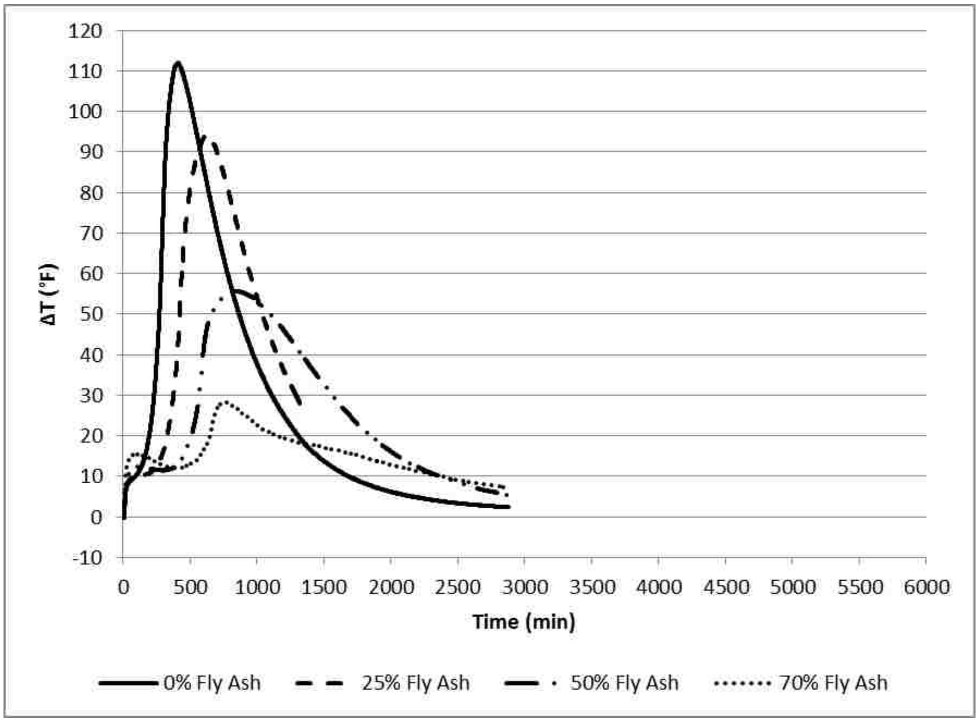

Figure C.11. Thermal Curve Plots for Combination 3-1

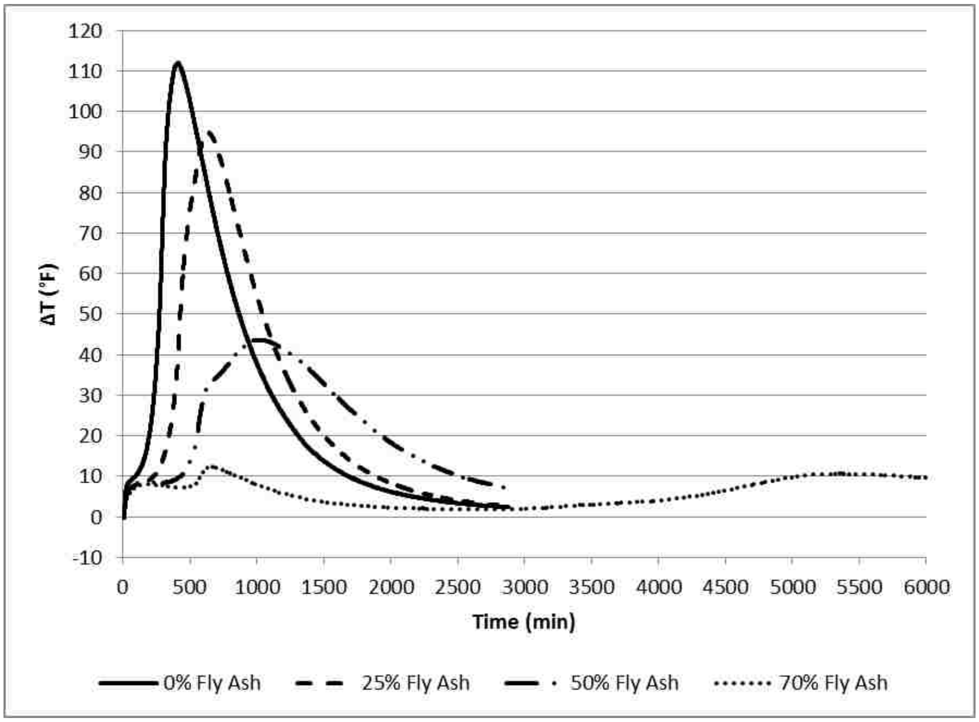

Figure C.12. Thermal Curve Plots for Combination 3-2

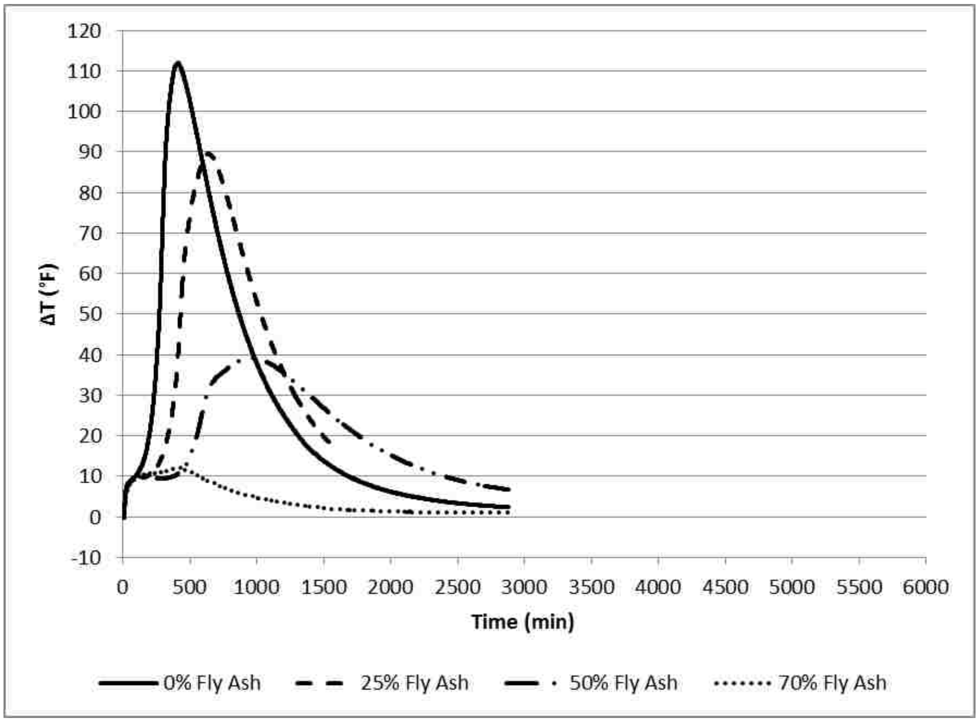

Figure C.13. Thermal Curve Plots for Combination 3-3

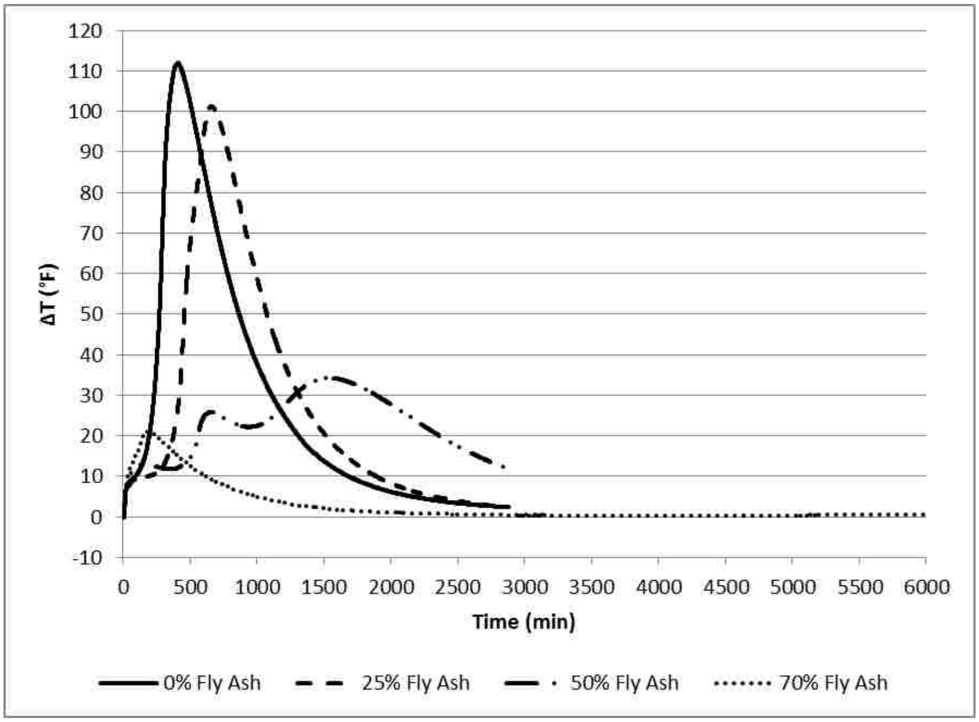

Figure C.14. Thermal Curve Plots for Combination 3-4

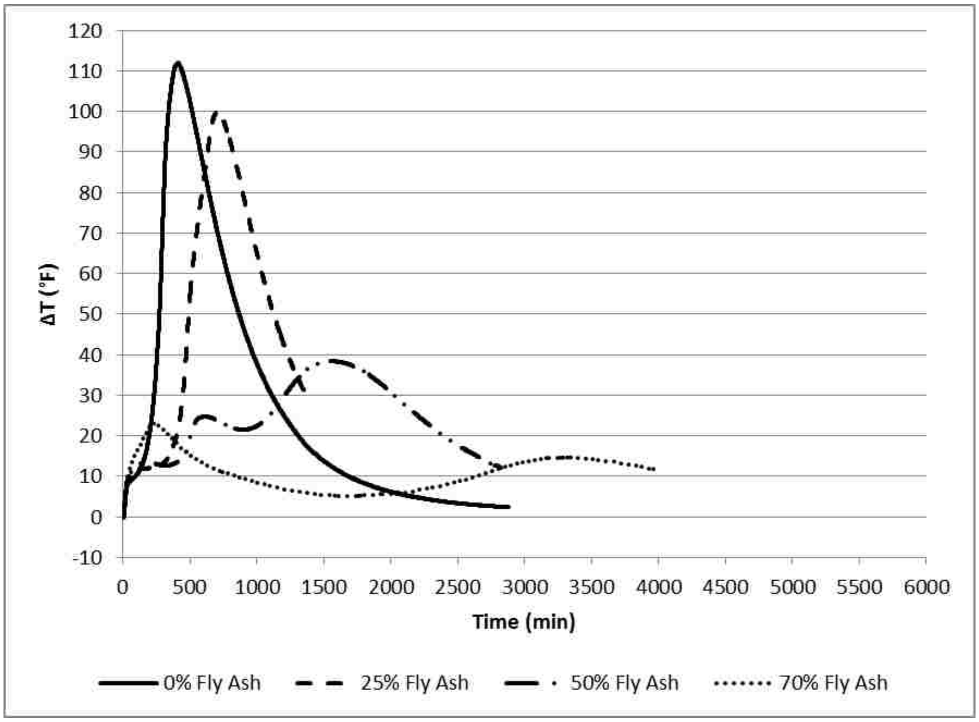

Figure C.15. Thermal Curve Plots for Combination 3-5

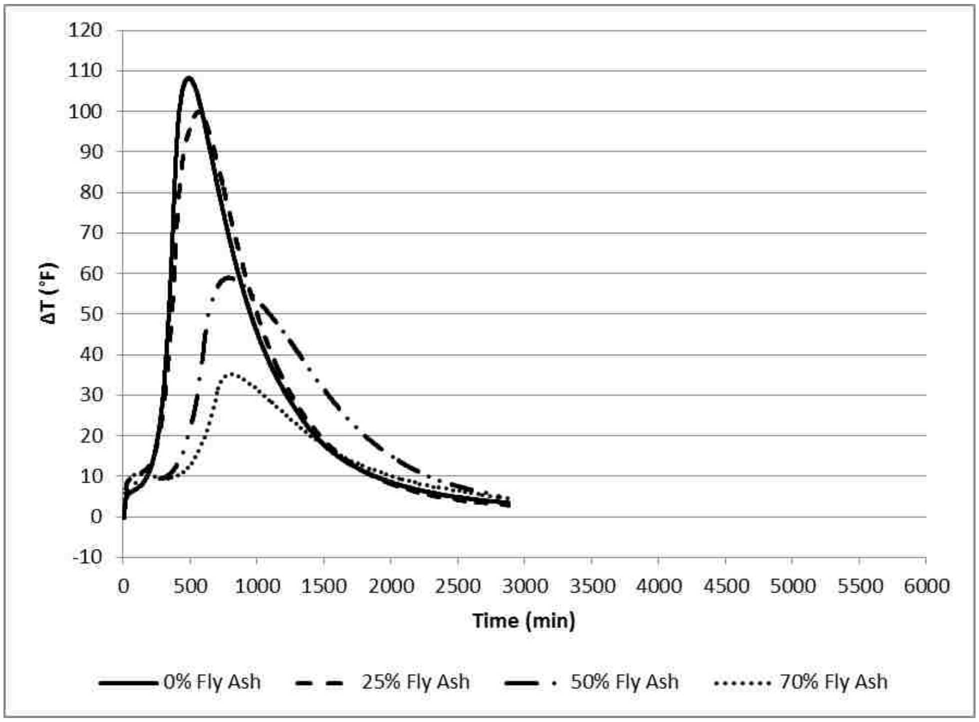

Figure C.16. Thermal Curve Plots for Combination 4-1

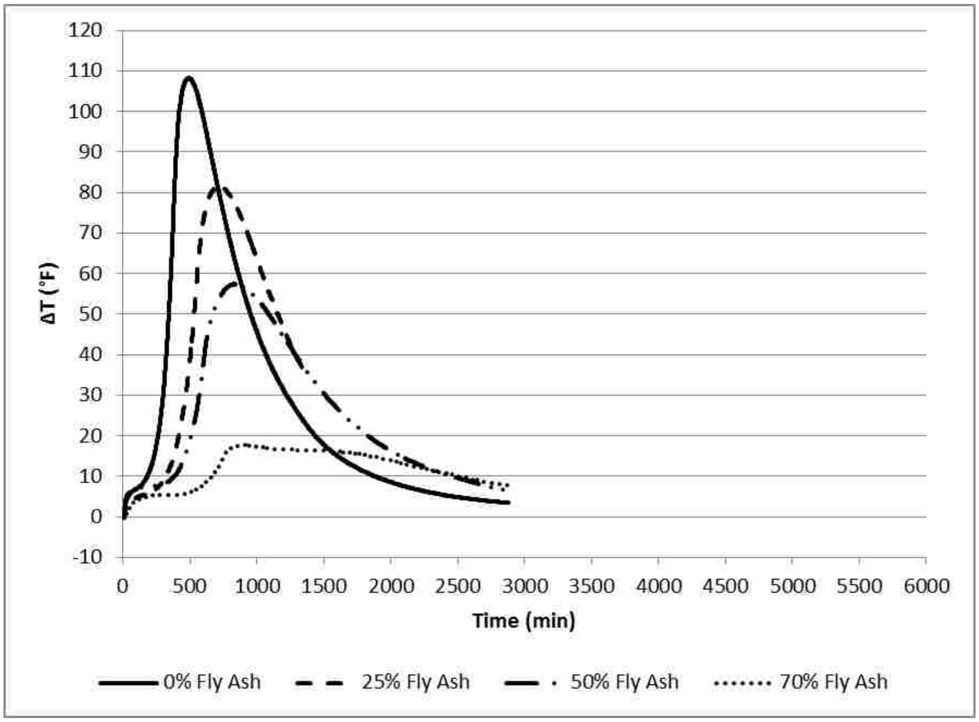

Figure C.17. Thermal Curve Plots for Combination 4-2

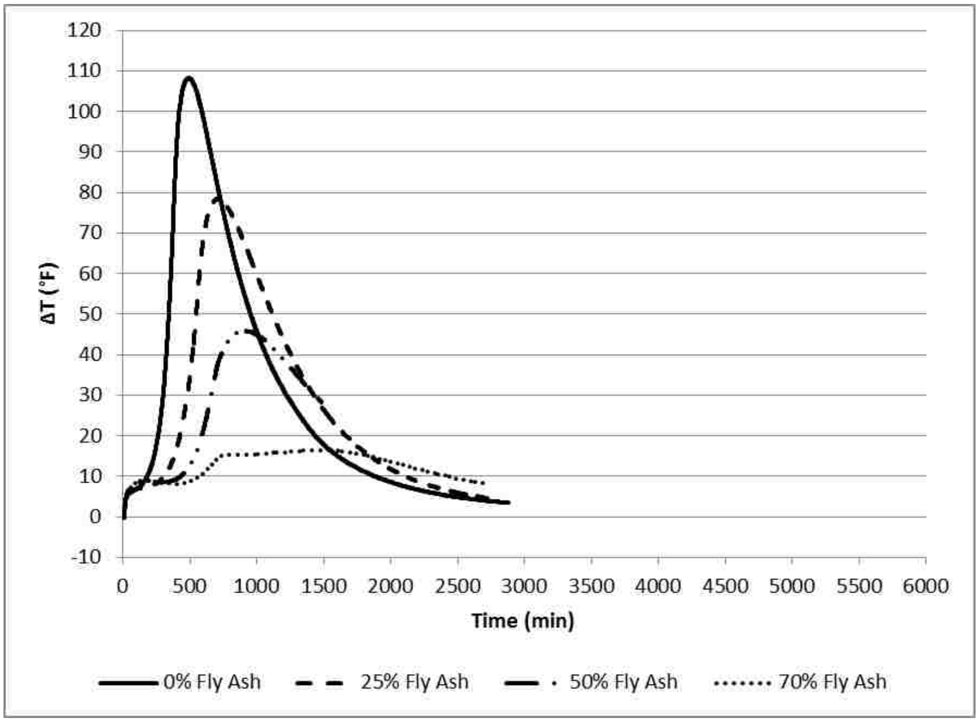

Figure C.18. Thermal Curve Plots for Combination 4-3

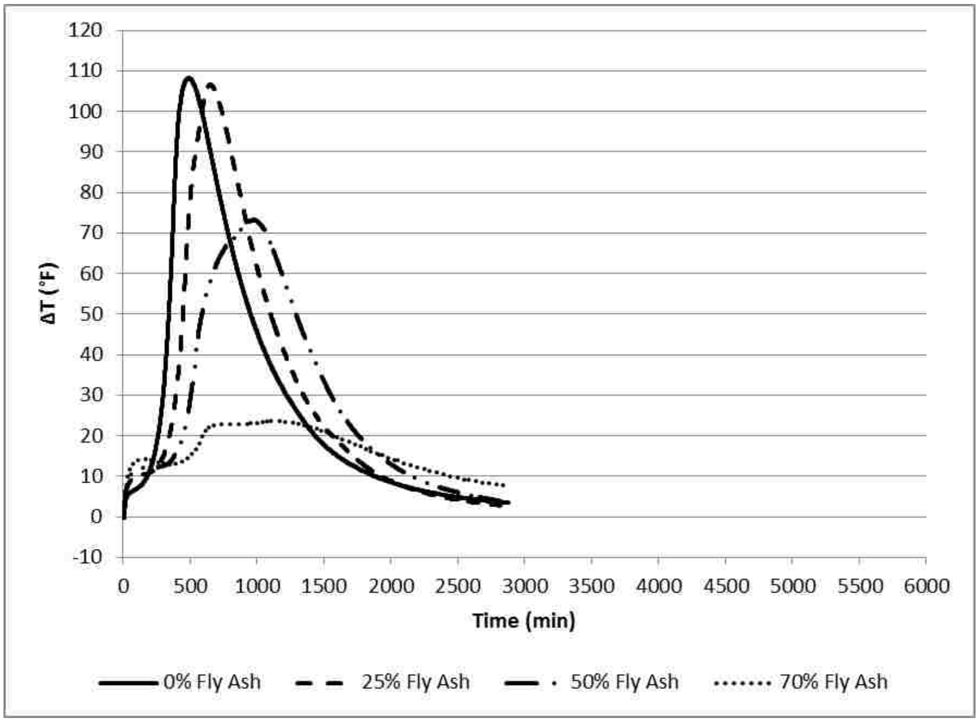

Figure C.19. Thermal Curve Plots for Combination 4-4

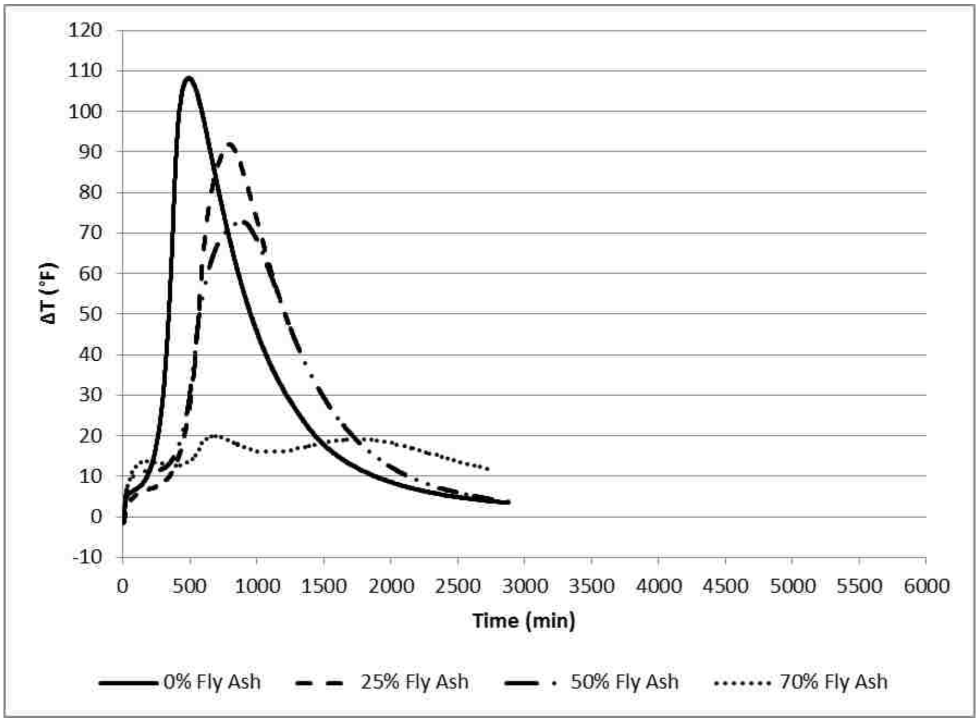

Figure C.20. Thermal Curve Plots for Combination 4-5

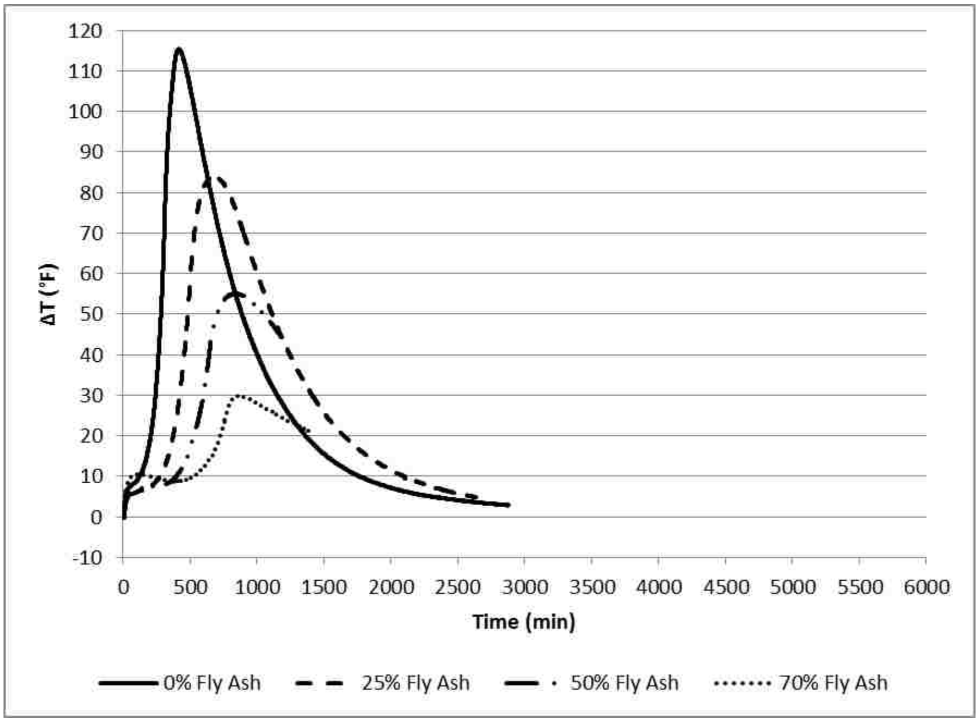

Figure C.21. Thermal Curve Plots for Combination 5-1

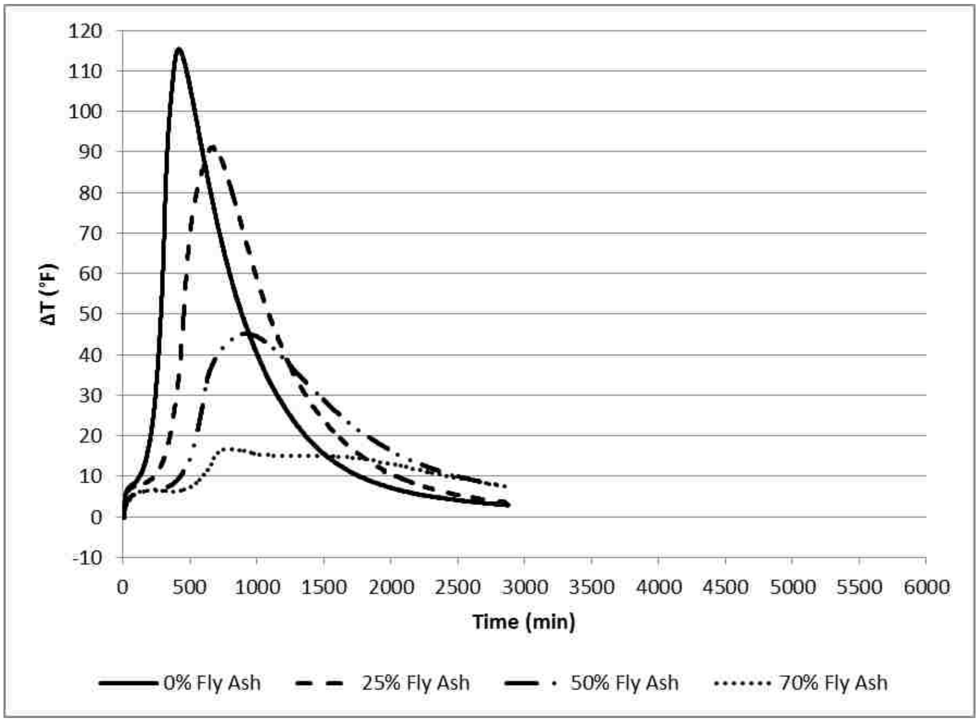

Figure C.22. Thermal Curve Plots for Combination 5-2

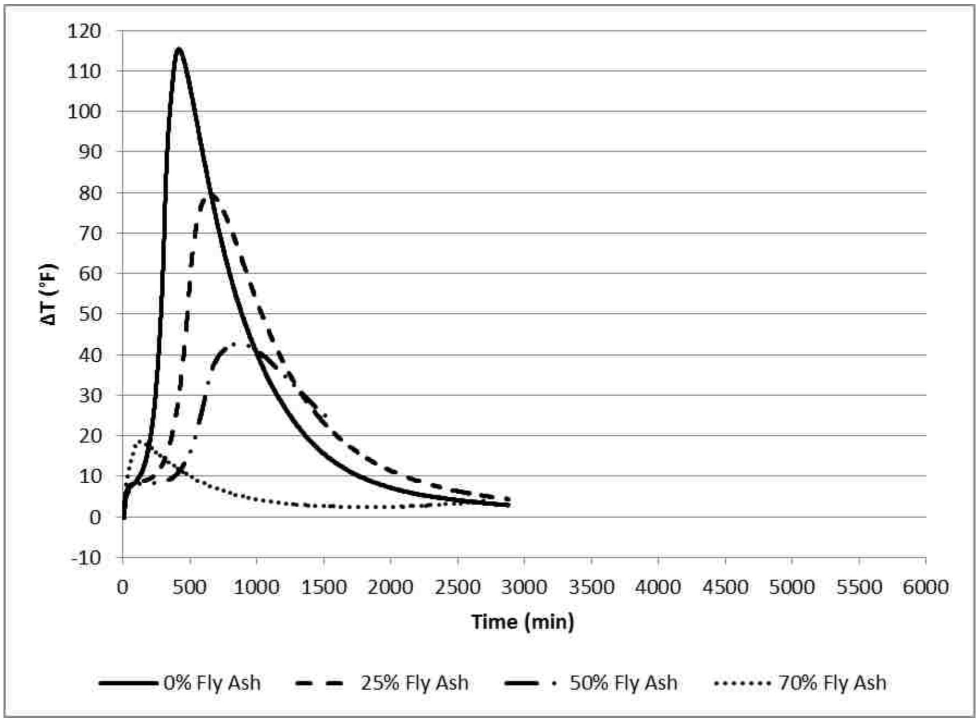

Figure C.23. Thermal Curve Plots for Combination 5-3

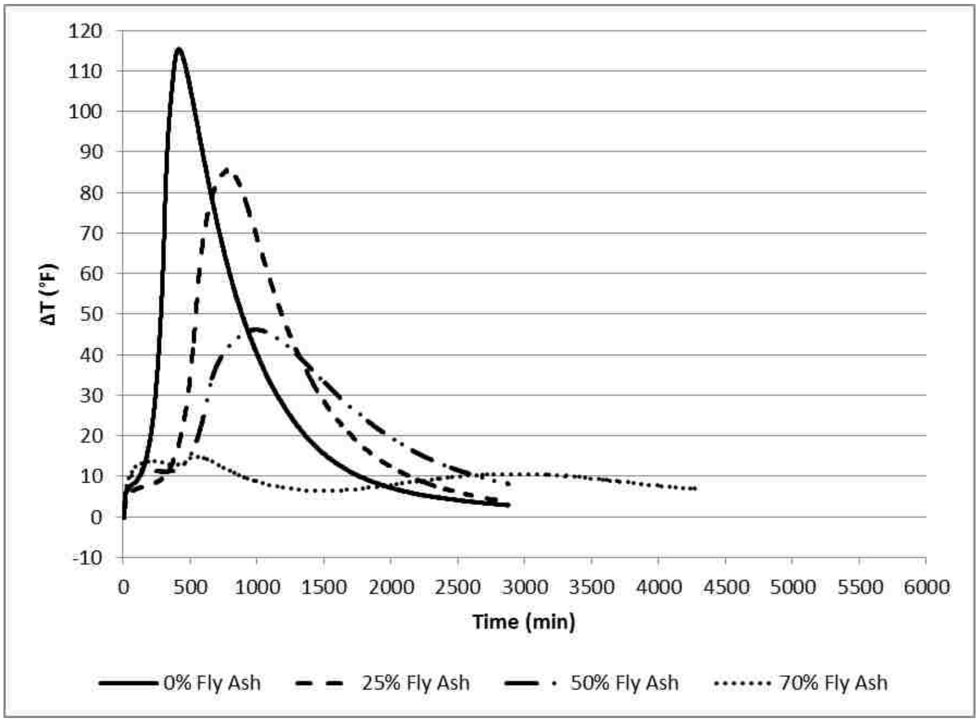

Figure C.24. Thermal Curve Plots for Combination 5-4

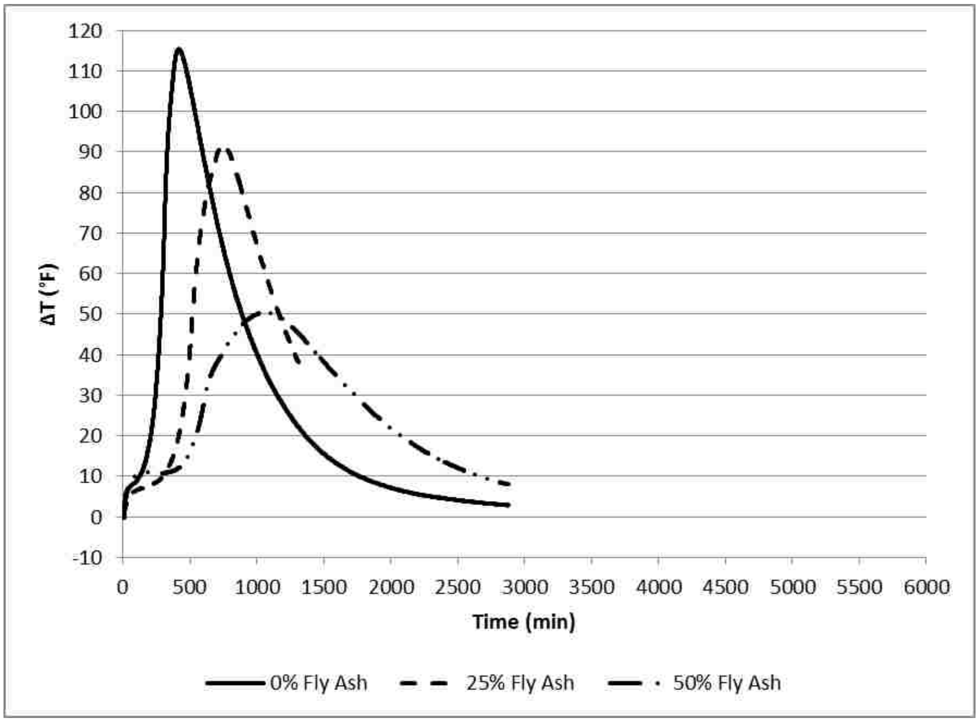

Figure C.25. Thermal Curve Plots for Combination 5-5

APPENDIX D

MAIN STUDY THERMAL CURVES

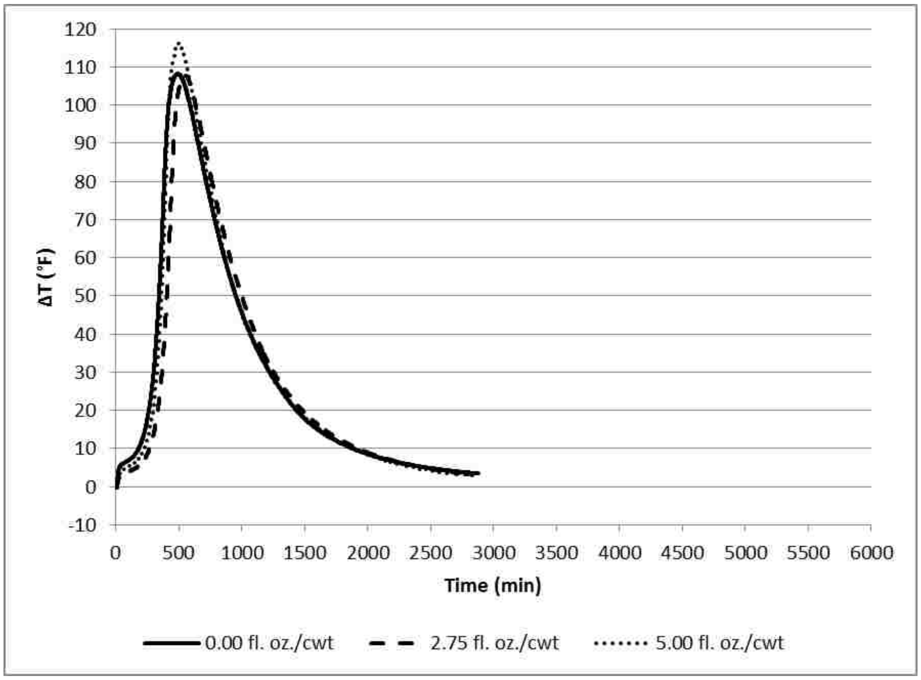

Figure D.1. Effect of Water Reducer on Combination 4-1 with 0% Fly Ash

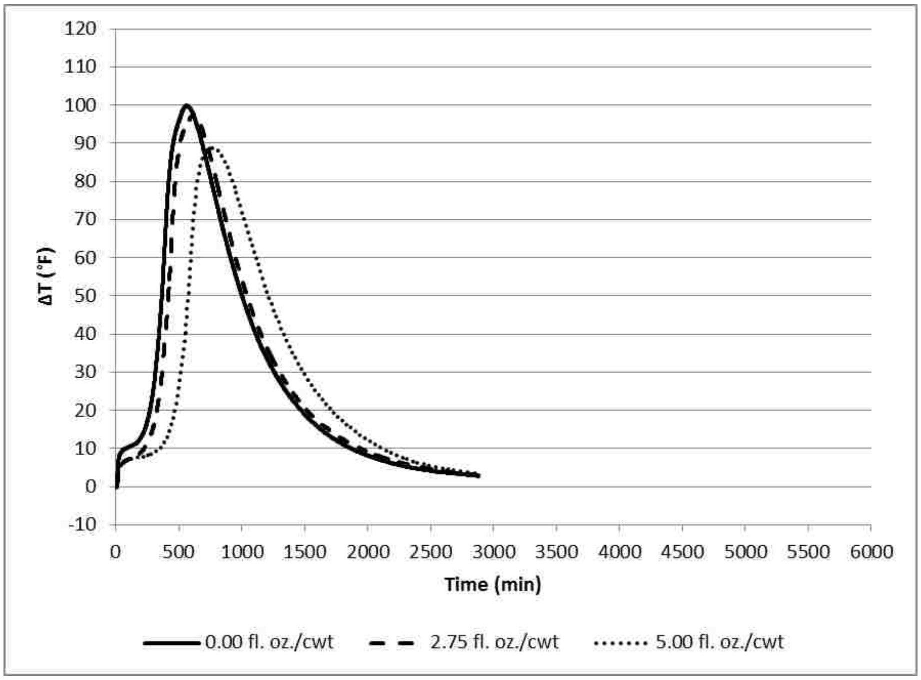

Figure D.2. Effect of Water Reducer on Combination 4-1 with 25% Fly Ash

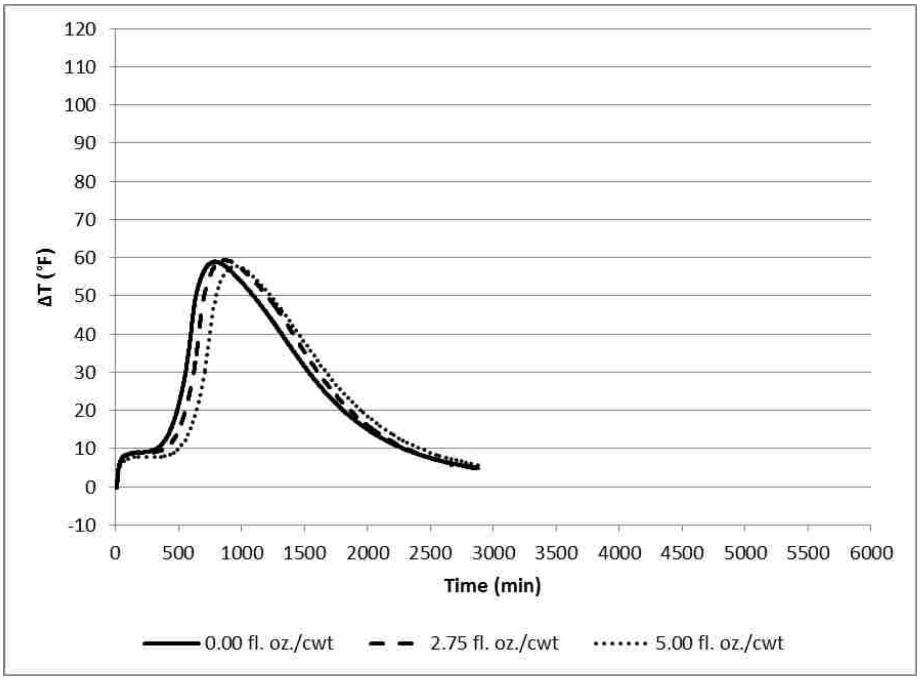

Figure D.3. Effect of Water Reducer on Combination 4-1 with 50% Fly Ash

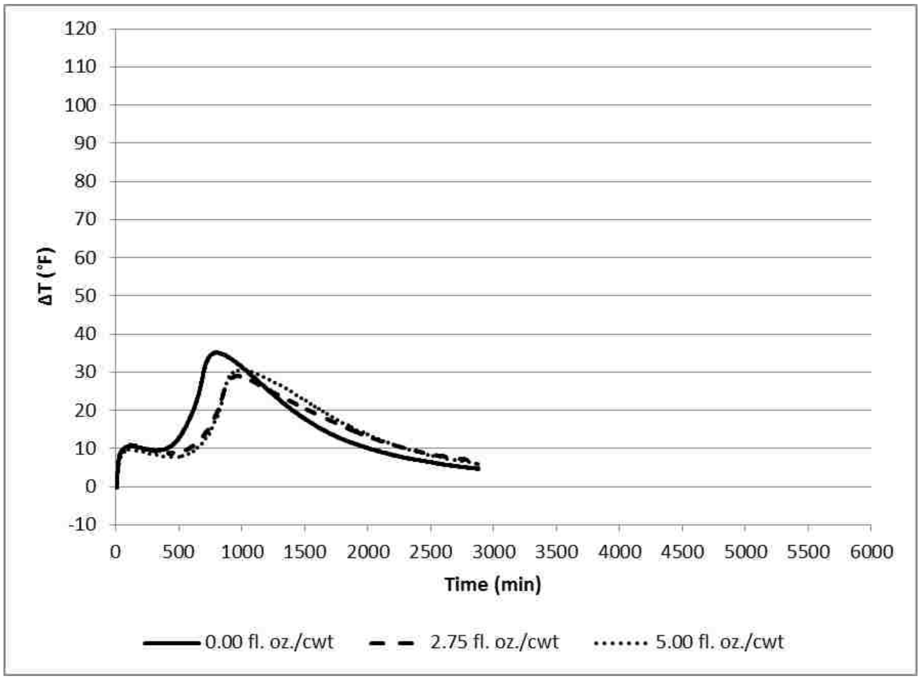

Figure D.4. Effect of Water Reducer on Combination 4-1 with 70% Fly Ash

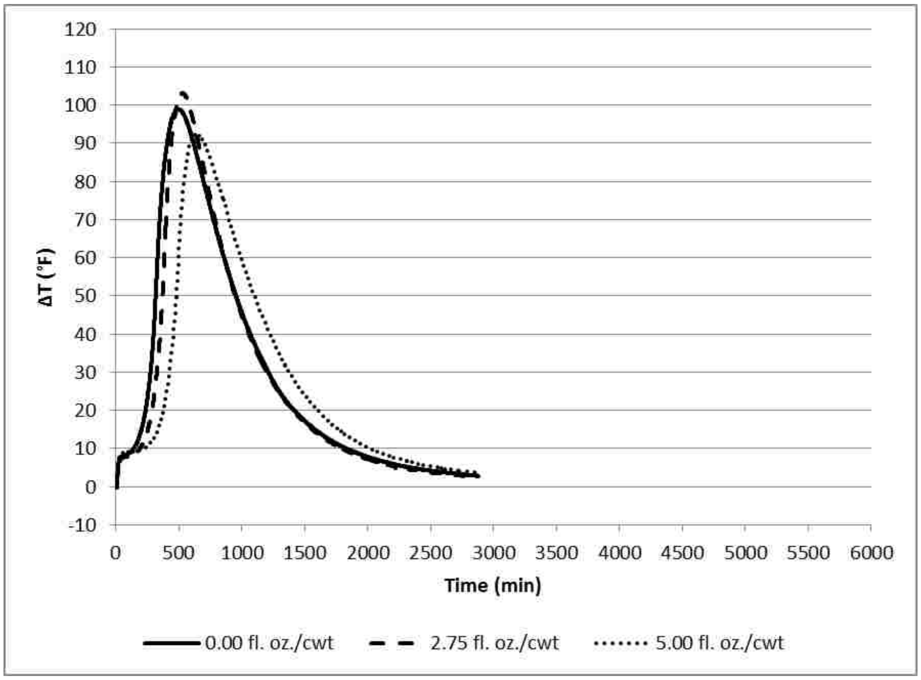

Figure D.5. Effect of Water Reducer on Combination 1-3 with 0% Fly Ash

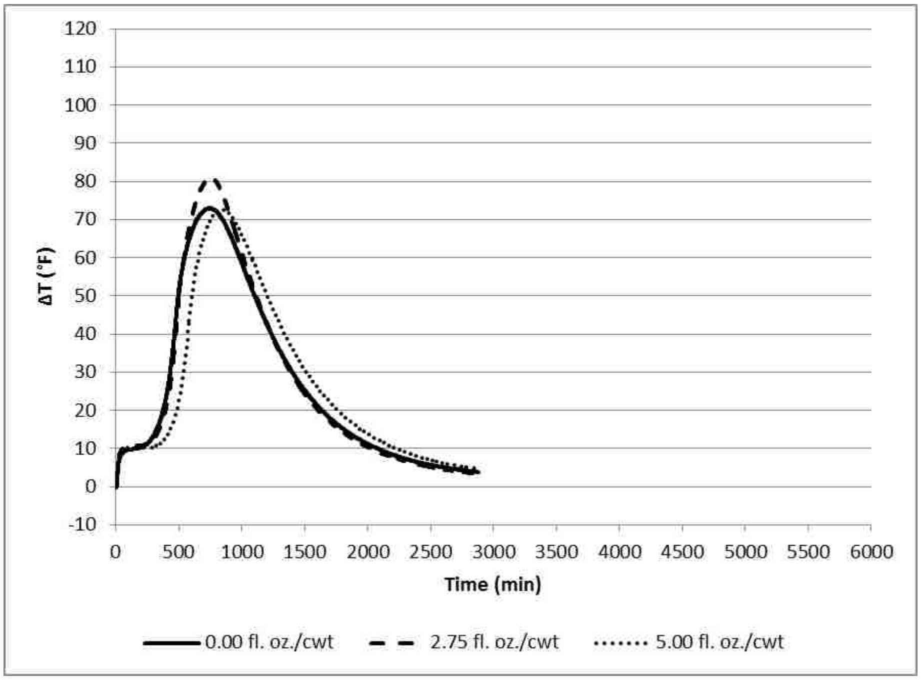

Figure D.6. Effect of Water Reducer on Combination 1-3 with 25% Fly Ash

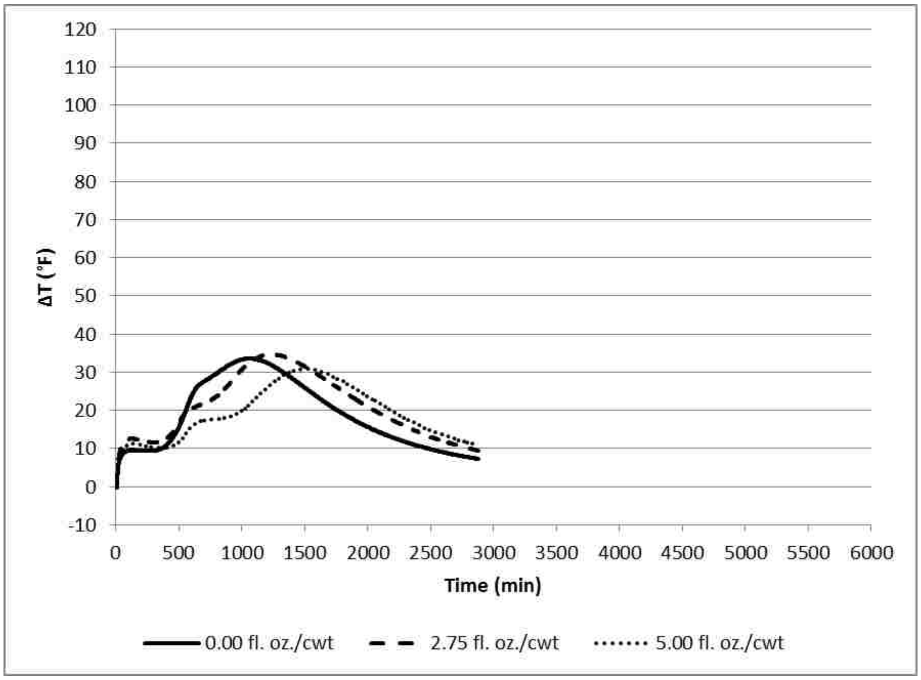

Figure D.7. Effect of Water Reducer on Combination 1-3 with 50% Fly Ash

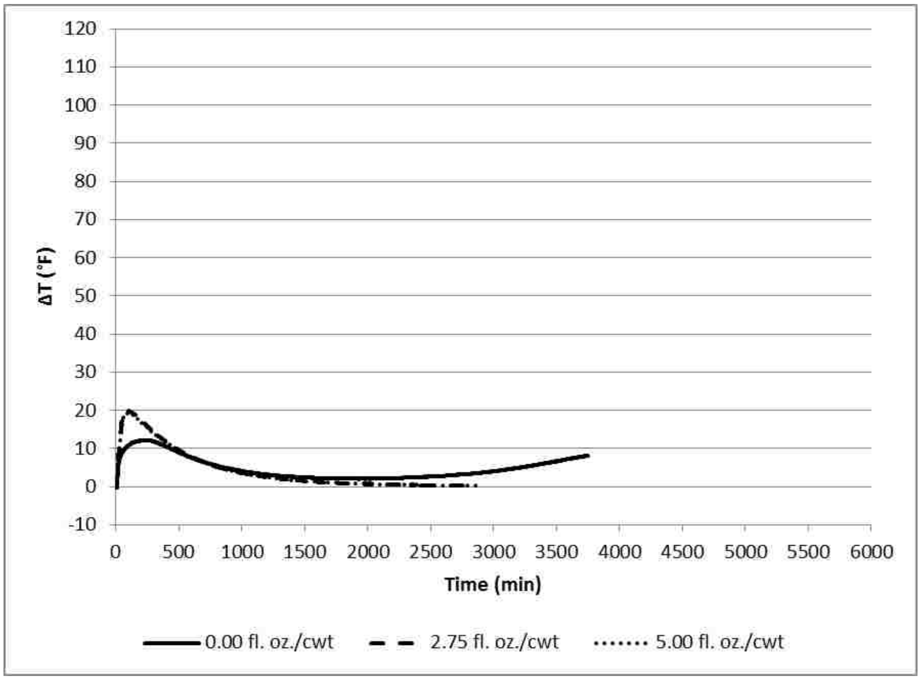

Figure D.8. Effect of Water Reducer on Combination 1-3 with 70% Fly Ash

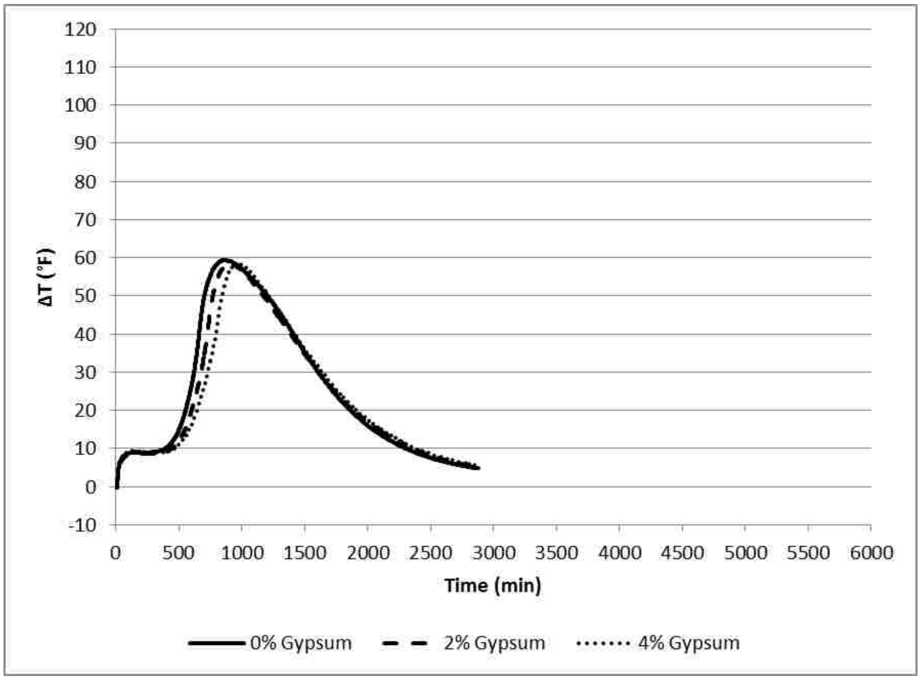

Figure D.9. Effects of Gypsum on Combination 4-1 with 50% Fly Ash and Low Dosage of Water Reducer

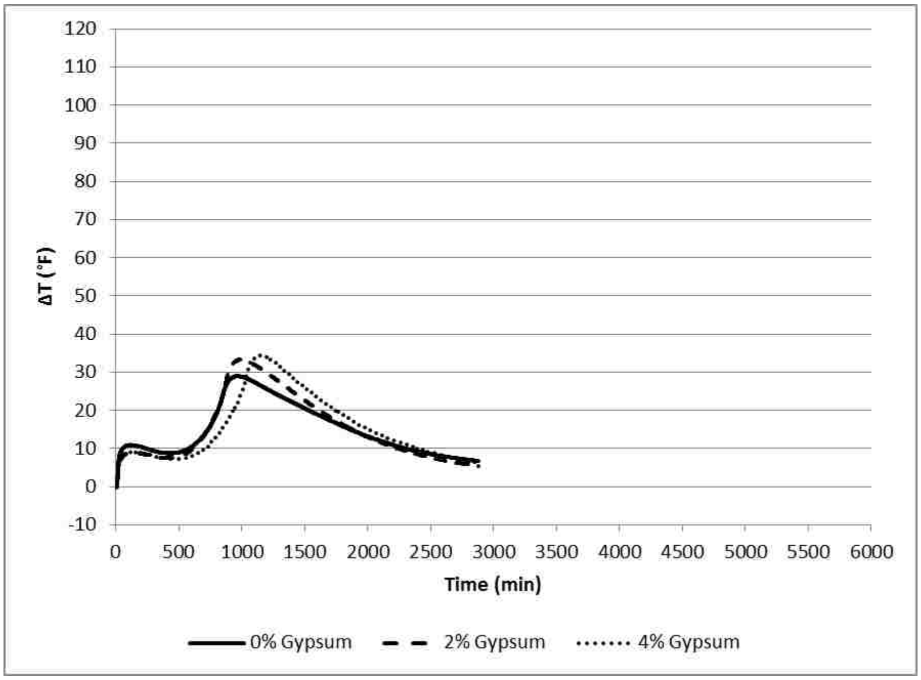

Figure D.10. Effects of Gypsum on Combination 4-1 with 70% Fly Ash and Low Dosage of Water Reducer

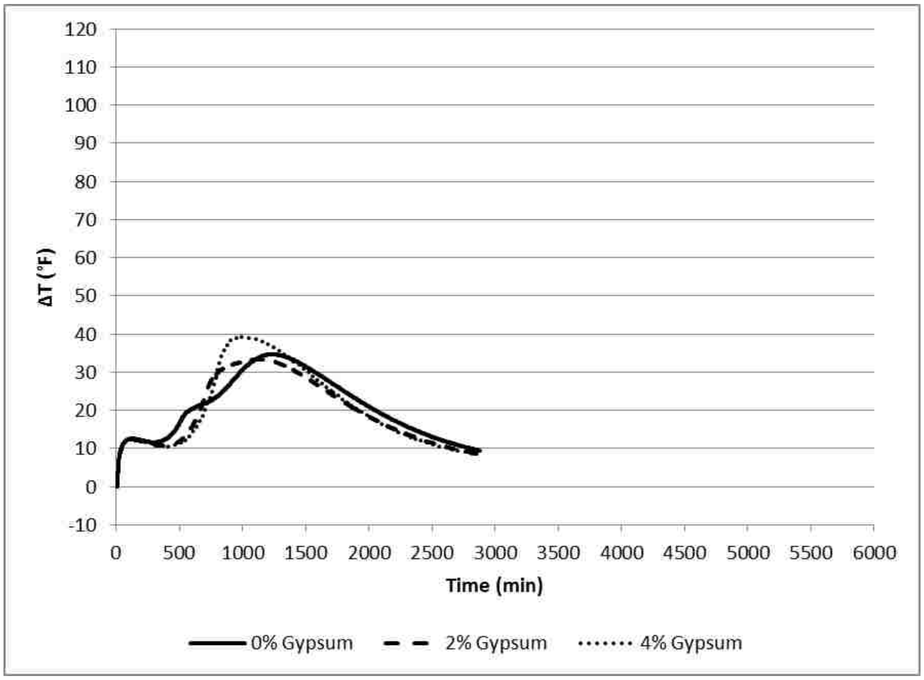

Figure D.11. Effects of Gypsum on Combination 1-3 with 50% Fly Ash and Low Dosage of Water Reducer

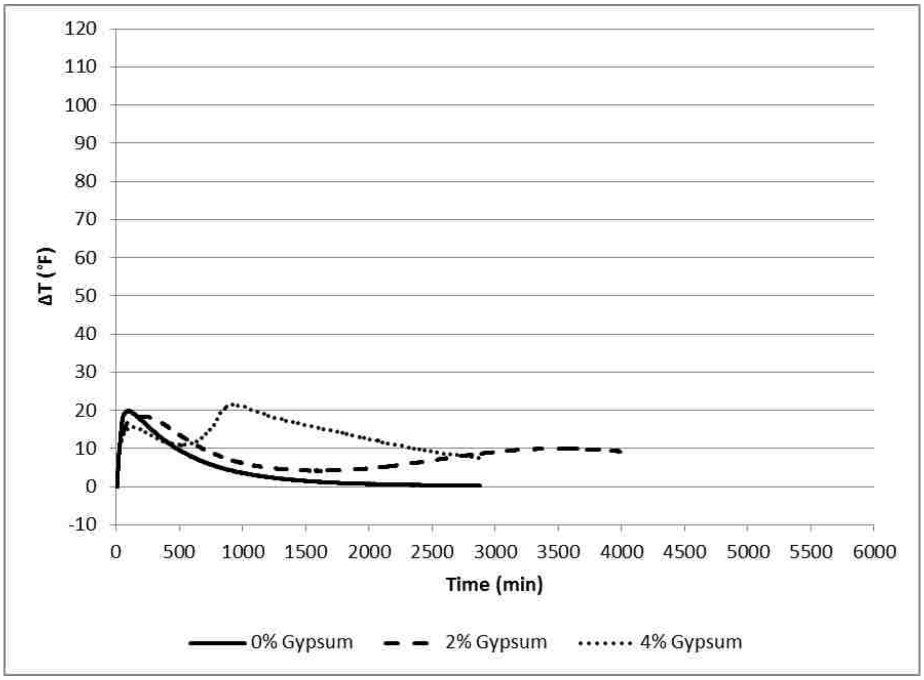

Figure D.12. Effects of Gypsum on Combination 1-3 with 70% Fly Ash and Low Dosage of Water Reducer

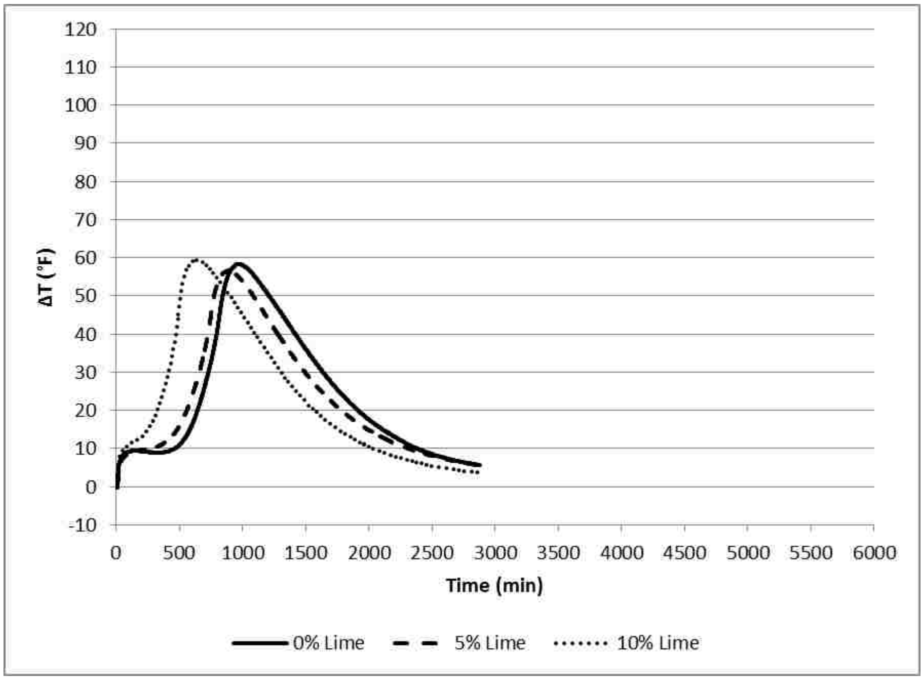

Figure D.13. Effects of Lime on Combination 4-1 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

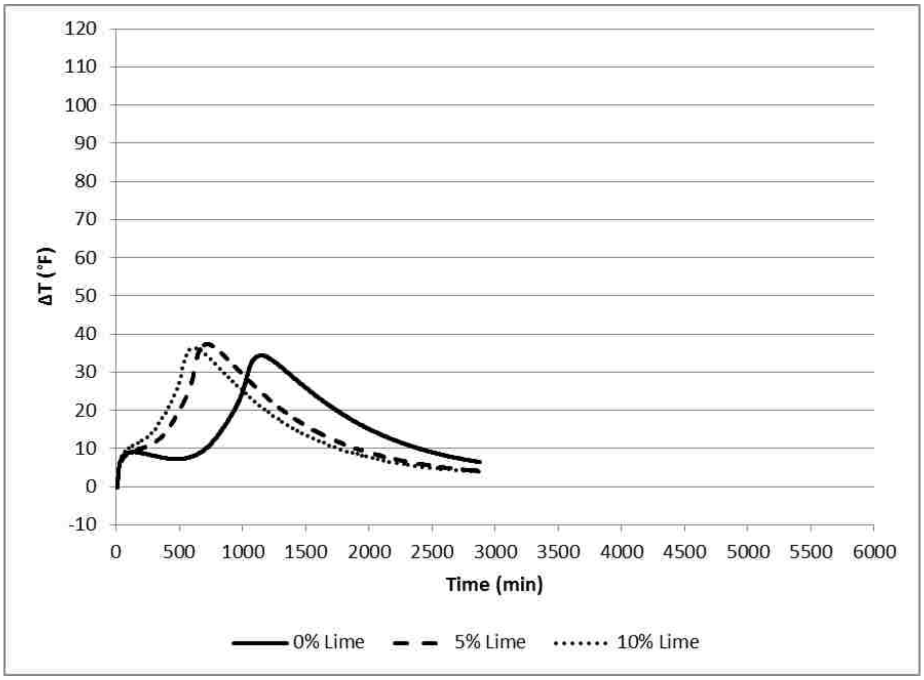

Figure D.14. Effects of Lime on Combination 4-1 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

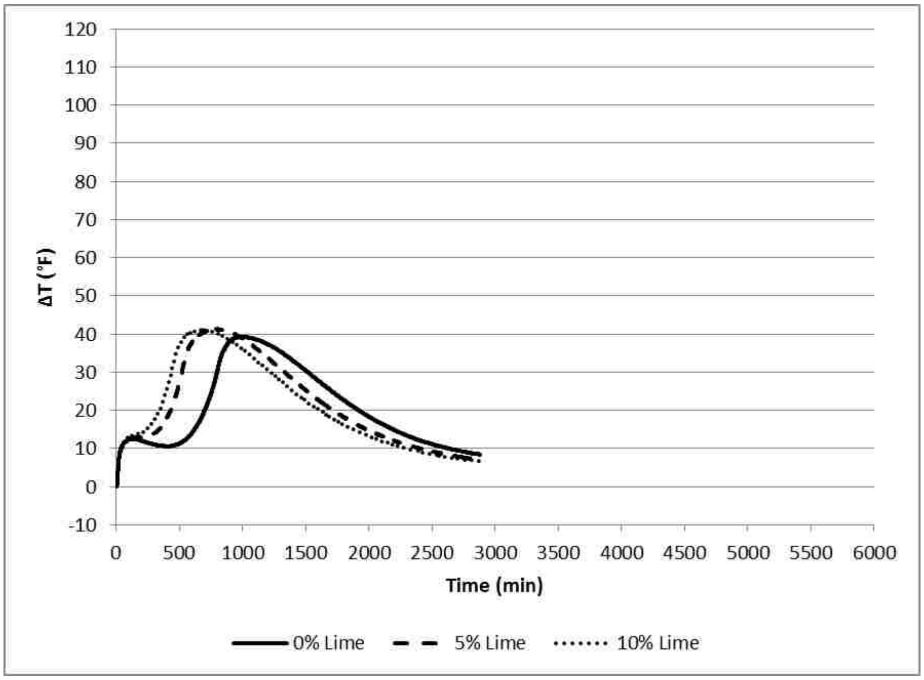

Figure D.15. Effects of Lime on Combination 1-3 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

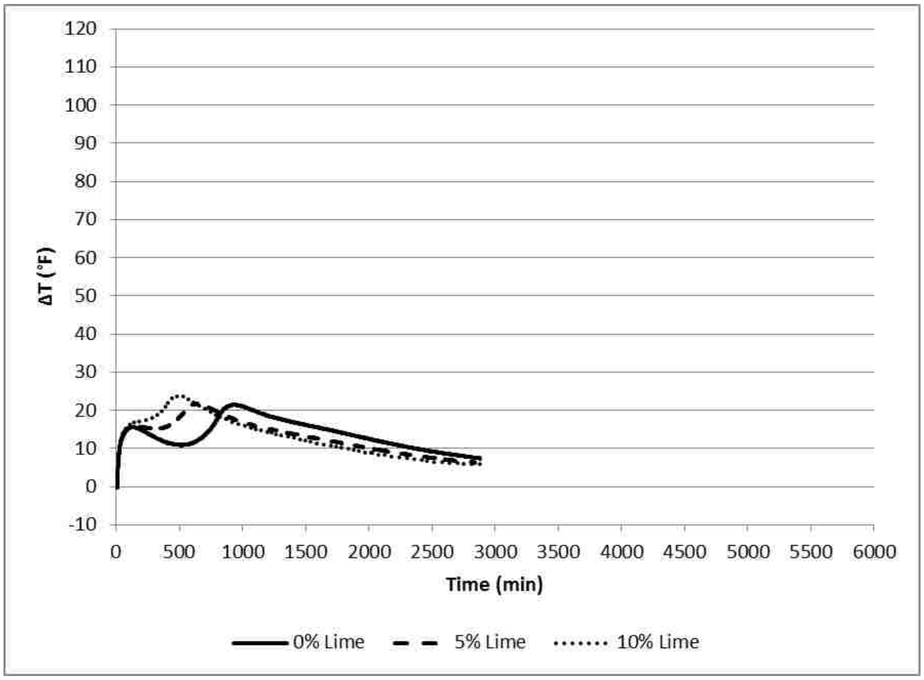

Figure D.16. Effects of Lime on Combination 1-3 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

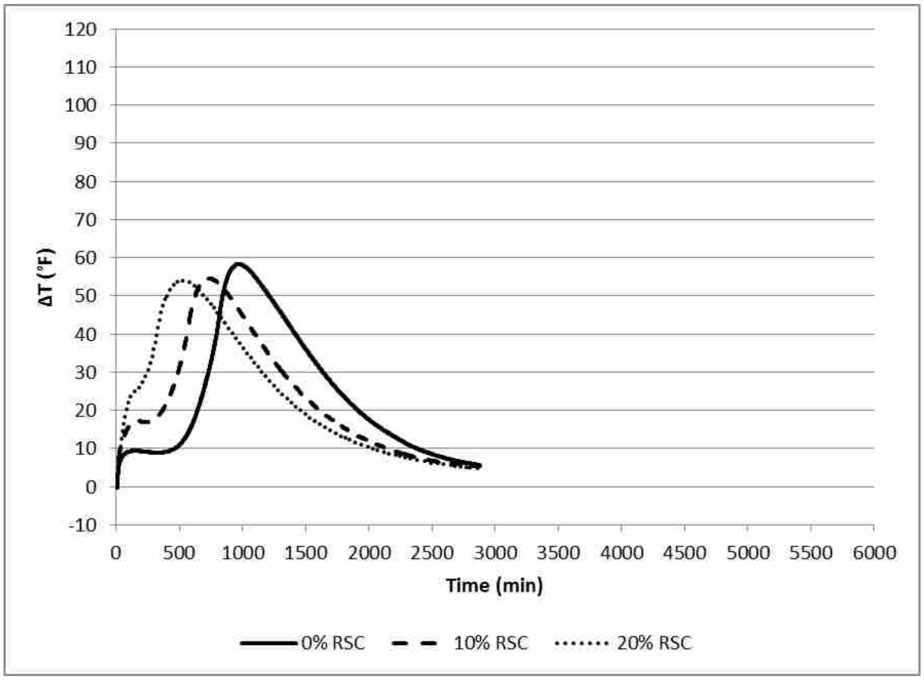

Figure D.17. Effects of Rapid Set Cement on Combination 4-1 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

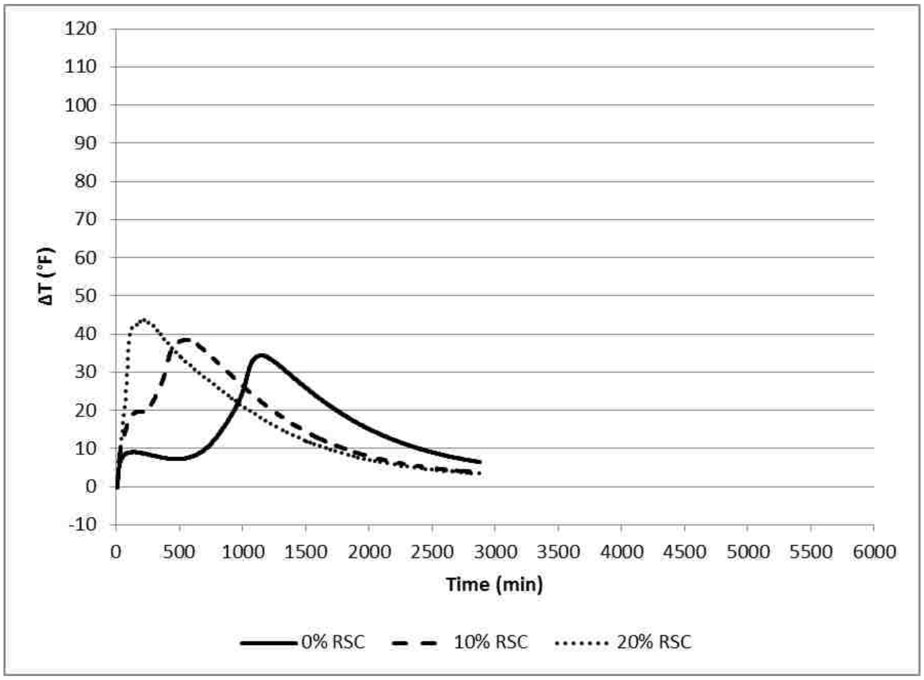

Figure D.18. Effects of Rapid Set Cement on Combination 4-1 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

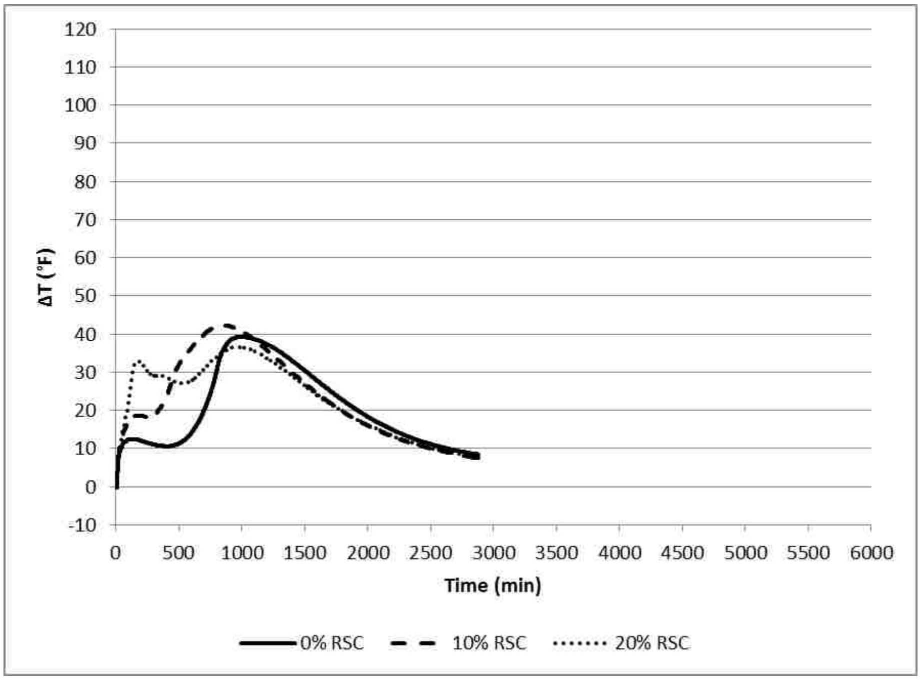

Figure D.19. Effects of Rapid Set Cement on Combination 1-3 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

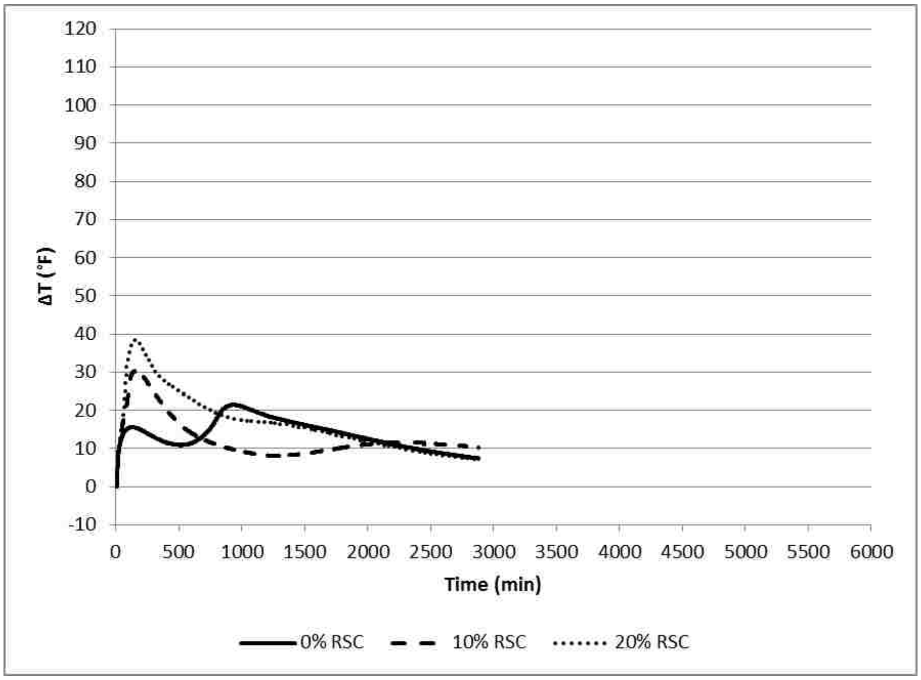

Figure D.20. Effects of Rapid Set Cement on Combination 1-3 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

APPENDIX E

SCREENING STUDY MINIATURE SLUMP PLOTS

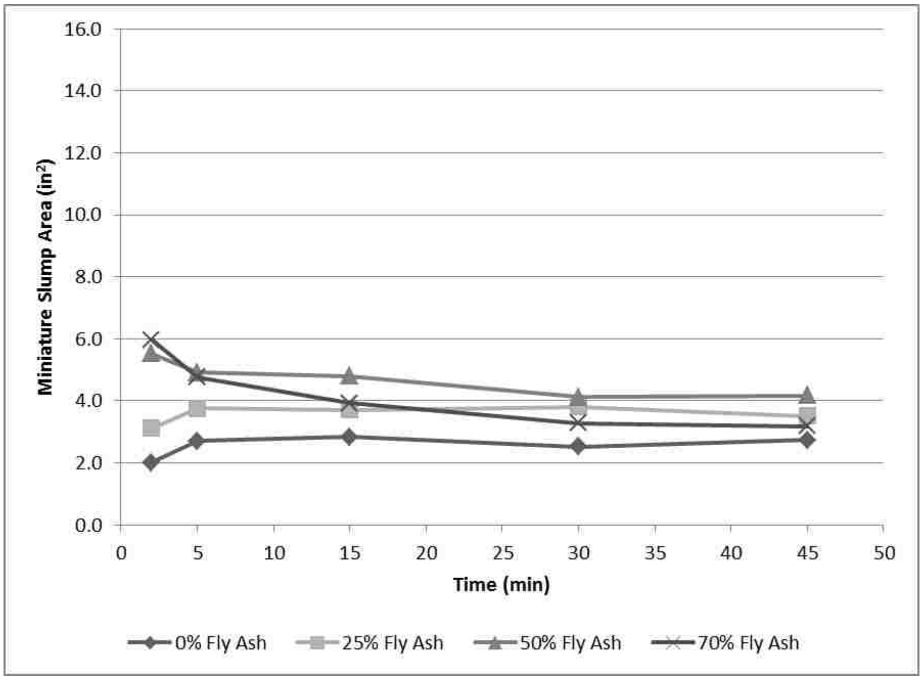

Figure E.1. Miniature Slump Plots for Combination 1-1

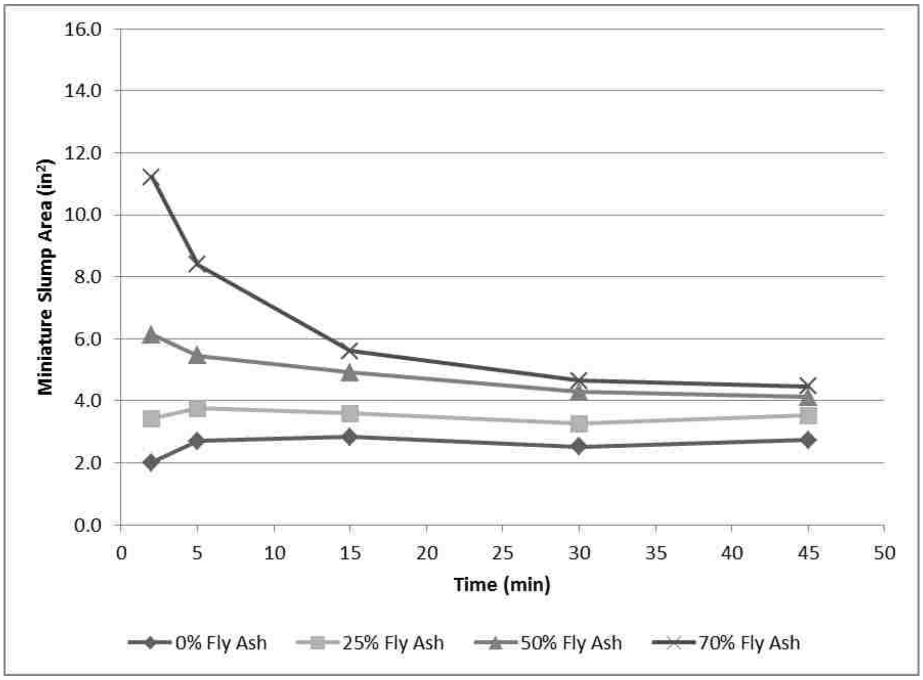

Figure E.2. Miniature Slump Plots for Combination 1-2

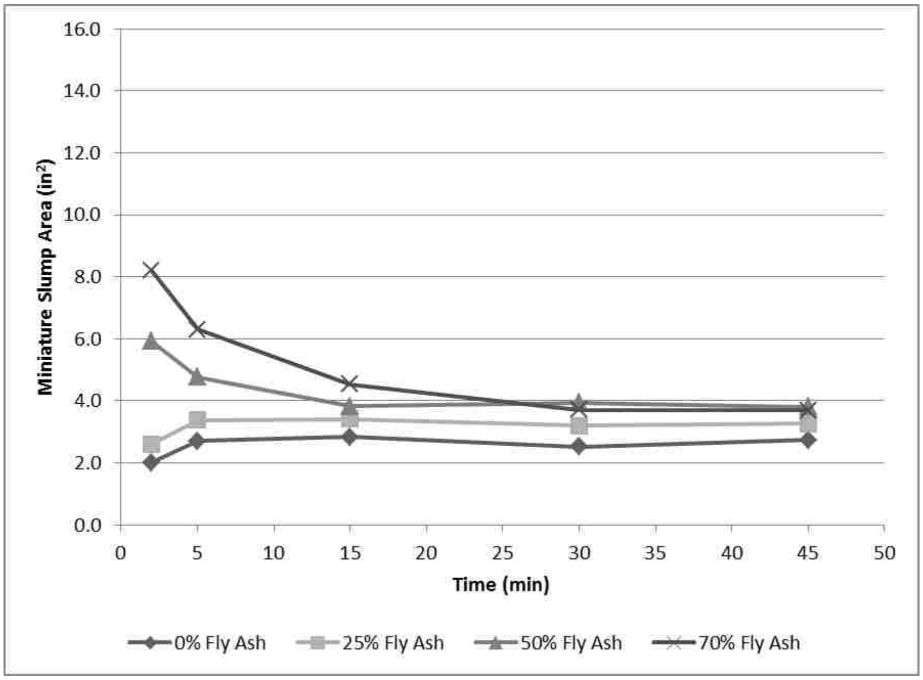

Figure E.3. Miniature Slump Plots for Combination 1-3

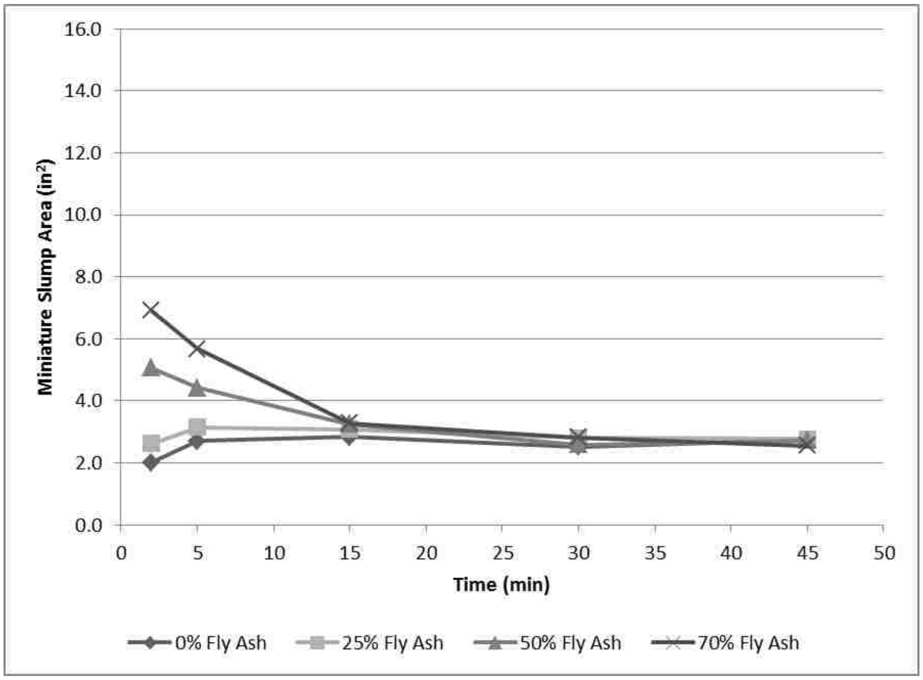

Figure E.4. Miniature Slump Plots for Combination 1-4

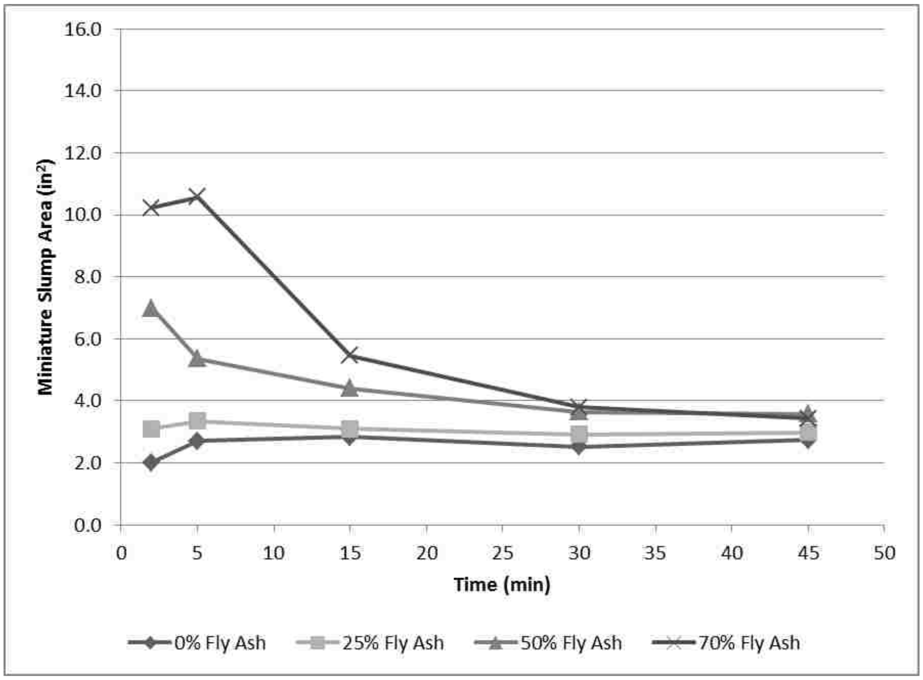

Figure E.5. Miniature Slump Plots for Combination 1-5

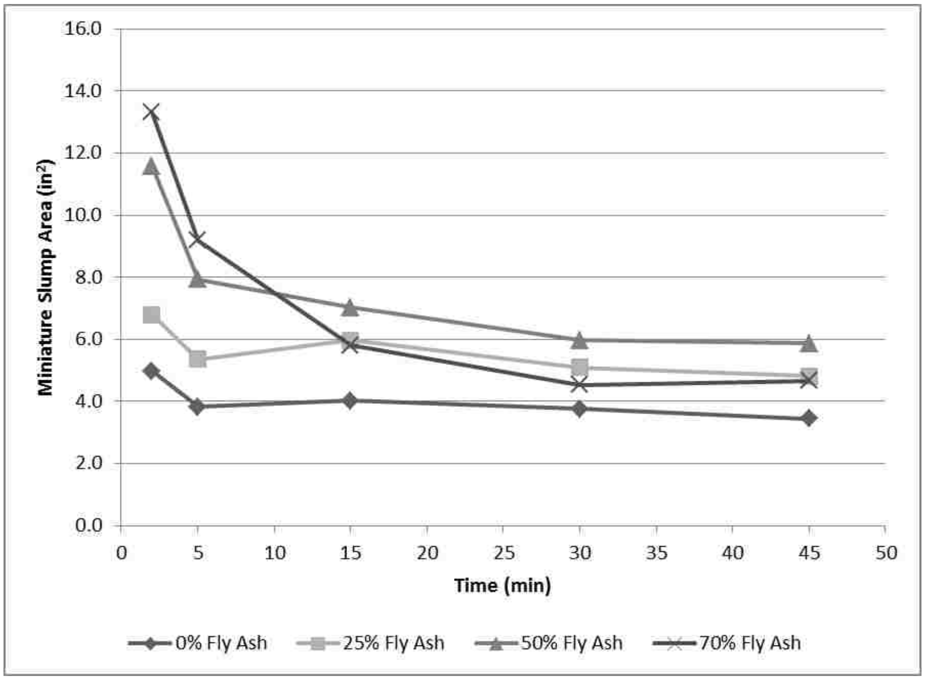

Figure E.6. Miniature Slump Plots for Combination 2-1

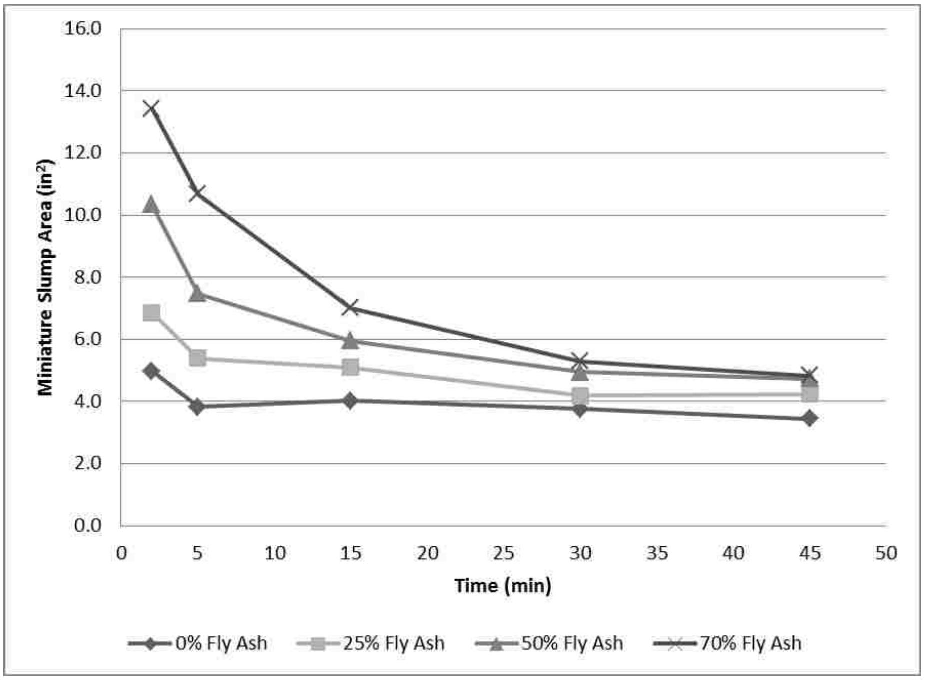

Figure E.7. Miniature Slump Plots for Combination 2-2

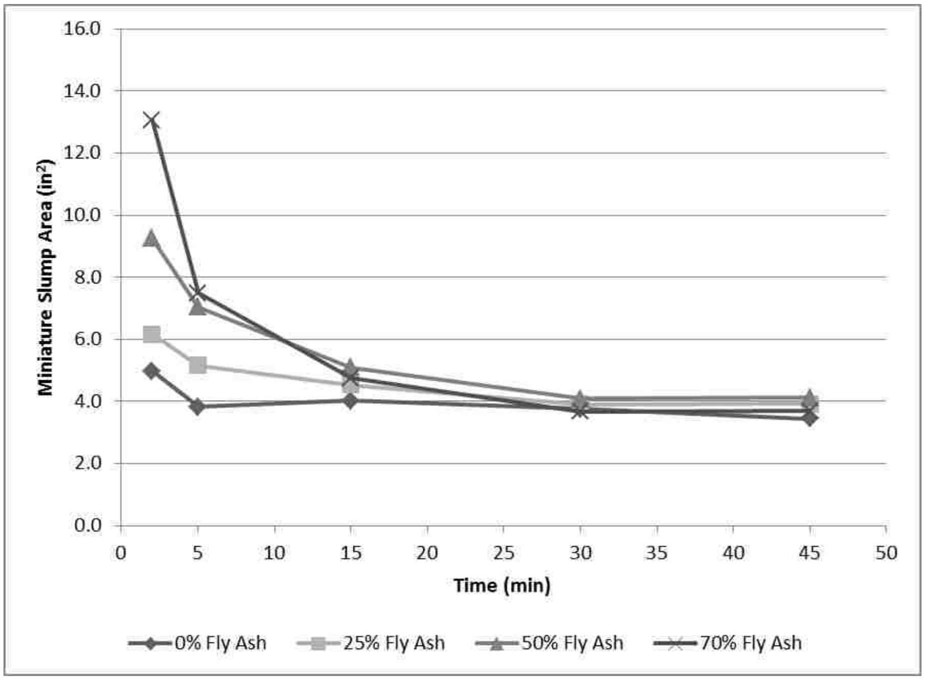

Figure E.8. Miniature Slump Plots for Combination 2-3

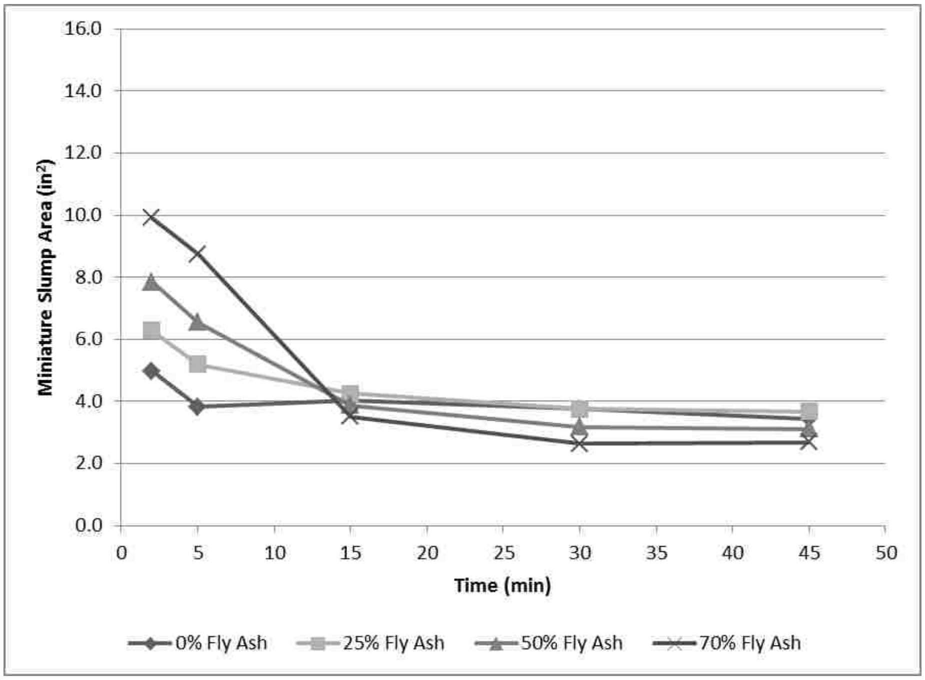

Figure E.9. Miniature Slump Plots for Combination 2-4

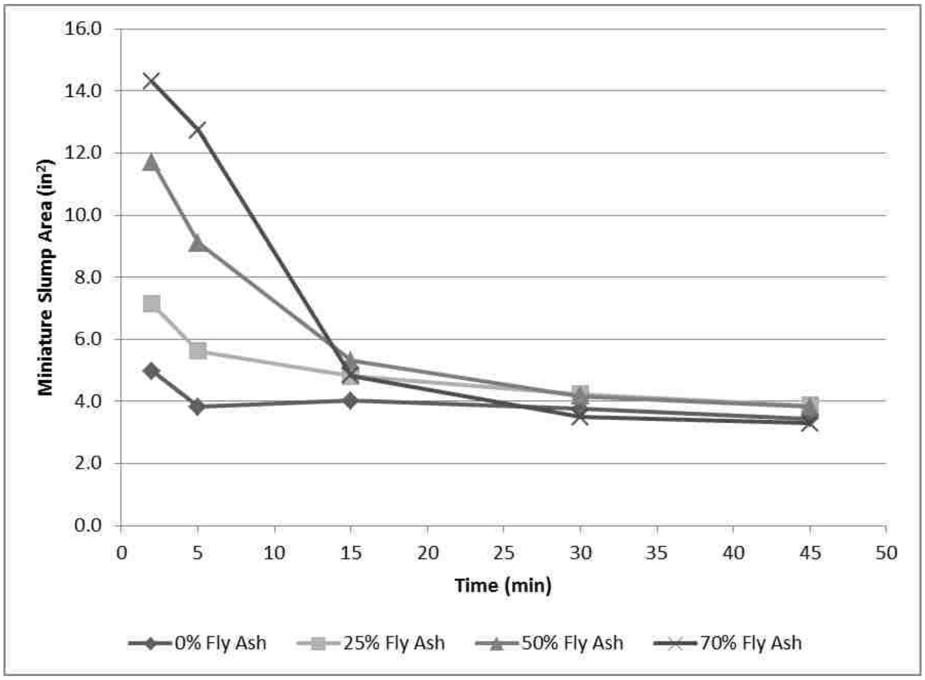

Figure E.10. Miniature Slump Plots for Combination 2-5

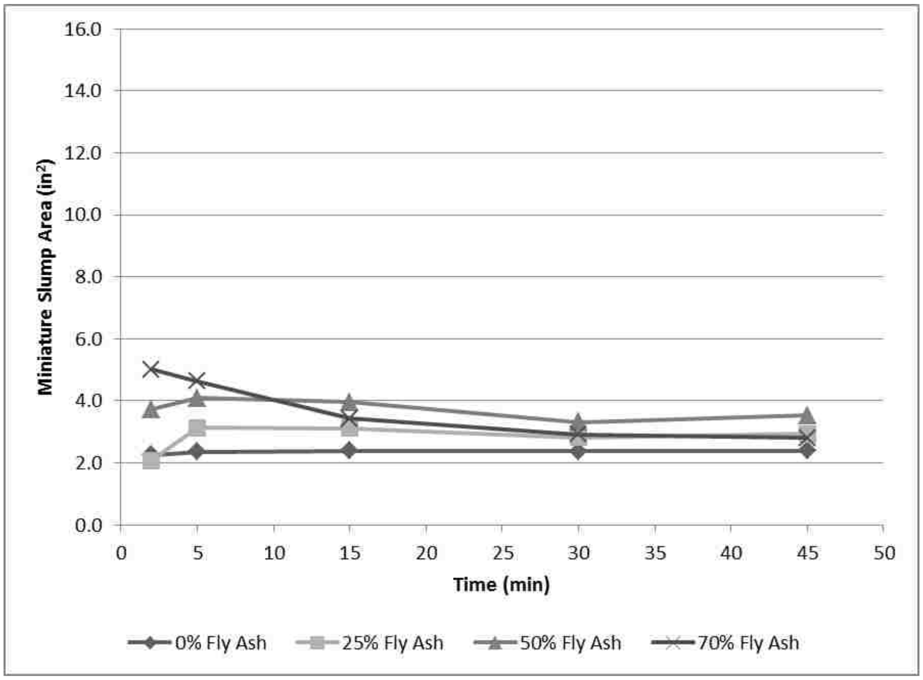

Figure E.11. Miniature Slump Plots for Combination 3-1

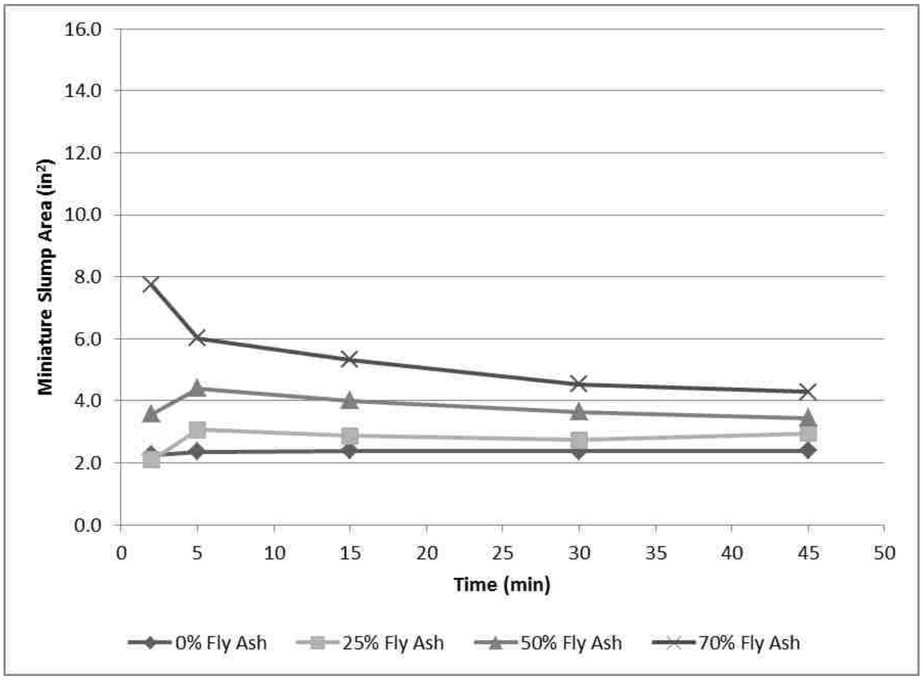

Figure E.12. Miniature Slump Plots for Combination 3-2

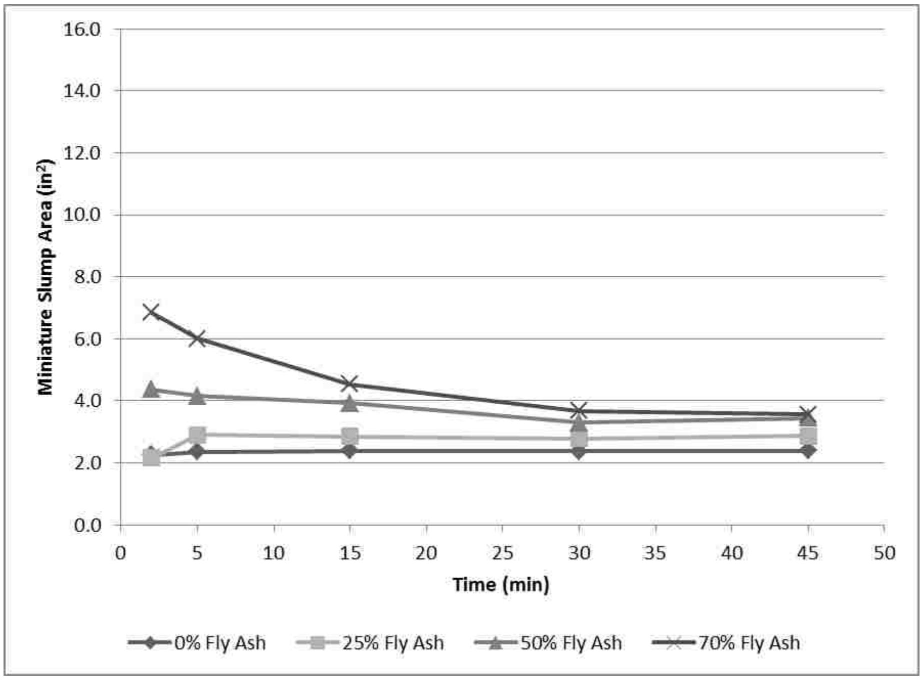

Figure E.13. Miniature Slump Plots for Combination 3-3

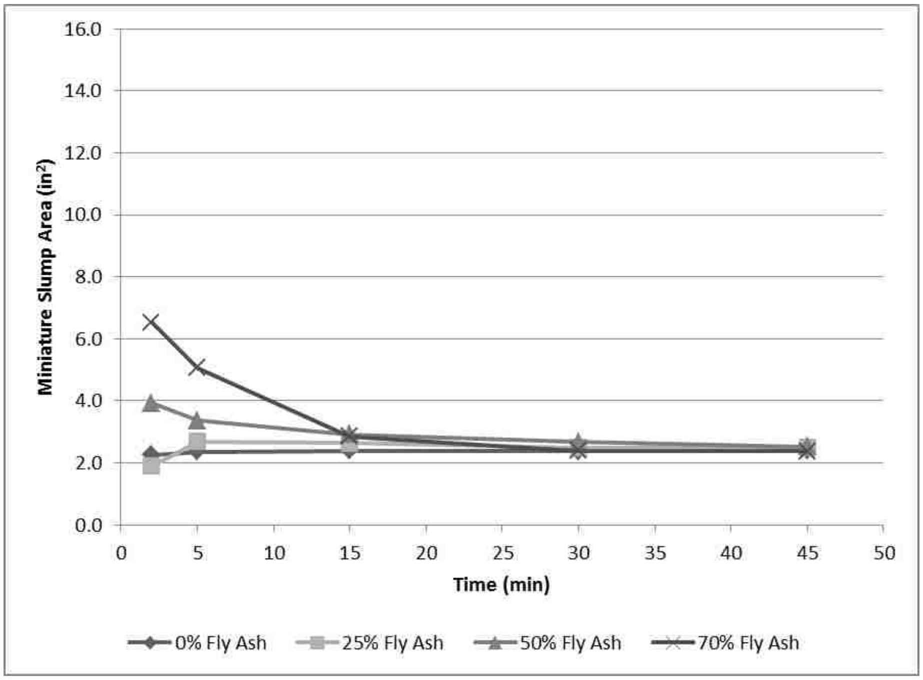

Figure E.14. Miniature Slump Plots for Combination 3-4

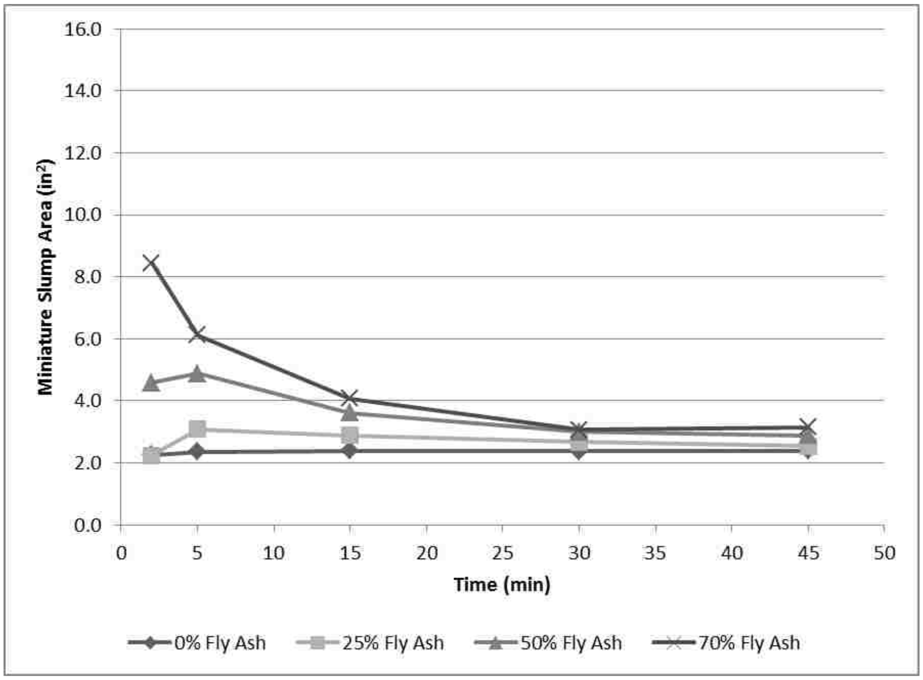

Figure E.15. Miniature Slump Plots for Combination 3-5

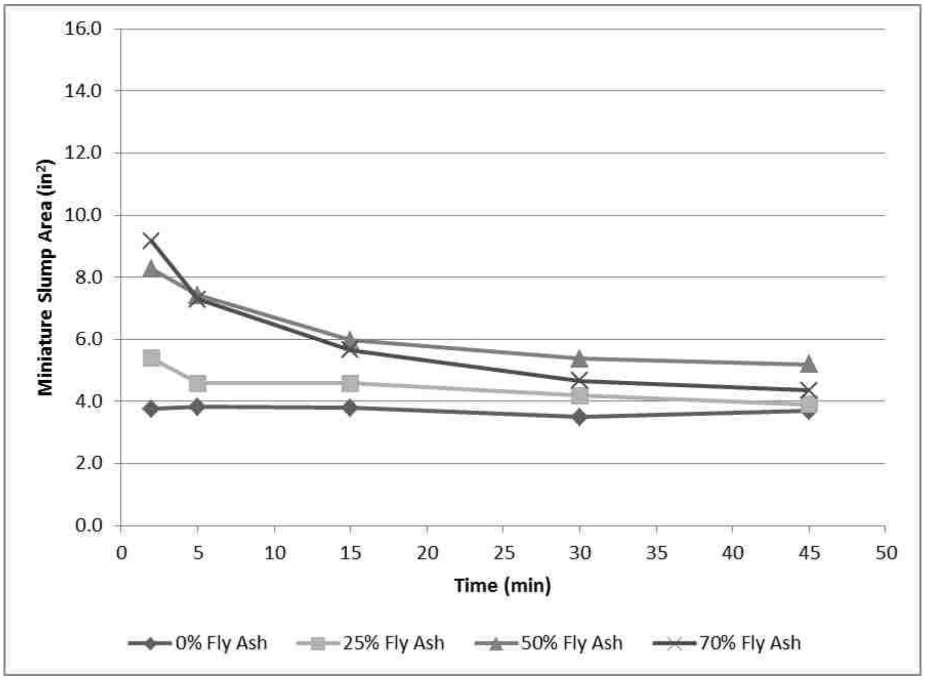

Figure E.16. Miniature Slump Plots for Combination 4-1

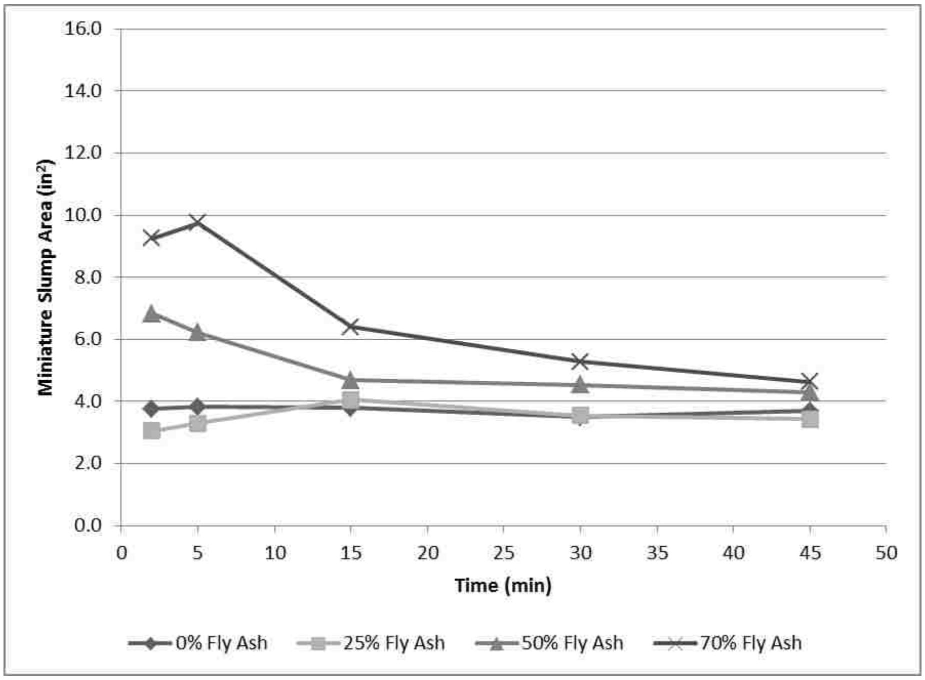

Figure E.17. Miniature Slump Plots for Combination 4-2

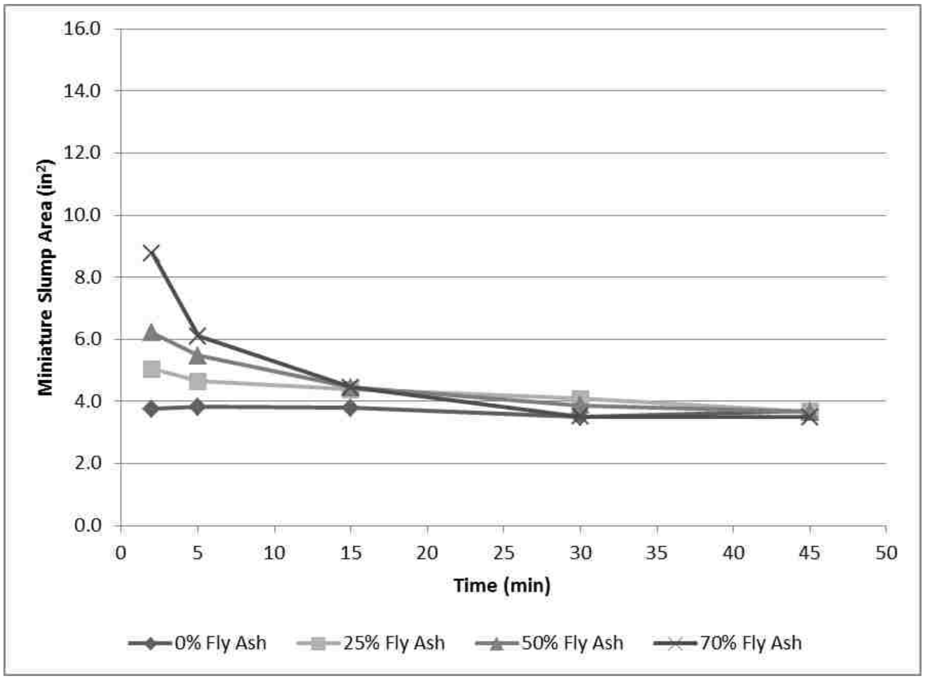

Figure E.18. Miniature Slump Plots for Combination 4-3

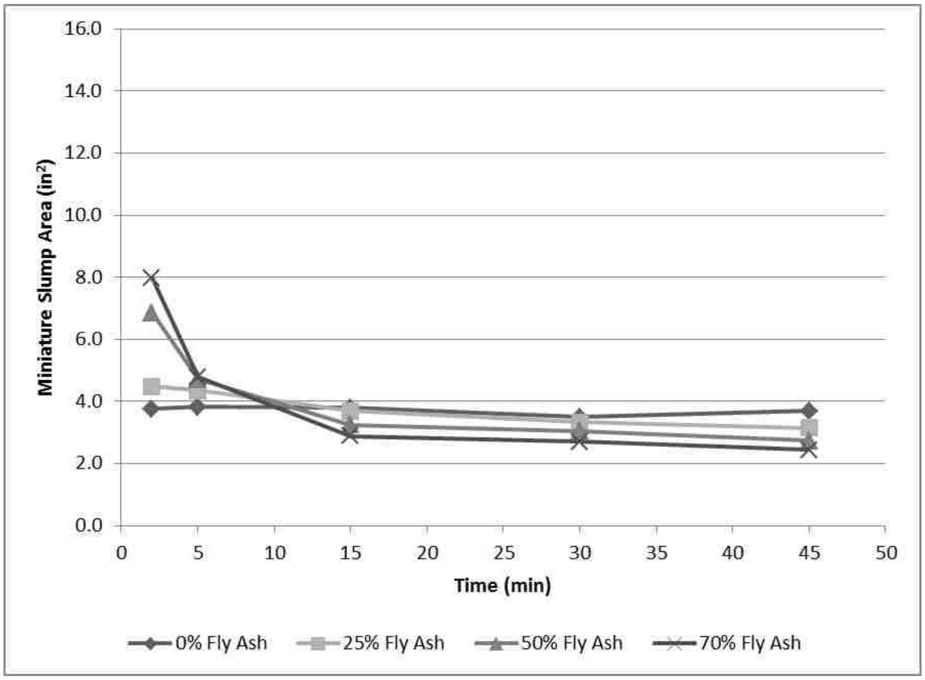

Figure E.19. Miniature Slump Plots for Combination 4-4

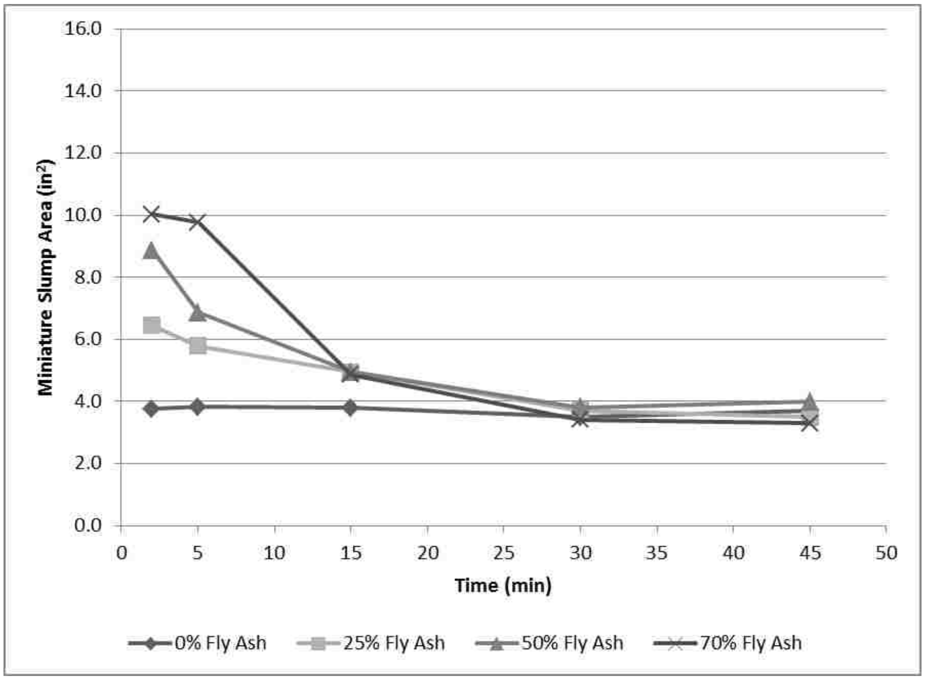

Figure E.20. Miniature Slump Plots for Combination 4-5

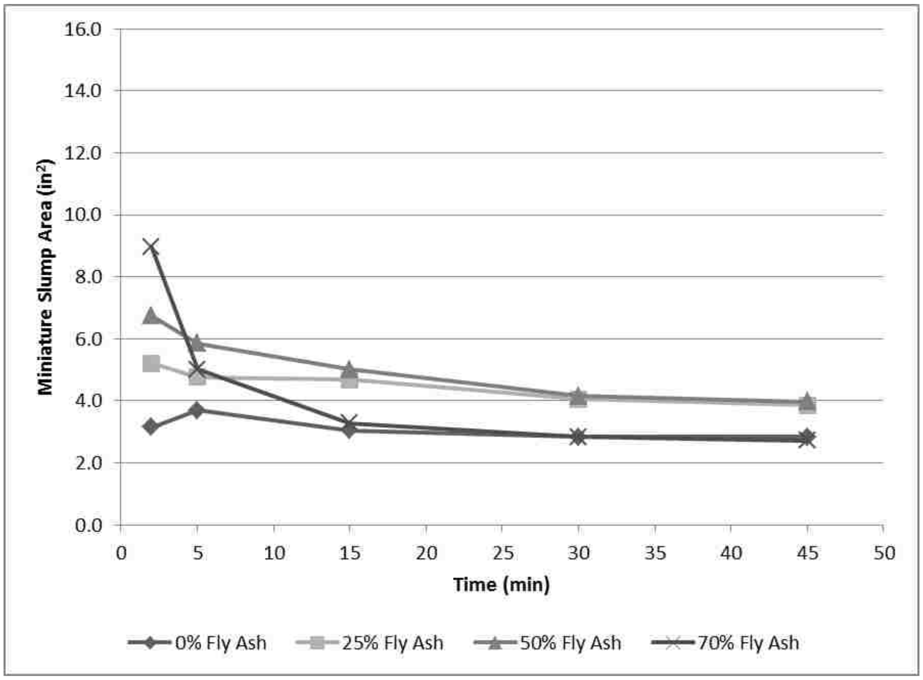

Figure E.21. Miniature Slump Plots for Combination 5-1

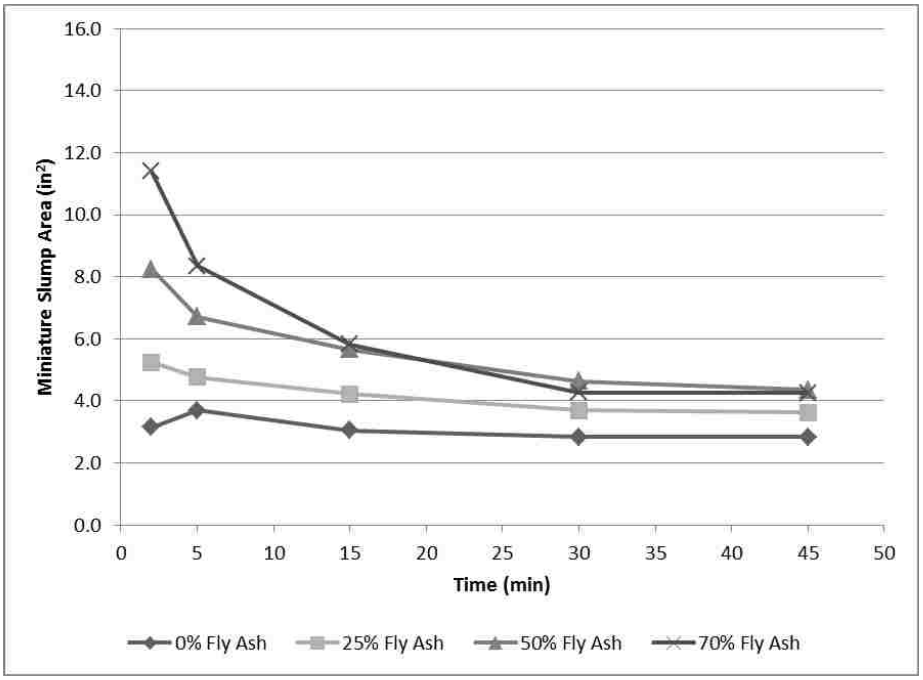

Figure E.22. Miniature Slump Plots for Combination 5-2

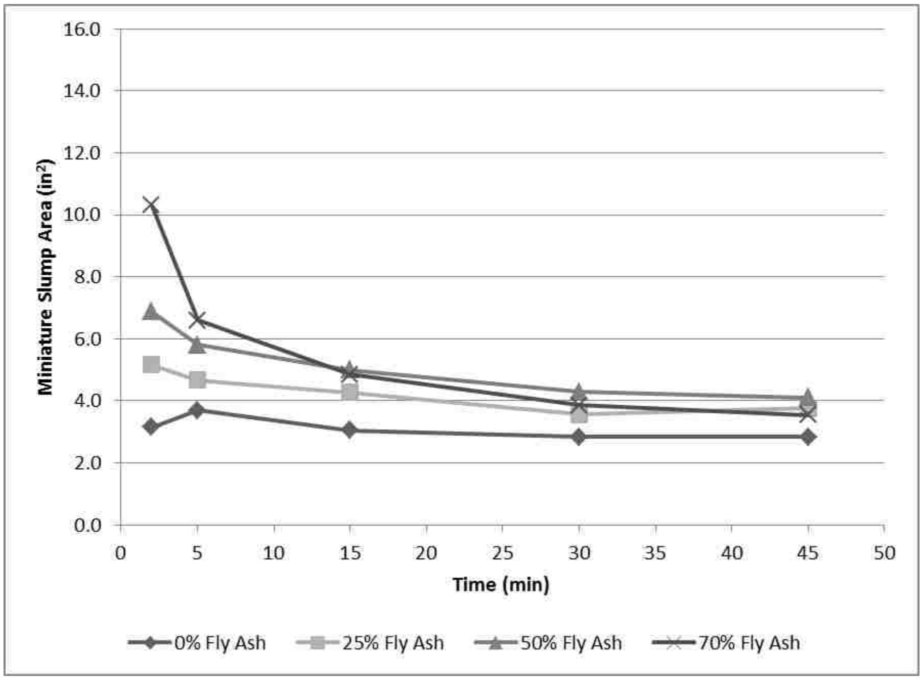

Figure E.23. Miniature Slump Plots for Combination 5-3

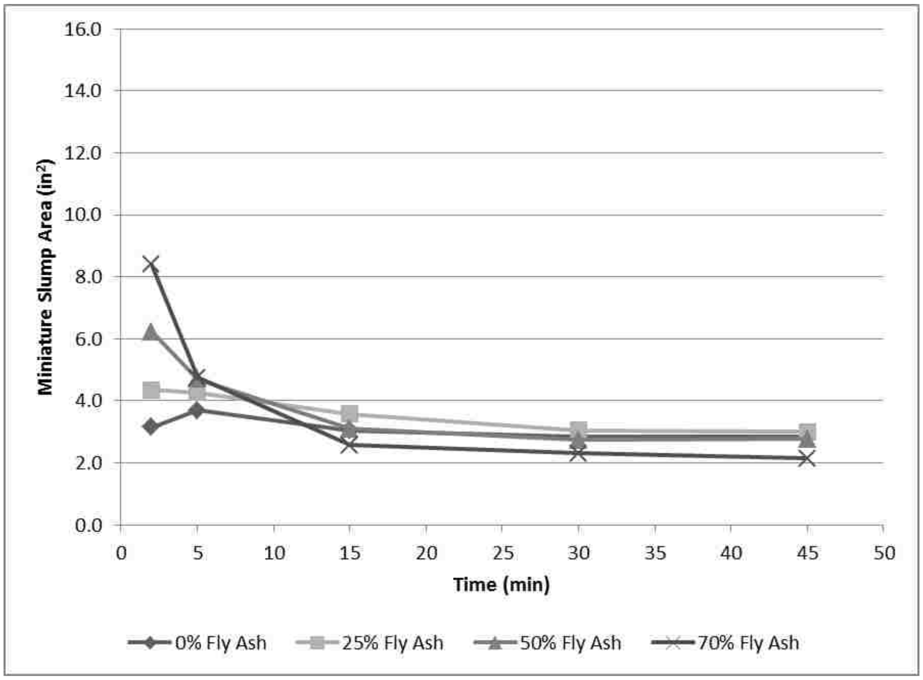

Figure E.24. Miniature Slump Plots for Combination 5-4

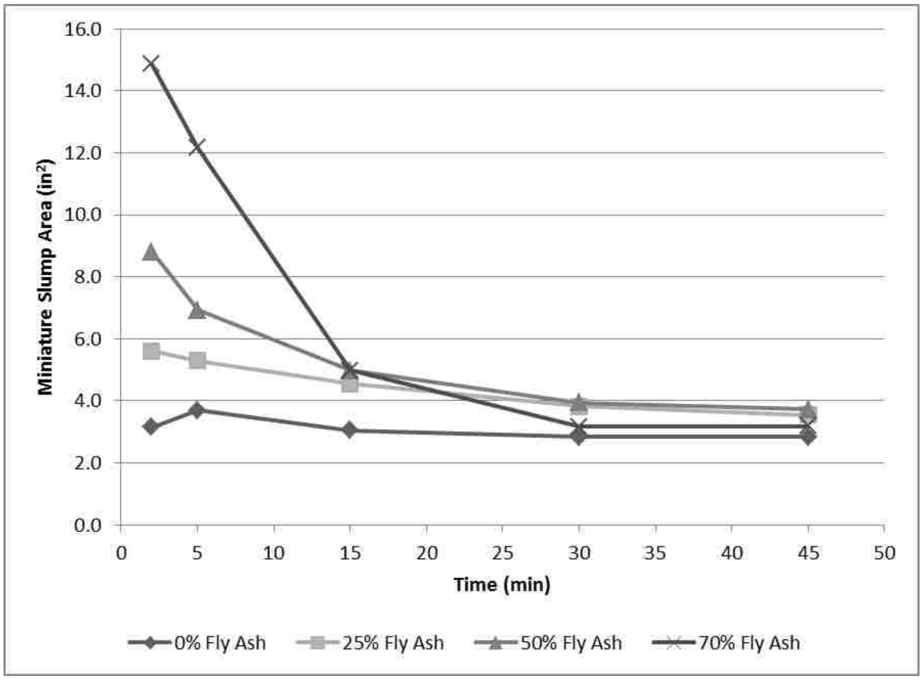

Figure E.25. Miniature Slump Plots for Combination 5-5

APPENDIX F

MAIN STUDY MINIATURE SLUMP PLOTS

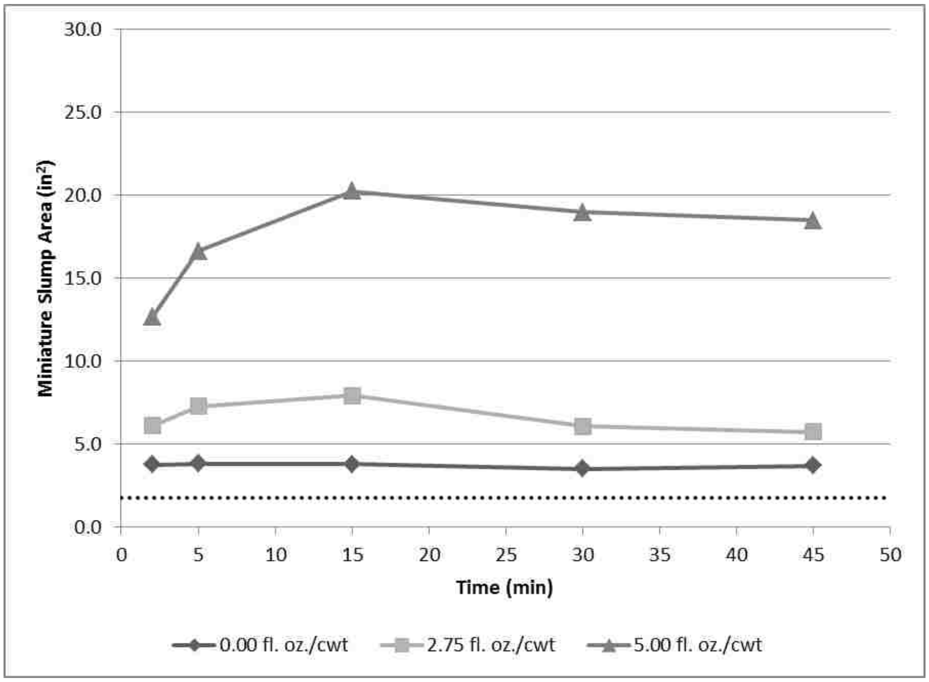

Figure F.1. Effect of Water Reducer on Combination 4-1 with 0% Fly Ash

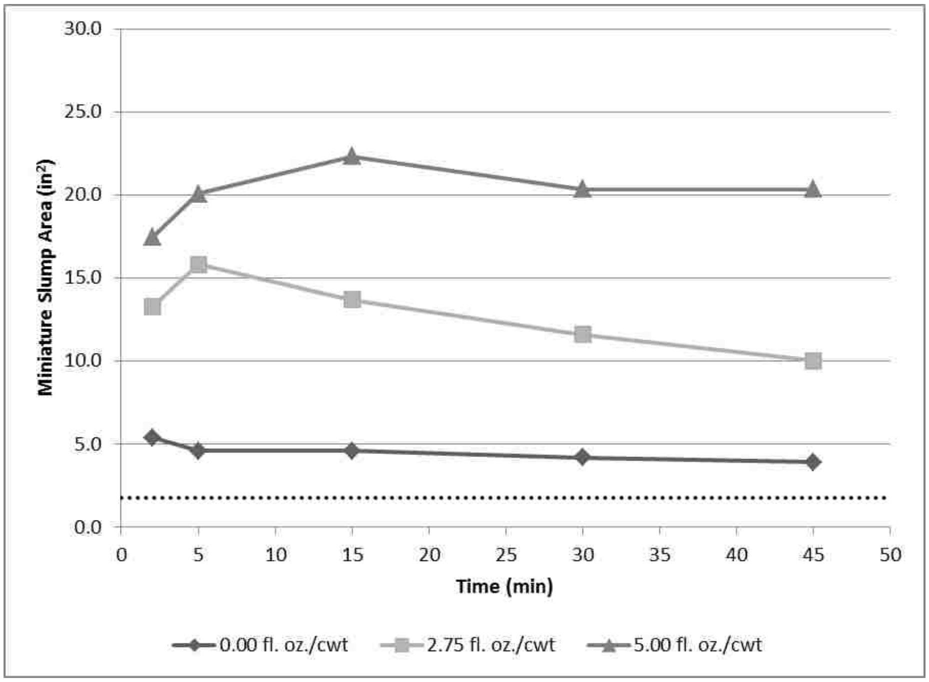

Figure F.2. Effect of Water Reducer on Combination 4-1 with 25% Fly Ash

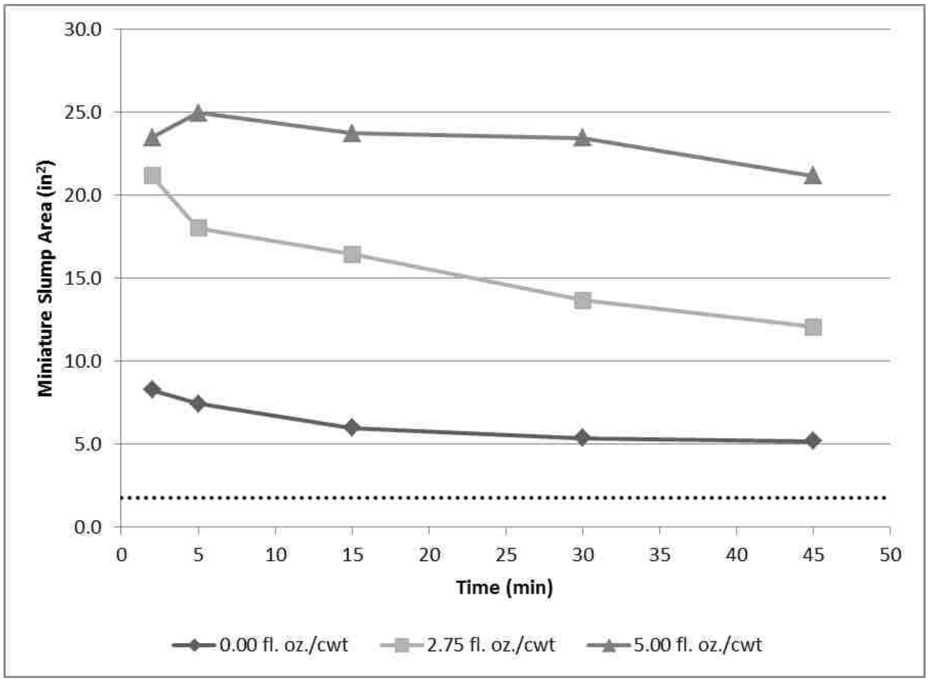

Figure F.3. Effect of Water Reducer on Combination 4-1 with 50% Fly Ash

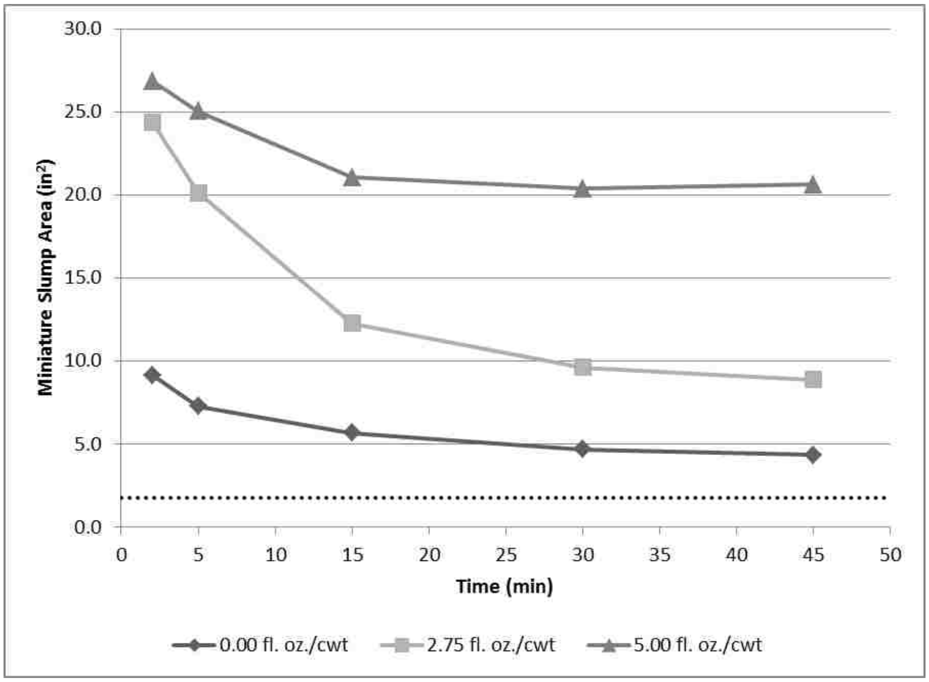

Figure F.4. Effect of Water Reducer on Combination 4-1 with 70% Fly Ash

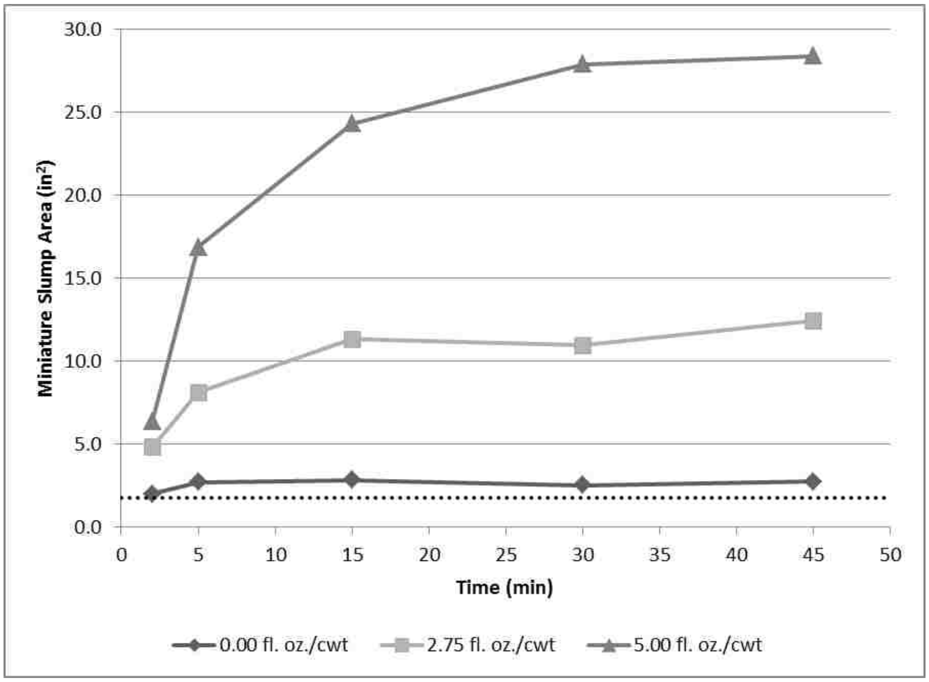

Figure F.5. Effect of Water Reducer on Combination 1-3 with 0% Fly Ash

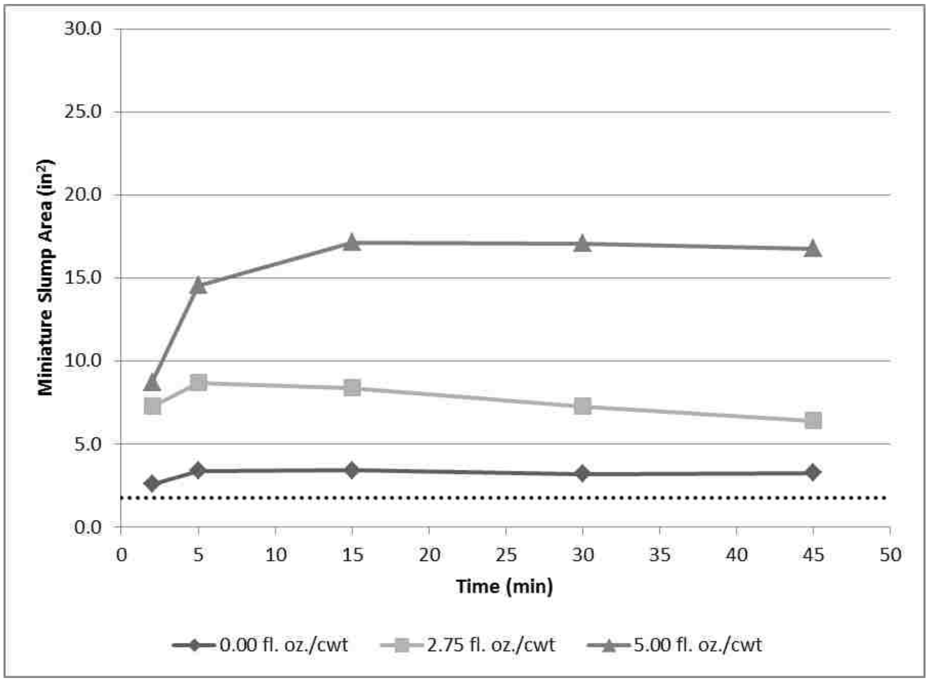

Figure F.6. Effect of Water Reducer on Combination 1-3 with 25% Fly Ash

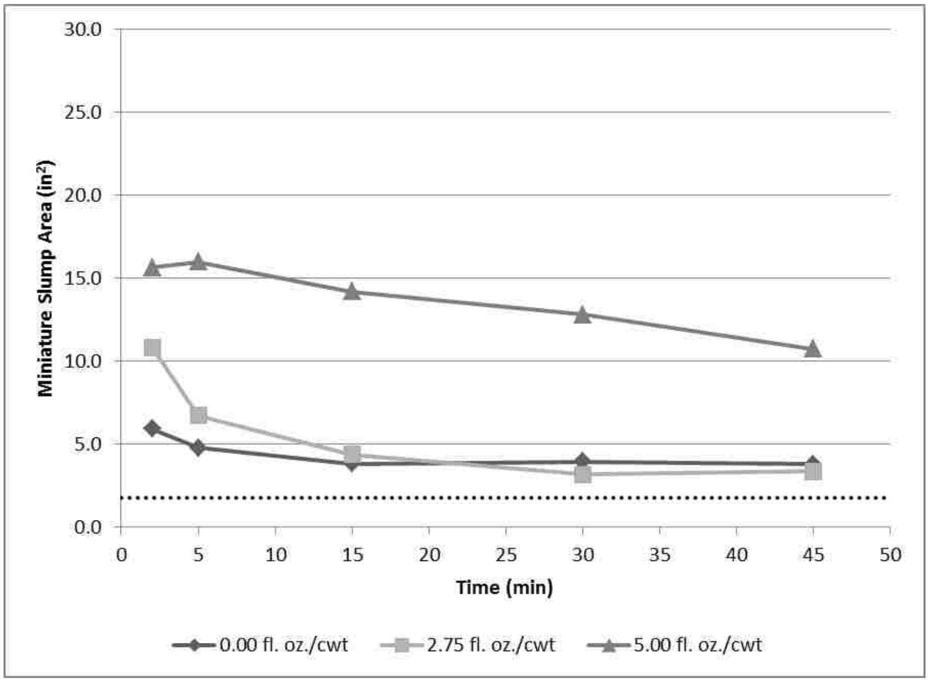

Figure F.7. Effect of Water Reducer on Combination 1-3 with 50% Fly Ash

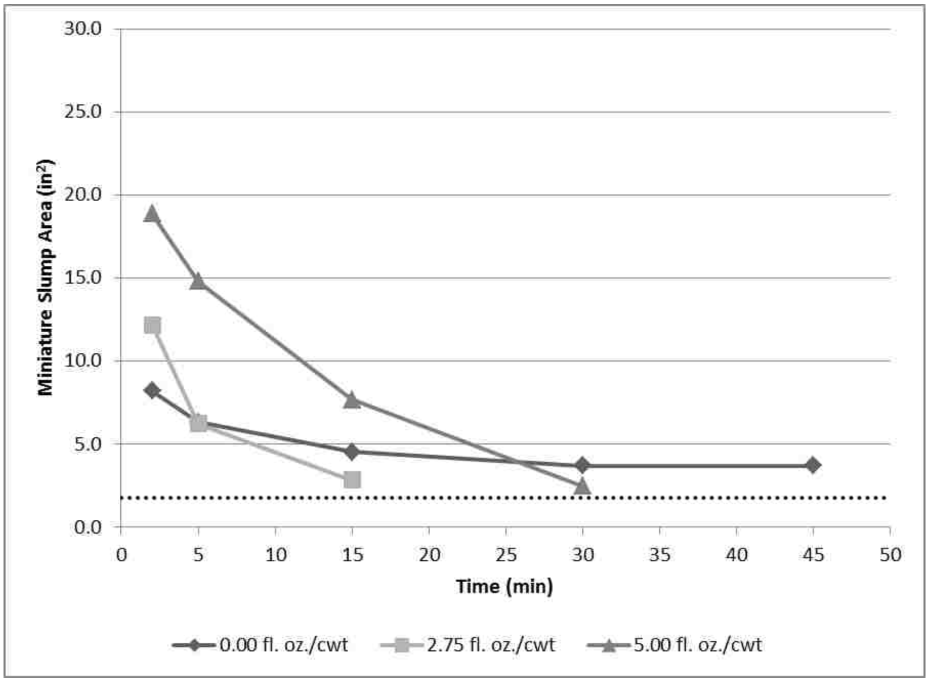

Figure F.8. Effect of Water Reducer on Combination 1-3 with 70% Fly Ash

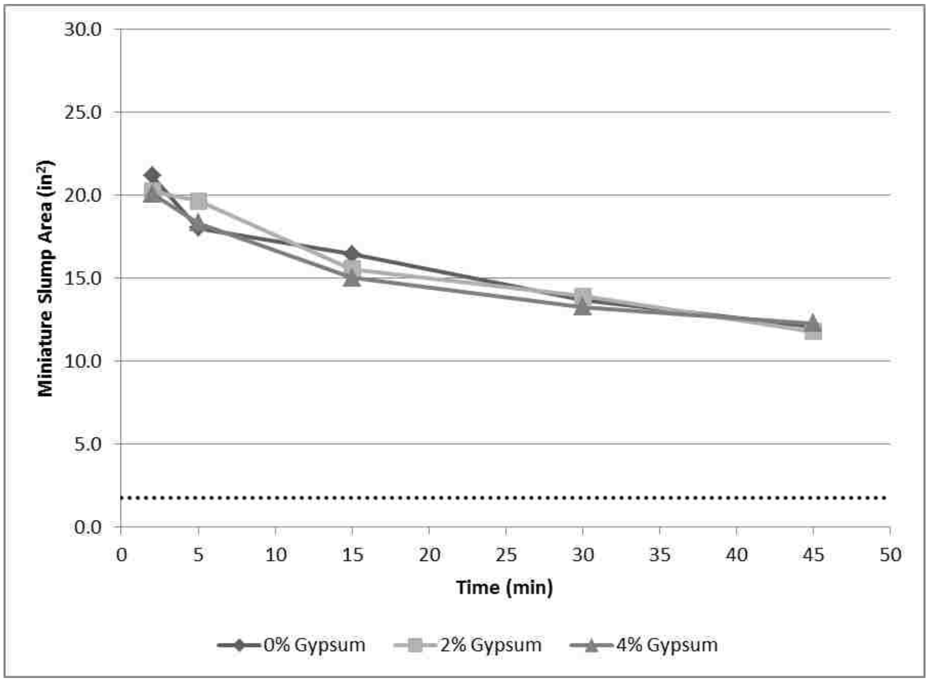

Figure F.9. Effects of Gypsum on Combination 4-1 with 50% Fly Ash and Low Dosage of Water Reducer

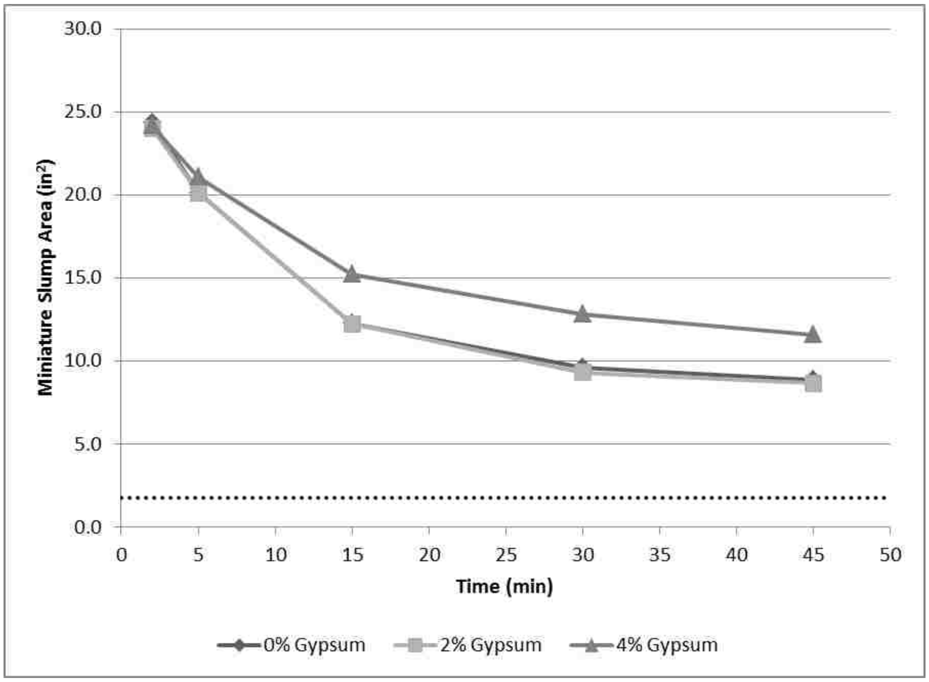

Figure F.10. Effects of Gypsum on Combination 4-1 with 70% Fly Ash and Low Dosage of Water Reducer

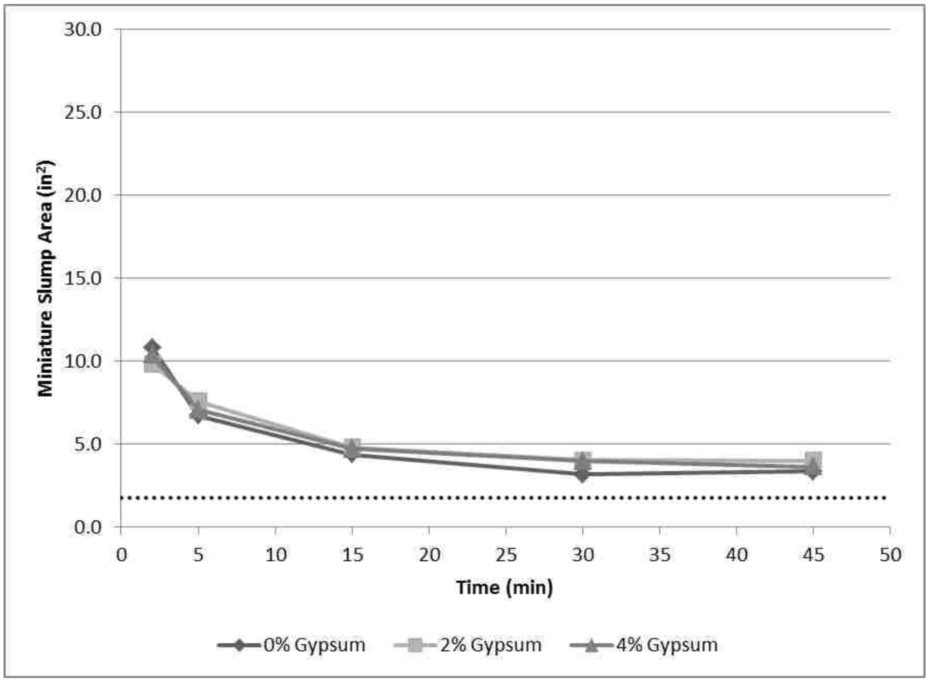

Figure F.11. Effects of Gypsum on Combination 1-3 with 50% Fly Ash and Low Dosage of Water Reducer

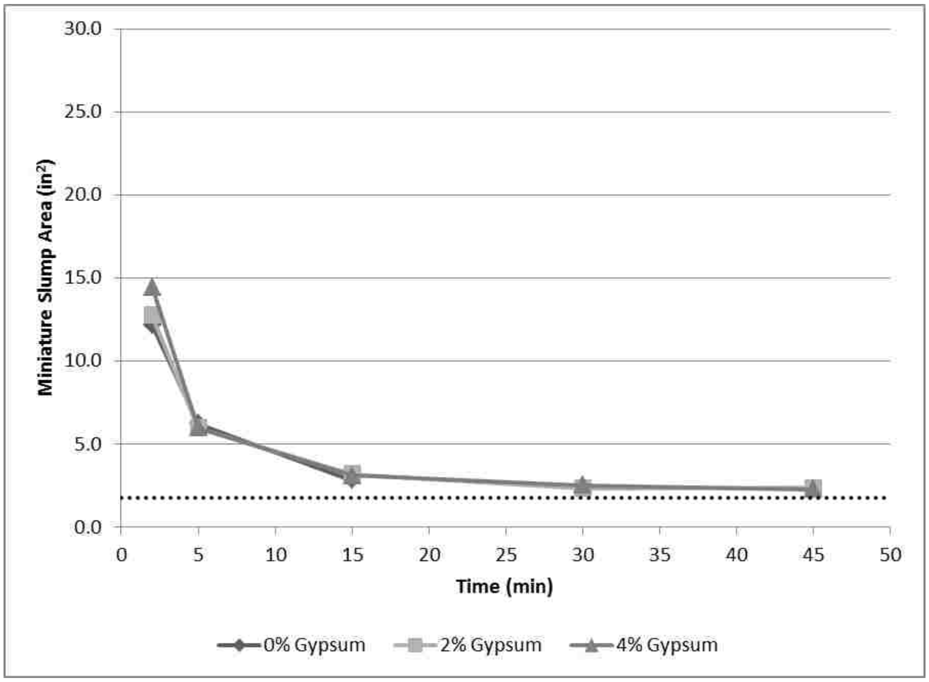

Figure F.12. Effects of Gypsum on Combination 1-3 with 70% Fly Ash and Low Dosage of Water Reducer

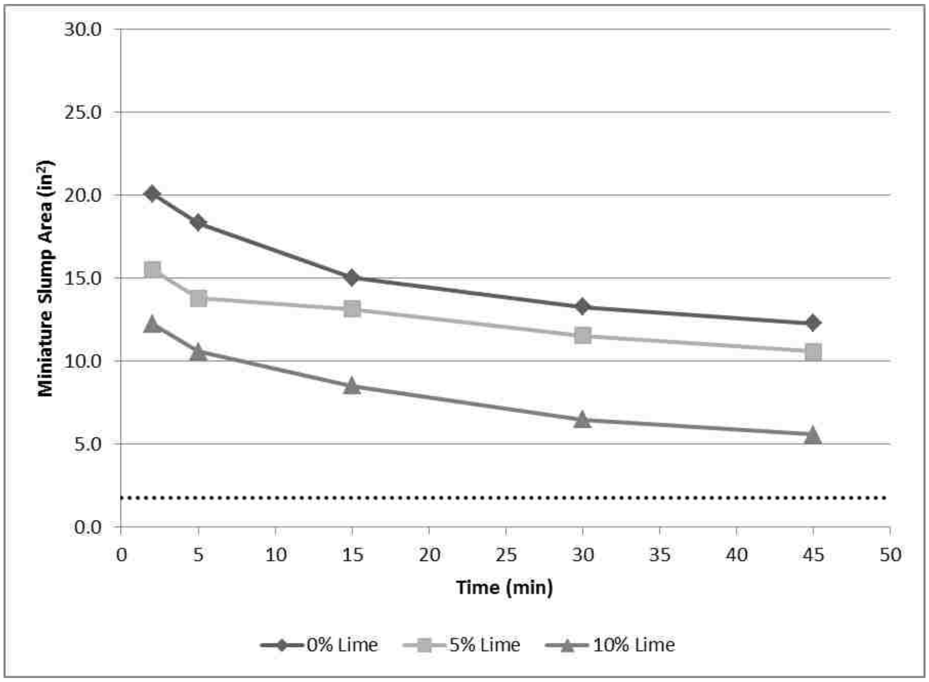

Figure F.13. Effects of Lime on Combination 4-1 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

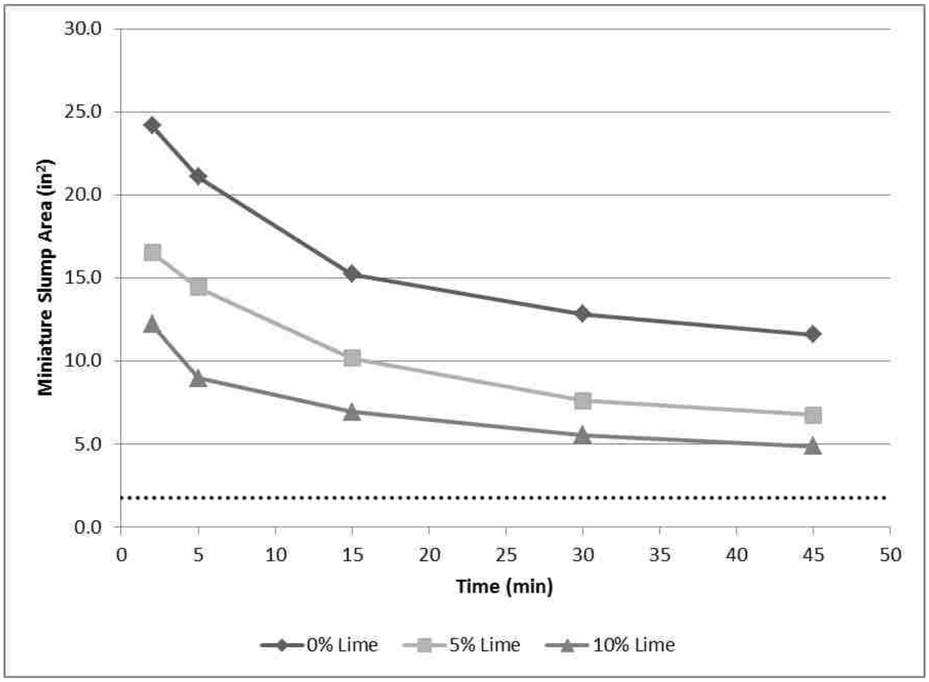

Figure F.14. Effects of Lime on Combination 4-1 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

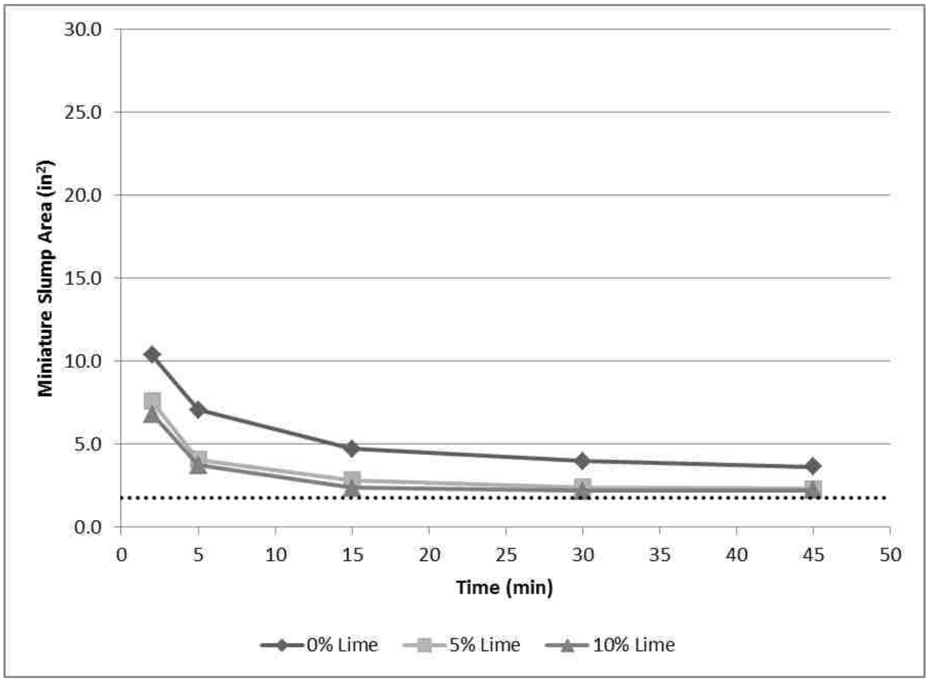

Figure F.15. Effects of Lime on Combination 1-3 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

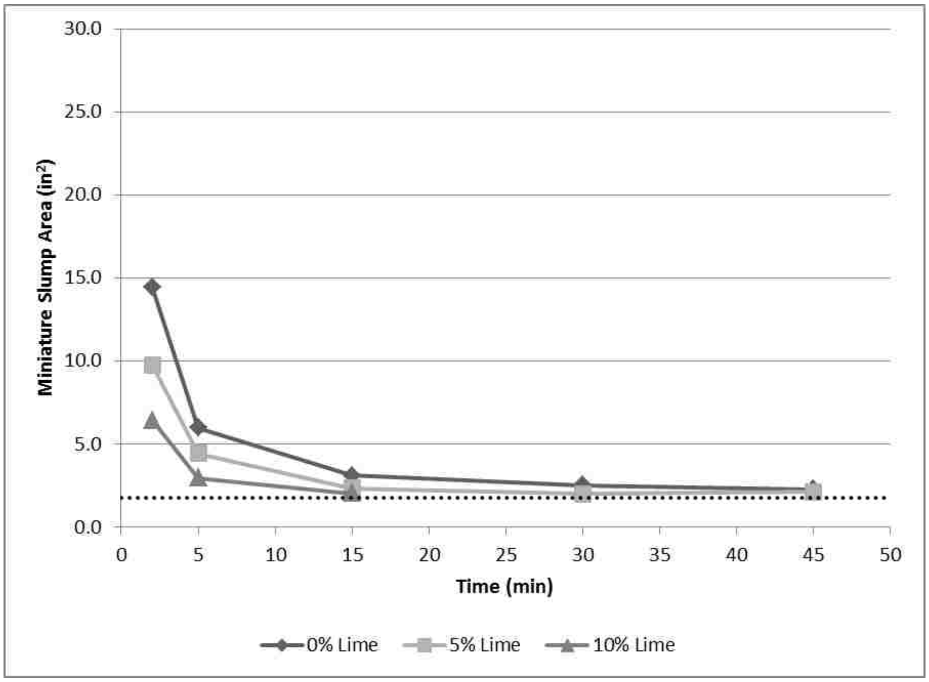

Figure F.16. Effects of Lime on Combination 1-3 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

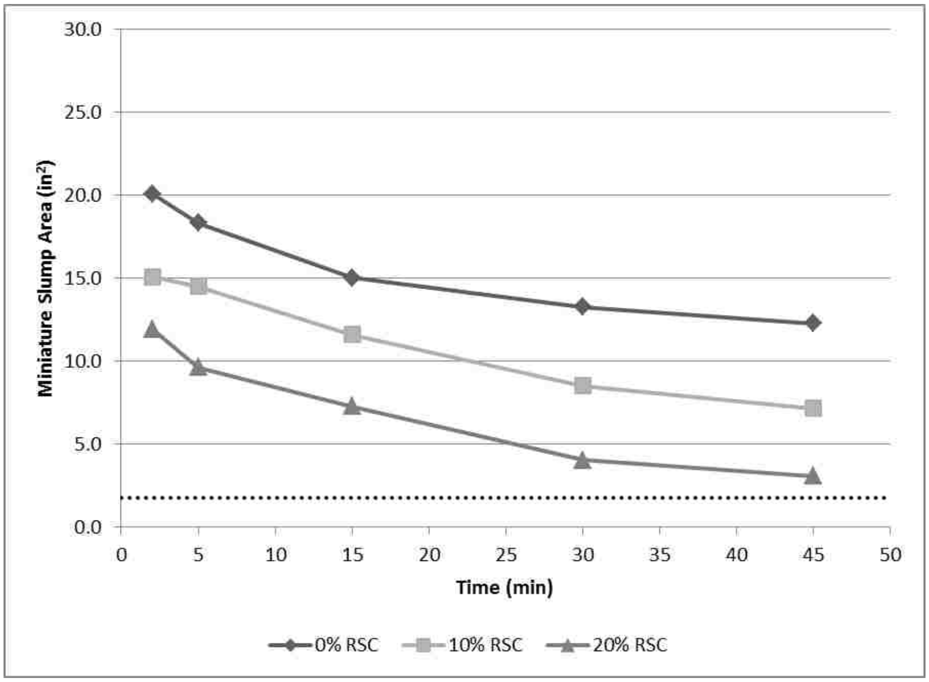

Figure F.17. Effects of Rapid Set Cement on Combination 4-1 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

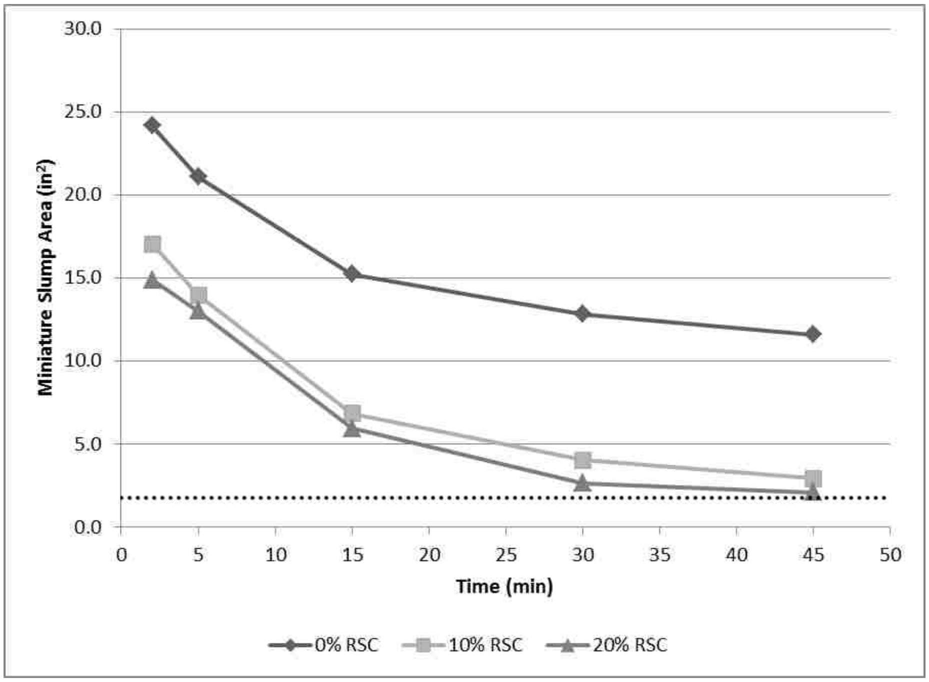

Figure F.18. Effects of Rapid Set Cement on Combination 4-1 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

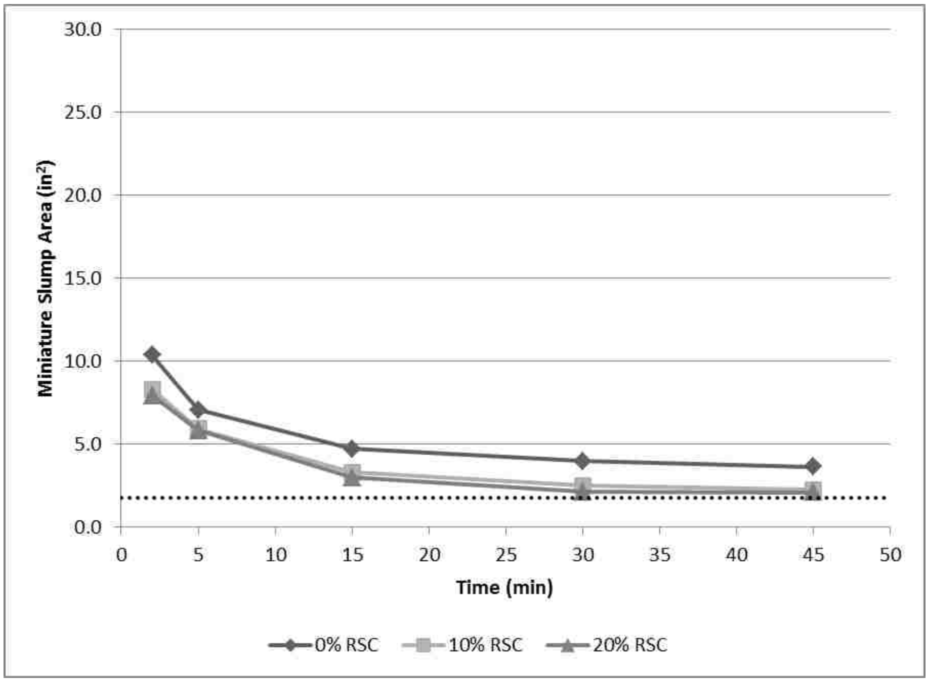

Figure F.19. Effects of Rapid Set Cement on Combination 1-3 with 50% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

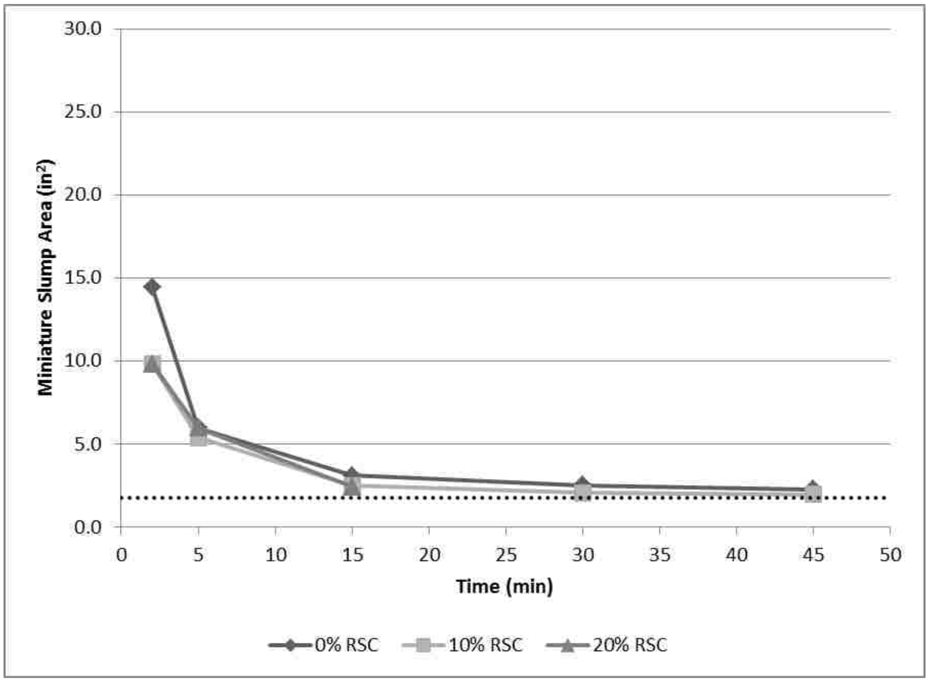

Figure F.20. Effects of Rapid Set Cement on Combination 1-3 with 70% Fly Ash, 4% Gypsum, and Low Dosage of Water Reducer

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VITA

Karl Wehking Beckemeier was born in North Kansas City, Missouri on April 27, 1987, to Kurt and Cynthia Beckemeier. He has one brother, Eric Beckemeier. Karl was raised in Hardin, Missouri and attended school in Norborne, Missouri, where he graduated in 2005. He then attended the Missouri University of Science and Technology and earned his Bachelors of Science degrees in Architectural Engineering and Civil Engineering. In December of 2012, he earned his Masters of Science degree in Civil Engineering from the Missouri University of Science and Technology.

While attending the Missouri University of Science and Technology, Karl was a member of Chi Epsilon, a civil engineering honor society, and Phi Kappa Phi, an honor society. He also was a Graduate Teaching Assistant for a construction materials course for four semesters, worked as a Research Assistant during his undergraduate and graduate studies, and held three summer internships with the Missouri Department of Transportation.

In June of 2010, Karl married Nickol Marie Enss. At the time of this writing, they reside in Louisville, Kentucky, where Karl is employed as a quality control engineer for a company that handles coal combustion products.