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**LABORATORY AND FIELD EVALUATIONS OF
EXTERNAL SULFATE ATTACK**

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**LABORATORY AND FIELD EVALUATIONS OF
EXTERNAL SULFATE ATTACK**

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LABORATORY AND FIELD EVALUATIONS OF EXTERNAL SULFATE ATTACK

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External sulfate attack is a complex process that can result in concrete structures deteriorating prematurely. This dissertation describes a comprehensive evaluation of factors influencing external sulfate attack and includes both laboratory and field investigations. Significant emphasis was placed on evaluating the sulfate resistance of mortar and concrete containing high-calcium fly ash (Class C fly ash as per ASTM C 618). This investigation showed that these fly ashes generally reduced the sulfate resistance of mortar and concrete, but that sulfate resistance was possible through the incorporation of other supplementary cementing materials (silica fume and ultra fine fly ash) into these mixtures. Another key area of emphasis in this project was the correlation between accelerated laboratory tests and outdoor exposure site performance. The behavior of concrete exposed to various sulfate salts (sodium, magnesium, and calcium) was evaluated, both in static immersion tests and in outdoor sulfate trenches. It was found that the distress outdoors was exacerbated by physical sulfate attack, especially when concrete was exposed to sodium sulfate. It was found that lowering the water-to-cementitious ratio (w/cm) and incorporating appropriate dosages of suitable

supplementary cementing materials improved resistance to both chemical and physical forms of sulfate attack. Lastly, a comprehensive study of bridges throughout Texas discovered concrete structures suffering from possible external sulfate attack. The use of analytical techniques such as x-ray diffraction (XRD) and scanning electron microscopy (SEM) were used throughout the study to determine the presence of hydration products that may form with mortars and concrete specimens. Findings from this research will be implemented in specifications in Texas for the use of Class C fly ash use in concrete in areas that may have sulfate soils and groundwater.

Table of Contents

List of Tables	x
List of Figures.....	xii
Chapter 1. Introduction.....	1
1.1 Background.....	1
1.2 Research objectives.....	2
1.3 Outline of Dissertation.....	5
Chapter 2. Literature Review.....	7
2.1 Internal sulfate attack.....	7
2.2 Thaumasite attack	11
2.3 External sulfate attack.....	12
2.3.1 Types of sulfates	12
2.3.1.1 <i>Calcium sulfate</i>	13
2.3.1.2 <i>Sodium sulfate</i>	13
2.3.1.3 <i>Magnesium sulfate</i>	15
2.4 Physical sulfate attack.....	15
2.5 Preventing sulfate attack.....	19
2.5.1 Internal sulfate attack.....	19
2.5.2 Thaumasite formation	19
2.5.3 External sulfate attack.....	19
2.5.3.1 <i>Permeability</i>	20
2.5.3.2 <i>Sulfate-resistant cements</i>	20
2.5.3.3 <i>Supplementary cementing materials</i>	21
2.5.4 Physical sulfate attack.....	25
2.6 Characterization of sulfate exposure conditions	25
2.6.1 Water samples	26
2.6.2 Soil samples	26
2.7 Structures suffering from sulfate attack.....	28
2.8 Test methods and specifications	28
2.9 Research needs.....	31
Chapter 3. Evaluation of the Sulfate Resistance of Mortars Containing High-Calcium Fly Ashes.....	32
3.1 Introduction.....	32
3.1.1 Research significance.....	32
3.2 Experimental methods	33
3.2.1 Materials	33
3.2.2 ASTM C 1012 test procedure	35
3.2.3 X-ray diffraction	36
3.2.4 Scanning electron microscopy.....	37
3.3 Experimental results and discussion	38
3.3.1 Expansion limits.....	38
3.3.2 Evaluation of Class C fly ash.....	40

3.3.2.1 Expansions	40
3.3.1.2 X-Ray diffraction.....	49
3.3.1.3 Scanning electron microscopy	51
3.3.2 Ternary blends	59
3.3.2.2 X-Ray diffraction.....	62
3.3.2.3 Scanning electron microscopy	64
3.3.3 Fly ash investigation	65
3.4 Summary	67
Chapter 4. Evaluation of Concrete Prisms in Various Sulfate Solutions including Outdoor Exposure Site Testing	70
4.1 Introduction.....	70
4.2 Experimental methods	71
4.2.1 Materials	71
4.2.1.1 Aggregates	71
4.2.1.2 Cement	71
4.2.1.3 Supplementary cementing materials	72
4.2.2 Outdoor sulfate exposure site design and test procedure.....	72
4.2.2.1 Exposure site design	73
4.2.2.2 Concrete prism testing regime	75
4.2.3 Mortar bar testing using ASTM C 1012	78
4.2.4 Sulfate profiling	78
4.2.5 Physical sulfate attack testing	80
4.4 Results and discussion	81
4.4.1 Calcium sulfate	82
4.4.1.1 Cement composition and w/cm	82
4.4.1.2 Supplementary cementing materials	87
4.4.1.3 Mortar and concrete comparisons.....	91
4.4.2 Sodium sulfate	93
4.4.2.1 Cement composition and w/cm	93
4.4.2.3 Supplementary cementing materials	100
4.4.3.1 Comparison of mortar to concrete.....	109
4.4.3 Magnesium sulfate	111
4.4.3.1 Cement composition and w/cm	111
4.4.3.2 Supplementary cementing materials	114
4.4.3.3 Comparison between concrete and mortars	120
4.4.2.2 Physical sulfate testing	121
4.5 Discussion.....	125
4.6 Conclusions.....	128
Chapter 5. Evaluation of Concrete Structures for Potential Deterioration due to External Sulfate Attack	130
5.1 Introduction.....	130
5.2 Experimental methods	133
5.2.2 Soil samples	134
5.2.3 Concrete powder samples	135

5.2.4 Concrete cores.....	135
5.3 Results and discussion	136
5.3.1 Childress District	136
5.3.1.1 Site 5.....	137
5.3.1.2 Site 9.....	138
5.3.1.3 Site 10.....	139
5.3.1.4 Summary of Childress District findings.....	140
5.3.2 Paris District.....	141
5.3.2.1 Site 22.....	141
5.3.2.2 Site 57.....	144
5.3.2.3 Summary of Paris District findings.....	145
5.3.3 El Paso District	145
5.3.3.1 Site 3.....	146
5.3.3.2 Site 31.....	147
5.3.3.3 Site 32.....	149
5.3.3.4 Site 27.....	150
5.3.3.5 Summary of El Paso findings.....	158
5.4 Conclusions.....	159
Chapter 6: Conclusions and Future Work.....	161
6.1 Conclusions.....	161
6.2 Suggested future work	164
Appendix A: Mortar Cube Strengths for ASTM C 1012 Testing.....	167
Appendix B: ASTM C 1012 Results	171
Appendix C: Concrete Mixture Expansions and Mass Change Results.....	174
Appendix D: District and County Maps	176
References:.....	183
Vita.....	187

List of Tables

Table 2-1: Cement chemistry notations used throughout this dissertation	12
Table 2-2: Sulfate exposure classification for water-soluble sulfates in soil or	26
Table 3-1: Chemical data for the portland cements used in this study	34
Table 3-2: Chemical analysis of fly ashes tested in the study	34
Table 3-3: Chemical analysis of other SCMs tested in the study	35
Table 3-4: Expansion measurements from FA1 in ASTM C 1012 Testing	41
Table 3-5: Expansion measurements from FA2 in ASTM C 1012 Testing	42
Table 3-6: Semi-quantitative Rietveld analysis of select mortar mixtures at 18 months .	51
Table 3-7: Semi-quantitative Rietveld analysis of ternary blends with FA1 and FA2.....	63
Table 4-1: Expansion and mass change data from mixtures placed in calcium sulfate conditions	83
Table 4-2: Expansion and mass change data from mixtures with Class C fly ash placed in calcium sulfate conditions.....	88
Table 4-3: Comparison between mortar bars and concrete prisms evaluated using calcium sulfate solution in ASTM C 1012 storage conditions	92
Table 4-4: Expansion and mass change data for mixtures without SCMs, exposed to sodium sulfate solution	94
Table 4-5: Expansion and mass change data for concrete with Type I cement and Class C fly ash, exposed to sodium sulfate solution	102
Table 4-6: Expansion and mass change data for concrete with Type I/II cement and Class C fly ash, exposed to sodium sulfate solution.....	103
Table 4-7: Expansion and mass change data for concrete with Type V cement and Class C fly ash, exposed to sodium sulfate solution.....	104
Table 4-8: Expansion and mass change data for concrete with ternary SCM blends exposed to sodium sulfate solution	105
Table 4-9: Expansion and Mass Change Data for Concrete with Various Cements (Type I, II, or V) in combination with Class F fly ash and exposed to sodium sulfate solution	106
Table 4-10: Comparison between mortar bars and concrete prisms evaluated using sodium sulfate solution in ASTM C 1012 storage.....	110
Table 4-11: Expansion and mass change data for mixtures without SCMs, exposed to magnesium sulfate solution.....	112
Table 4-12: Expansion and mass change data for concrete with Type I cement and Class C fly ash, exposed to magnesium sulfate solution	115
Table 4-13: Expansion and mass change data for concrete with Type I/II cement and Class C fly ash, exposed to magnesium sulfate solution	116
Table 4-14: Expansion and mass change data for concrete with ternary SCM blends exposed to magnesium sulfate solution	118
Table 4-15: Comparison between mortar bars and concrete prisms evaluated using magnesium sulfate solution in ASTM C 1012 storage conditions	121
Table 5-1: Sulfate content of concrete powders from locations in the Childress District	140

Table 5-2: Semi-quantitative XRD Rietveld analyses from columns SO and NO in the Childress District	140
Table 5-3: Semi-quantitative Rietveld analyses taken from two sections from a culvert at Site 22	142
Table 5-4: XRD results from Site 57 in the Paris District	144
Table 5-5: Sulfate content of concrete powder taken from the riprap at site 31	148
Table 5-6: Concrete mixtures made for ROW markers in west Texas	154

List of Figures

Figure 2-1: Exposure block containing non-reactive aggregates and heat cured up to 183 °F (83 °C), showing no signs of distress after 3 years.....	9
Figure 2-2: Exposure block containing highly-reactive aggregate and heat-cured up to 183 °F (83 °C), showing signs of significant cracking after 3 years.....	10
Figure 2-3: Exposure block containing highly-reactive aggregate showing less cracking after 3 years.....	11
Figure 2-4: Solubility curve for sodium sulfate /water system (Berkeley 1904).....	17
Figure 2-5: Relationship between C ₃ A content in fly ash to 6 month expansion in ASTM C 1012 testing (Shashiprakash and Thomas 2001).....	23
Figure 2-6: The effect of ternary blends with silica fume and Class C fly ash on expansion of mortars compared to mortars using only Class C fly ash (Shashiprakash and Thomas 2001)	24
Figure 3-1: Expansions of FA1 at different replacement dosages.....	45
Figure 3-2: Expansions of FA3 at different replacement dosages.....	46
Figure 3-3: Expansion of FA8 fly ash at different replacements.....	48
Figure 3-4: Mortar mixture with 40% FA8 after 56 days in ASTM C 1012 testing	48
Figure 3-5: SEM image and EDS spectrum of 25% FA2 after 18 months storage in sodium sulfate solution showing ettringite pockets.....	53
Figure 3-6: SEM image and EDS spectrum of 20% FA1 after 18 months of storage showing gypsum formation around aggregates	54
Figure 3-7: SEM image and EDS spectrum of 20% FA1 mortar after 18 months storage in sodium sulfate showing possible conversion of gypsum into ettringite.....	55
Figure 3-8: SEM image and EDS spectrum analysis of 40% FA1 after 18 months in sodium sulfate solution ettringite and gypsum formations.....	57
Figure 3-9: SEM image and EDS spectrum analyses of 35% FA2 after 18 months of storage in sodium sulfate showing gypsum formation around aggregates	58
Figure 3-10: Mortar mixtures with 20% FA1 and ternary blends	60
Figure 3-11: Mortar mixtures with 40% FA1 and ternary blends	61
Figure 3-12: SEM image and EDS spectrum of 40% FA1 with 5% SF after 18 months of storage in sodium sulfate storage showing a gypsum band along the sample edge and around aggregates	65
Figure 3-13: Quantitative XRD Rietveld analyses for FA1, FA2, and FA8.....	66
Figure 4-1: Outdoor sulfate exposure site located in Austin, TX. From left to right, the trenches contain calcium sulfate, sodium sulfate and magnesium sulfate.....	73
Figure 4-2: The placement of prisms from each mixture into the outdoor exposure site or in the modified ASTM C 1012 testing.....	76
Figure 4-3: Placement of prisms in each outdoor exposure trench. The units are in inches.	77
Figure 4-4: Prisms were cut into 3 in (75mm) cubes to allow for milling for sulfates. Slices were also removed for SEM analysis.....	79
Figure 4-5: Temperature Cycle for mortars subjected to physical sulfate attack.....	80
Figure 4-6: Mixture designations used throughout this chapter.....	82

Figure 4-7: Concrete prism with a 0.4 w/cm placed vertically in the outdoor calcium sulfate exposure site. In this photograph, the left side shows the portion of the prism that was below the soil level.	84
Figure 4-8: Semi-quantitative Rietveld analysis showing differences in cement types for prisms at 0.4 w/cm, placed indoors in calcium sulfate.	86
Figure 4-9: Quantitative analysis showing differences in cement types for prisms at 0.7 w/cm placed indoors in calcium sulfate.	87
Figure 4-10: Semi-quantitative XRD analysis of profiled prisms containing Class C fly ash at a 0.4 w/cm.	90
Figure 4-11: Quantitative XRD analysis of profiled prisms containing Class C fly ash at a 0.4 w/cm to determine phase content at different milled depths	91
Figure 4-12: C1-7 prism submerged in the outdoor sodium sulfate exposure site after 18 months.	96
Figure 4-13: Mixture C5-7 after 18 months of outdoor exposure to sodium sulfate. This prism was placed vertically, with the section on the left fully submerged below sulfate-saturated soil.	97
Figure 4-14: Semi-quantitative XRD Rietveld analyses of concrete prisms at 0.4 w/cm, placed indoors in sodium sulfate solutions after 18 months	98
Figure 4-15: Semi-quantitative XRD Rietveld analysis of concrete prisms at 0.7 w/cm, placed indoors in sodium sulfate solutions after 18 months	99
Figure 4-16: Semi-quantitative XRD analysis from mixtures containing sulfate resistant cement at in the outdoor sulfate exposure site	100
Figure 4-17: Semi-quantitative XRD Analysis of Concrete prisms at 0.4 w/cm placed in sodium sulfate solutions for 18 months	108
Figure 4-18: Quantitative XRD analysis of prisms at 0.7 w/cm placed tested indoors in sodium sulfate solutions.	109
Figure 4-19: Semi-quantitative XRD analysis of concrete prisms at 0.4 w/cm placed in indoor magnesium sulfate conditions	113
Figure 4-20: Semi-quantitative XRD Rietveld analysis of prisms placed in magnesium sulfate conditions	114
Figure 4-21: Semi-quantitative XRD Rietveld analysis of prisms containing SCMs in indoor magnesium sulfate conditions	119
Figure 4-22: Semi-quantitative XRD Rietveld analysis of prisms with SCMs placed indoors in magnesium sulfate solution	120
Figure 4-23: Physical sulfate testing of non-air-entrained mortars containing Type V cement (w/cm=0.7)	123
Figure 4-24: Physical sulfate testing of air-entrained and non-air-entrained mortars (w/cm=0,7) immersed in 30% sodium sulfate solution and subjected to temperature changes.	124
Figure 4-25: Mortar specimens before and after physical sulfate testing. The mixture contained Type V cement at 0.7w/cm. The disk on the left was prior to testing and the disk on the right went through 150 cycles.	125
Figure 5-1: Site locations discussed within this chapter	132
Figure 5-2: Calibration curve for sulfate using the turbidimeter	134

Figure 5-3: Damage to the lower part of a wall below US 83 in Childress District.....	138
Figure 5-4: Damage to a bridge column on FM 2278, south of Childress, Texas.....	139
Figure 5-5: Deterioration commonly found in culverts in the Paris District. The distress begins near the base of the culvert and continues up the side, likely in line with the highest level of water.	143
Figure 5-6: Deterioration of a culvert above the soil level, with no deterioration visible below the level of the soil (after excavation).....	143
Figure 5-7: Deteriorated concrete columns from a bridge in the Paris District.....	144
Figure 5-8: Riprap deterioration occurring on the embankment below a bridge.....	147
Figure 5-9: Riprap deterioration at Site 31 in the El Paso District	148
Figure 5-10: Deteriorated riprap at Site 32 located on FM 652 in the El Paso District..	149
Figure 5-11: ROW marker deteriorating in west Texas.....	151
Figure 5-12: Location of the removed and replaced ROW markers along SH 54 north of Van Horn, Texas	153
Figure 5-13: Placement of new ROW marker in the existing location of the deteriorated ROW marker	154
Figure 5-14: The sulfate content of soils taken from each of the ROW locations using ASTM C 1580 and TEX-135-E Test Methods	155
Figure 5-15: Semi-quantitative XRD Rietveld analyses from ROW markers in the El Paso District.....	156
Figure 5-16: New ROW marker with Class C fly ash at 0.4 w/cm after 3 months of exposure in gypsiferous soils	158

Chapter 1. Introduction

1.1 Background

Sulfate attack is a complex form of deterioration that has damaged concrete structures throughout the world. Sulfate attack is particularly complex because the source of sulfates can be external or internal (delayed ettringite formation), and the distress can be chemical in nature, due to alteration of hydration of products, or physical in nature, due to phase changes in the penetrating sulfate solution. This dissertation focuses exclusively on external sulfate attack, but includes both chemical and physical manifestations of this form of attack.

The research described herein was funded by the Texas Department of Transportation (TxDOT) under TxDOT Project 4889, “Sulfate Resistance of Concrete Exposed to External Sulfate Attack” and was initiated as a joint research project between the University of Texas at Austin and the University of New Brunswick. The project was initiated in September 2004 and will be completed in August 2009. A summary of research performed at both universities will be integrated into the final project report to be submitted to The Texas Department of Transportation (TxDOT) in 2009. The remainder of this chapter provides a brief summary of the project objectives and describes how the remaining chapters are organized and presented.

1.2 Research objectives

Although sulfate attack has been recognized as a cause of concrete distress for many years, it remains a controversial, confusing, and complex topic. There are many unresolved issues, far too many to be tackled in a single investigation. The research described in this dissertation aims to address several of these lingering issues, especially those that are particularly relevant to the state of Texas. The key technical issues that were evaluated include:

- **Sulfate resistance of concrete containing ASTM C 618 Class C fly ash.**

This is particularly an issue in Texas, where Class C fly ash is widely available, and in some parts of the state (e.g., Lubbock), it is the only type of fly ash available. Research is needed to determine the impact of fly ash chemistry and mineralogy on sulfate resistance and to identify the mechanisms responsible for the poor sulfate resistance exhibited by certain Class C fly ashes. Lastly, and perhaps most importantly from a practical point of view, research is needed to identify methods by which concrete containing Class C fly ash can be made sulfate-resistant (i.e., incorporation of silica fume or ultra-fine fly ash in ternary systems).

- **Sulfate resistance of concrete exposed to gypsiferous soils.** There is much debate today regarding the potential for deterioration of concrete exposed to gypsiferous or gypsum-bearing soils. Because gypsum (calcium sulfate) is much less soluble than other common forms of sulfate, such as sodium sulfate and magnesium sulfate, it has been suggested that there is less potential for sulfate-induced distress (Rebel et al. 2005). This

uncertainty related to this solubility-related issue is compounded by the fact that the vast majority of laboratory studies have used more aggressive sulfate solutions, primarily sodium sulfate, and as such, there is a general lack of information on how damaging gypsum can be to concrete. Given that gypsum is by far the most common form of sulfate in soils and groundwater in Texas, this is obviously a critical issue and a key focus of this study.

- **Determination of severity of exposure.** The general approach recommended by the American Concrete Institute (ACI 2001), as well as other agencies, to preventing sulfate attack starts with defining the severity of exposure to which a given concrete structure will be subjected. This involves sampling either groundwater or soil from the subject site and analyzing it for sulfate content. The measured sulfate content would then be used to select an appropriate preventive measure, such as concrete mixtures with lower water/cementitious materials (w/cm) ratios, and potentially containing low-C₃A cements and/or supplementary cementing materials (SCMs). The measurement of sulfates in groundwater is quite straightforward and is not a contentious issue as one only has to measure the sulfate concentration using appropriate analytical techniques. However, when one attempts to measure the concentration of sulfates in a soil sample, the solubility of different sulfate forms becomes critical. The issue is that one must extract sulfate from the subject soil by diluting it

with water, and as such, the solubility of the sulfate contained in the soil affects the values obtained for a given extraction ratio (or water:soil ratio). There is no clear consensus on what specific extraction ratio should be used for soil analysis, with values ranging from 1:1 to as high as 20:1 (currently recommended in ACI 201 – Guide to Durable Concrete). Sodium and magnesium sulfate are very soluble and are not impacted much by changes in extraction ratio, as even lower extraction ratios (i.e., 1:1 or 2:1) tend to extract most of the sulfates from the subject soil. Gypsum-based soils, however, are highly impacted by varying extraction ratios as increases in extraction ratios yield proportionally higher sulfate contents. Because the sulfate concentration generated from soil analysis is directly linked to levels of sulfate protection, this is clearly a key issue, especially in Texas, where gypsum is the primary sulfate form.

- **Resistance of concrete to physical sulfate attack.** In recent years, a relatively new form of sulfate-induced distress has been recognized, one in which sulfates penetrate into concrete and lead to deterioration without chemically altering the hydration products within the concrete (Folliard and Sandberg 1994; Haynes et al. 1996; Flatt and Scherer 2002). This distress, known as physical salt attack or physical sulfate attack, results from phase changes within the penetrating sulfate solution, which triggers crystallization pressures that can physically degrade concrete. Research is

needed to determine which salts can cause this form of distress and how this deterioration can be prevented.

- **Correlation between laboratory tests and field performance.** To date, there is very little correlation between accelerated laboratory tests (using ASTM C 1012 or other standard tests) and the actual performance of concrete subjected to external sulfates. This is particularly relevant given that physical salt attack may be more prevalent than previously thought in the field and is not considered or triggered in standard, accelerated laboratory tests such as ASTM C 1012.

The above research objectives were addressed in this project through a combination of laboratory tests, forensic and mechanistic evaluations, field studies, and the development of an outdoor sulfate exposure site in Austin, Texas. The details of these evaluations are described later in this dissertation. It is hoped that the collective findings presented in this dissertation, coupled with the results of parallel work performed at the University of New Brunswick, will help to advance the state of the art and improve the future performance of concrete exposed to external sulfates.

1.3 Outline of Dissertation

The remainder of this dissertation is organized into to the following chapters, with additional detailed information included as appendices:

- **Chapter 2** presents a brief review of literature on sulfate attack, with primary emphasis on external sulfate attack.

- **Chapter 3** describes a comprehensive study on the resistance of mortars to sulfate-induced expansion (following ASTM C 1012).
- **Chapter 4** describes a study of the resistance of concrete mixtures to various sulfate environments, both in the laboratory and at the outdoor exposure site developed under this project in Austin, Texas
- **Chapter 5** summarizes the findings of various field investigations of transportation structures in the state of Texas exposed to sulfate-rich conditions.
- **Chapter 6** briefly summarizes the main conclusions from this study to date, describes additional research in progress under this TxDOT-funded project, and highlight additional research needs that were beyond the scope of this project.

Chapter 2. Literature Review

Concrete is a complex system composed of various materials that have to be selected and proportioned properly and subsequently mixed, transported, placed, and compacted using sound principles, in order to achieve the desired properties and ensure a long service life. When concrete is exposed to aggressive environments, all of the above becomes even more critical. Sulfate attack represents a major challenge in that it is a complex process, in which the sources of sulfate can be internal such as delayed ettringite formation (DEF) or external, and the manifestations of distress can either be chemical or physical in nature. The research described in this dissertation focuses exclusively on external sulfate attack, and as such, the literature review presented in this chapter has a similar focus. However, for completeness a brief description of other sulfate-related durability problems, such as DEF and thaumasite attack is provided first, for completeness, followed by a more detailed review of external sulfate attack. .

2.1 Internal sulfate attack

Internal sulfate attack, also known as delayed ettringite formation (DEF), is a form of premature concrete deterioration that has occurred within the past couple of decades. It is triggered when high internal concrete temperatures are encountered (typically above 158° F (70 ° C)) during the initial hydration stage. These extreme high temperatures can occur in pre-cast concrete yards during steam curing or in certain cast-in place structures, most often mass concrete elements. Several researchers have shown that 158° F (70 °C) is the minimum critical temperature needed for delayed ettringite formation (Drimalas 2004;

Famy 1999; Ramlochan 2002), although every concrete mixture is different and exhibits different threshold temperatures. In addition, mixtures incorporating sufficient dosages of SCMs can chemically suppress DEF even when extreme temperatures are encountered. For mixtures that are susceptible to DEF, temperatures greater than 158° F (70 °C) can result in ettringite incongruously dissolving and sulfates and aluminates being trapped within the calcium-silica-hydrate (C-S-H) (Heinz and Ludwig 1987). These trapped sulfates are the source of attack on concrete as they are an “internal” source. These sulfates are released by the C-S-H once a drop of pH occurs in the concrete. A drop in pH can occur from a number of items such as leaching or alkali silica reaction (ASR). Delayed ettringite formation is often associated with alkali silica reaction in field structures as ASR results in a reduction in pore solution pH, as alkalies become bound in ASR gel. Once the sulfates are released, they react with monosulfate to form ettringite, which when it forms in small pores leads to significant expansion and stress development. Expansion triggered by delayed ettringite formation can be over 2 %, which is quite dramatic.

As described previously, ASR is a known trigger for DEF, and the combined effects of these two mechanisms can be quite dramatic in terms of expansion and cracking. Further, it has been shown to be quite challenging to trigger DEF, without ASR, in large concrete blocks (Drimalas 2004). Figures 2-1 and 2-2 show two blocks made for testing in an outdoor exposure site and were heat-treated during initial curing with the internal temperature reaching 183 °F (83 °C) at the middle of each block. Both of the concrete

blocks are the same age. The block in Figure 2-1 contains a non-reactive sand and non-reactive coarse aggregate (with regard to ASR), while the block in Figure 2-2 contains a highly-reactive sand with the same non-reactive coarse aggregate as used in the block in Figure 2-1. The heat-treated block with reactive aggregate (Figure 2-2) shows considerably more cracking than the heat-treated block with non-reactive aggregates in Figure 2-1. A non-heat-treated block containing the same highly-reactive aggregate (Figure 2-3) has shown considerable cracking, but nowhere near as much cracking as the heat-treated block shown in Figure 2-2, highlighting the synergy in distress triggered by ASR plus DEF (Drimalas 2004).



Figure 2-1: Exposure block containing non-reactive aggregates and heat cured up to 183 °F (83 °C), showing no signs of distress after 3 years



Figure 2-2: Exposure block containing highly-reactive aggregate and heat-cured up to 183 °F (83 °C), showing signs of significant cracking after 3 years



Figure 2-3: Exposure block containing highly-reactive aggregate showing less cracking after 3 years

2.2 Thaumasite attack

Thaumasite formation has often been confused with ettringite formation due to the close chemical composition of the expansive phases. Thaumasite formation is known to occur when C-S-H is in contact with either calcium, carbon dioxide, carbonates, sulfates, or moisture at temperatures between 32-59 °F (0-15 °C) (Bensted 1999). A calcium carbonate silicate sulfate hydrate forms, called thaumasite, which results in a significant loss of cohesion to occur within the hydrated cement paste. This type of distress can be prevented through proper materials selection and mixture proportioning, particularly by avoiding internal sources of carbonates that serve as key reactants in the process.

2.3 External sulfate attack

External sulfate attack, sometimes referred to as the “classical form of sulfate attack” is quite complex and still not fully understood. Sulfates can enter concrete through many external sources such as soils and groundwater. Sulfate can be of natural origin or derived from agricultural fertilizers or industrial effluents (Neville 1996). The specific types of sulfates that are found in soils and groundwater are discussed next.

2.3.1 Types of sulfates

The complexity of sulfate attack begins first with the variety of sulfates that can damage concrete. The most common sulfates that interact with concrete are calcium, sodium, and magnesium sulfate, which are listed in order of their aggressiveness. Each of these sulfate forms are discussed separately next, but one should bear in mind that it is common to find mixed sulfates present in the same groundwater or soil sample. Table 2-1 provides cement chemistry notations used throughout this dissertation.

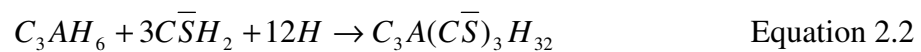
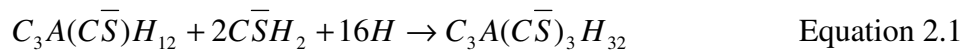
Table 2-1: Cement chemistry notations used throughout this dissertation

Chemical Name	Cement Chemistry Notation
Ettringite	$C_3A(C\bar{S})_3H_{32}$
Calcium Monosulfoaluminate	$C_3A(C\bar{S})H_{12}$
Gypsum	$C\bar{S}H_2$
Tricalcium Aluminate	C_3A or C_3AH_6
Sodium Sulfate	$N_2\bar{S}H_{10}$
Magnesium Hydroxide	$Mg(OH)_2$
Calcium Hydroxide	CH
Aluminum Hydroxide	AH ₃
Sodium Hydroxide	NH
Silica	S

2.3.1.1 Calcium sulfate

Calcium sulfate (gypsum) is generally believed to be the least aggressive of the three sulfates, mainly due to its lower solubility. The solubility of gypsum is approximately 1440 ppm, which is significantly less than that of sodium sulfate and magnesium sulfate. There are two essentially two different schools of thought on the issue of gypsum solubility and its impact on sulfate attack. One school of thought is that the inherently low solubility of gypsum limits its concentration in groundwater (or in the pore water of soil), and this low concentration limits the potential damage to concrete (Rebel et al. 2005). The other school of thought is that once calcium sulfate ions enter concrete, its solubility increases as it encounters the highly-alkaline pore solution within the concrete, and the higher sulfate concentrations can then more aggressively attack the hydrated cement paste (Hansen and Pressler 1947).

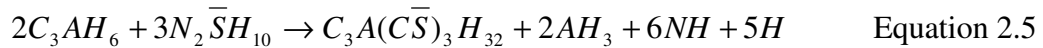
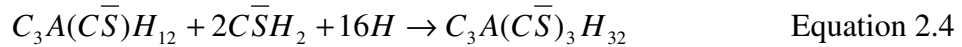
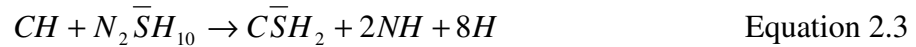
Specifically, as shown in equation 2.1, calcium sulfate will react with monosulfoaluminate and water to form ettringite, which can result in expansion and cracking. Calcium sulfate also reacts with tricalcium aluminate to form ettringite as shown in Equation 2.2.



2.3.1.2 Sodium sulfate

Attack from sodium sulfate is more complex than attack from calcium sulfate because more phases are affected. Sodium sulfate may attack concrete in two different ways.

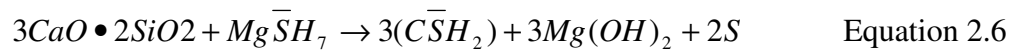
The first form of attack (Equation 2.3) involves sodium sulfate reacting with calcium hydroxide (portlandite) to form gypsum. Gypsum can then react with monosulfoaluminate (Equation 2.4) to form ettringite. Once the calcium hydroxide is depleted, gypsum formation will discontinue. Once the monosulfoaluminate becomes depleted, excess gypsum will form in the system and ettringite formation will cease (Gollop and Taylor 1992). The second form of attack (Equation 2.5) involves sodium sulfate reacting with tricalcium aluminate to form ettringite.



Tian and Cohen (2000) studied the expansion of alite (C_3S) caused by the formation of gypsum. In the case of a pure alite paste, no aluminum should be available to form ettringite. Cement pastes made with and without silica fume were placed in a 5% sodium sulfate solution. After 360 days in sodium sulfate, the alite paste, without silica fume, began to expand, and x-ray diffraction analyses showed that this expansion was due to gypsum formation (Tian and Cohen 2000). These findings suggest that gypsum formation can, in fact, lead to expansion, in addition to the loss of mass or cohesion that is typically observed when gypsum forms.

2.3.1.3 Magnesium sulfate

Magnesium sulfate is the most complex of the three types of sulfates. It can react with all hydrated cement products and is generally considered to be the most damaging form of sulfate. Magnesium sulfate will react with calcium silicate to form gypsum plus magnesium hydroxide and a silica gel, as shown in Equation 2.6. This formation of magnesium hydroxide (brucite) is known to form a barrier which may provide protection to the concrete and it also tends to internally affect pore solution pH. Brucite formation does have its downfall in that it needs a high amount of calcium hydroxide to form. Once the CH is depleted, the magnesium sulfate will seek more calcium. In this case, decalcification of the C-S-H will occur, due to a removal of calcium (Gollop and Taylor 1992).



2.4 Physical sulfate attack

The previous examples of external sulfate attack due to interactions with calcium, sodium, and magnesium sulfate resulted in chemical alterations of the hydrated cement paste, for example leading to the formation of gypsum or ettringite or to the decalcification of C-S-H. However, damage triggered by external sulfates may also be physical in nature, without any such chemical alterations. A common form of physical salt attack in concrete occurs when sodium sulfate penetrates into concrete and phase changes occur between anhydrous sodium sulfate (thenardite) and decahydrate sodium sulfate (mirabilite). These phase changes, typically triggered by changes in temperature,

lead to significant crystallization pressures that can impart stresses and cracking in concrete. Neville (2004) reported that this transformation of thenardite to mirabilite can result in tensile hoop stresses stressing the range of 1450-2900 psi (10-20 MPa). This stress is quite high and could easily damage concrete (Neville 2004).

In the early 1990's, Folliard and Sandberg (1994) proposed that crystallization of sodium sulfate within concrete, triggered by temperature changes, was the predominant cause of distress due to physical salt or sulfate attack. Figure 2-4 shows the solubility curve for sodium sulfate, which shows the change between thenardite and mirabilite at approximately 91 °F (33 °C). After cycling concrete specimens in 30% sodium sulfate solution from 41° to 86 °F (5° to 30 °C), substantial mass loss occurred in the samples. X-ray diffraction on these samples did not show any sign of ettringite formation or any other deleterious product from chemical attack. In parallel tests, it was shown that the total volume of the sodium sulfate/water solution increased by approximately 3 % as crystallization was triggered upon a temperature drop. In essence, this type of distress is similar to freeze-thaw distress in that physical distress is triggered by a volume change of the water or solution inside concrete. Samples cycled from 95° to 230 °F (35° to 110 °C) did not show any weight loss and the majority of these samples gained weight (Sandberg and Folliard 2004), confirming that the distress only occurs when temperatures drop below about 91 °F (33 °C) and when a high concentration of sodium sulfate is present in the pores of concrete.

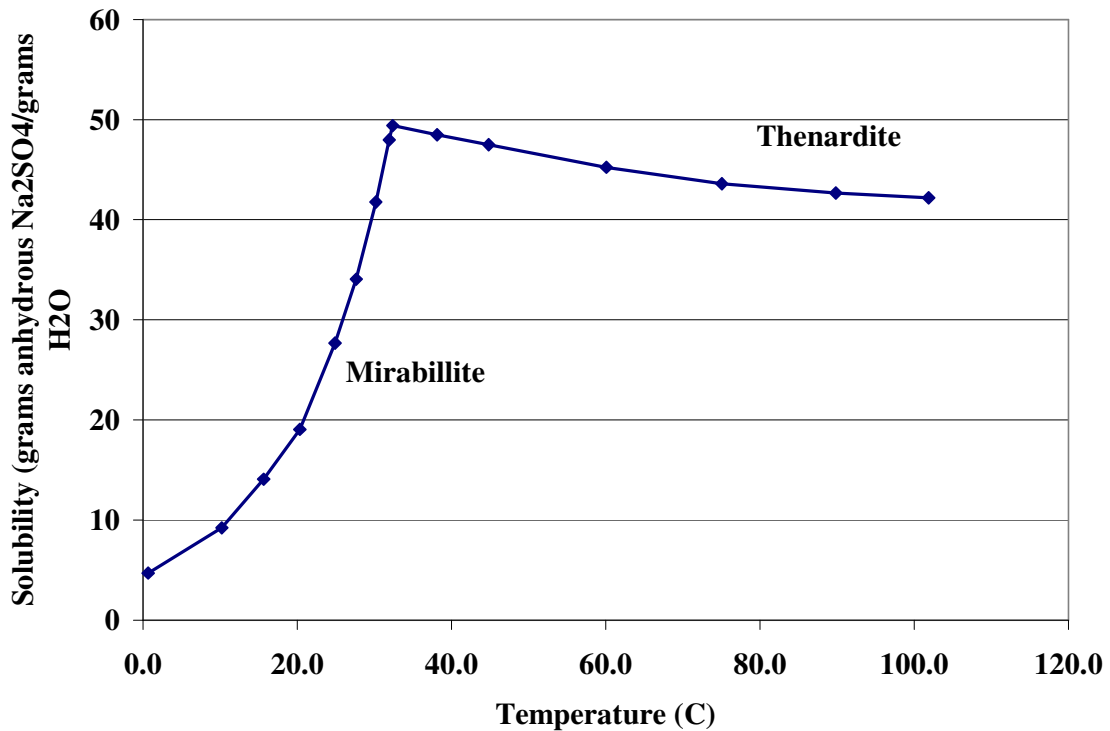


Figure 2-4: Solubility curve for sodium sulfate /water system (Berkeley 1904)

Since the 1940's, the Portland Cement Association (PCA) has studied the long-term durability of concrete specimens stored in outdoor environments in Sacramento, California. The PCA study is comprised of four research phases since its inception and has focused on the areas of cement content, cement composition, cement types, SCMs, w/cm, and various types of coatings. The fourth phase, initiated in 1982, is comprised of research on mineral admixture replacements, w/cm, and coatings. Concrete beams measuring 6 in x 6 in x 30 in (150 mm x 150 mm x 760 mm) were cast and shipped to Sacramento, California one year after being cast. The beams were then halfway submerged in soil containing 10% sodium sulfate. The beams were annually inspected and assigned a rating between 1-5 with 5 showing the most deterioration (Stark 1989).

The first PCA bulletin report in 1989 reported that the most important parameter influencing sulfate resistance was the w/cm of concrete (Stark 1989). It was also reported that cement type (e.g., Type I vs. Type II vs. Type V) had minimal influence on sulfate resistance for concrete mixtures with either low or high w/cm, but a significant difference was noted for mixtures with intermediate w/cm values. Interestingly, mixtures containing fly ash or GGBFS reduced sulfate resistance in 29 of 30 mixtures, when compared to a control mixture. Beams with coatings were reported to behave well, but it was proposed that this protection may only be temporary as the epoxy coating showed signs of peeling away from the concrete (Stark 1989). The distress reported in concrete beams was attributed to external, chemical sulfate attack in this 1989 bulletin, and there was no mention of other distress mechanisms.

In 2002, a second bulletin on the PCA site determined that damage on the concrete beams was only occurring above the soil level, and that very little damage was reported below ground or in parallel tests in which beams were stored indoors (without substantial variations in temperature). Stark (2002) proposed that the main mechanism of distress was physical sulfate (or salt) attack, a form of distress that had been identified as being a key deterioration factor in various papers published between the 1989 and 2002 PCA bulletins, some of which are described next. The main findings from this 2002 bulletin suggest that physical sulfate attack is a much more significant form of distress in field

concrete than had been previously reported and suggests that the overall topic of sulfate attack is even more complex than ever.

2.5 Preventing sulfate attack

This section briefly summarizes recommended methods of preventing sulfate attack in concrete, including both internal and external sulfate attack, and for cases where the deterioration is physical or chemical in nature.

2.5.1 Internal sulfate attack

Internal sulfate attack or DEF can be prevented by minimizing curing temperatures (nominally below 70 °C) or by chemically suppressing DEF through the use of suitable dosages of SCMs (e.g., >25% fly ash, >35% slag) (Ramlochan 2002; Drimalas 2004).

2.5.2 Thaumasite formation

Keeping the temperature above 59 °F (15 °C) would be beneficial for not allowing for thaumasite formation; however, this is not possible for many structures throughout the world. A lower permeability concrete may help prevent thaumasite by not allowing the transport of necessary ions through the concrete. ACI recommends a maximum w/cm of 0.45 to help prevent the thaumasite form of sulfate attack (ACI 2001). Lastly, one should avoid excessive carbonate fines in concrete as these serve as key reactants in the process.

2.5.3 External sulfate attack

External sulfate attack can be prevented through proper material selection and mixture proportioning. This section briefly summarizes viable means of preventing sulfate attack,

including discussions on the universal importance of reducing permeability and the direct benefits of using lower w/cm, sulfate-resistant cements, and SCMs.

2.5.3.1 Permeability

Concrete with a low w/cm yields a microstructure with reduced porosity and permeability which reduces the rate of ingress of sulfate ions. Cement paste with a w/cm of 0.7 is approximately 10 times more permeable to that a comparable mixture with a 0.55 w/cm (Powers et al. 1954). A significant correlation between higher permeability and greater expansion was reported with concretes exposed to 5% sodium sulfate (Khatri 1997), and Al-Amouti (2002) reported similar findings for concrete exposed to sodium sulfate, but not with magnesium sulfate solutions. To achieve low permeability, one must not only use a low w/cm (i.e., less than 0.45) but also ensure adequate curing. As described later, the incorporation of SCMs into concrete mixtures is the most powerful method of reducing sulfate ingress.

2.5.3.2 Sulfate-resistant cements

Sulfate-resistant cement was developed to limit the C_3A in the cement to prevent sulfate attack. The lower C_3A cement primarily reduces the amount of ettringite that can form. However, sulfate-resistant cement does not stop the attack on calcium hydroxide and C-S-H (Mehta 1993). ASTM C-150 limits the C_3A content of Type V cement to 5 % and the C_3A content of Type II cement to 8 % maximum. It is also generally believed that the alumina in the aluminoferrite phase of portland cement can participate in sulfate attack, and as such, ASTM C 150 states that the $C_4AF + 2C_3A$ in Type V cement should not exceed 25%, unless specific performance tests show satisfactory results (ACI 201.2R-01

2001). This guide will be referred to in this dissertation as ACI 201.2R-01. In localities that do not have availability of Type V cement, the use of Type II cement with suitable SCMs can provide comparable sulfate resistance to Type V cement (ACI 2001). The U.S. Bureau of Reclamation has shown Type V cement to be beneficial in its long term studies and considers sulfate-resistant cement to be a viable means of improving performance in a sulfate environment (Eglinton 1998).

Gollop and Taylor (1995) employed various analytical techniques to investigate the microstructure of cement paste cubes with ordinary portland and sulfate-resistant cements after 6 months submerged in magnesium and sodium sulfate solutions. Sulfate-resistant cement cubes still provided the same deleterious. Brucite formation was noticed along the edge of the sample but again at a lesser degree than that found in the ordinary portland cement cube (Gollop and Taylor 1995).

2.5.3.3 Supplementary cementing materials

Most SCMs, when used in sufficient dosages, can be quite effective in preventing sulfate attack by lowering permeability, reducing CH content, and diluting the reactive components emanating from the portland cement. Many studies have been conducted to show the benefits of incorporating various SCMS in concrete to improve sulfate resistance, and only a select few of these are cited herein for conciseness.

Generally, ground-granulated blast furnace slag (GGBFS) is quite effective in controlling sulfate attack, with replacement levels from 25 to 50% providing moderate to severe exposure protection, respectively. Mortars containing 45 to 72% GGBFS (by mass replacement of cement) were reported by Hooton and Emery (1990) to provide satisfactory sulfate resistance after 10 years of storage in 3000 mg/l sodium sulfate solution. One potential issue with slag is that the typical 1% sulfur content in blast furnace slags occurs mainly as sulfide in glass phase and is released upon hydration as other constituents. The release of the sulfide cannot be ignored when considering the effects on sulfate attack (Taylor and Gollop 1997). ACI 201.2R-01 recommends the use of between 40 and 70 % by mass of slag to control sulfate attack (ACI 201 2001).

Many studies have shown that low calcium fly ash is generally more effective than high calcium fly ash in preventing sulfate-induced expansion and cracking. Dunstan (1980) worked with creating a resistance factor R that based the sulfate resistance of fly ash on calcium and iron oxide content of the fly ash. In the study, higher calcium oxide fly ash would fail the resistance factor. Tikalsky also studied a variety of fly ashes and found that high calcium fly ashes do not perform well in sulfate environments (Tikalsky and Carrasquillo 1993).

The use of Class F fly ash (CaO content less than 20%) has long been found to be effective for sulfate resistance when dosages between 25 and 35% by mass are used. However, some high-lime Class C fly ashes produce concrete with poor sulfate

resistance, sometimes even worse than control mixtures without fly ash. Shashiprakash and Thomas (2001) found that this led to increased expansion when compared with the high-C₃A cement used on its own. The reasons why high-lime ashes were less effective than low-lime ashes in controlling sulfate attack were identified as:

- Some high-calcium fly ashes contain C₃A (also some CH)
- Lower consumption of lime due to reduced pozzolanicity
- Presence of reactive calcium-aluminates in glass phase
- Production of reactive aluminate hydrates

Figure 2-5 shows the strong relationship between the CaO content of the fly ash and the expansion at six months in ASTM C 1012 testing. More research is needed to better differentiate the behavior of different high-lime ashes; using CaO as an index of potential expansion may not hold for all fly ashes.

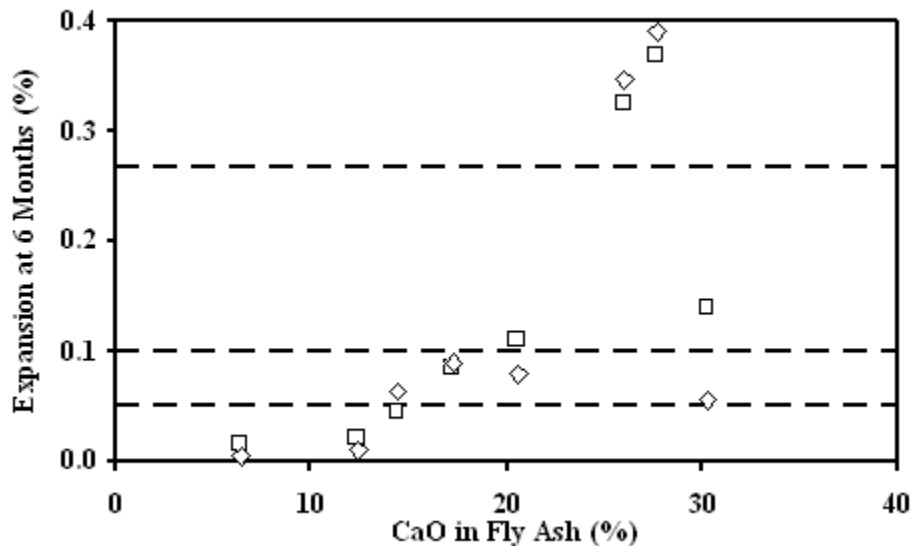


Figure 2-5: Relationship between C₃A content in fly ash to 6 month expansion in ASTM C 1012 testing (Shashiprakash and Thomas 2001)

In addition to linking the mineralogy and chemistry of fly ashes to sulfate resistance, Shashiprakash and Thomas (2001) also performed significant research on combining high-CaO ashes with silica fume, with emphasis on mixtures with between 3 and 6% percent silica fume (by mass of total cementitious materials). Figure 2-6 shows the effects of just a small dosage of silica fume (3%) on the sulfate resistance of concrete with a high-calcium fly ash.

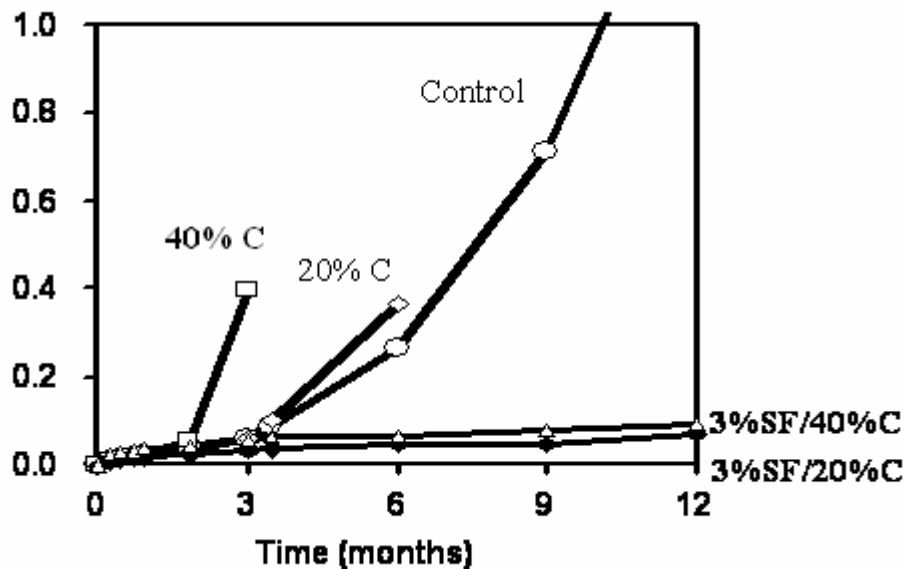


Figure 2-6: The effect of ternary blends with silica fume and Class C fly ash on expansion of mortars compared to mortars using only Class C fly ash (Shashiprakash and Thomas 2001)

Metakaolin is a pozzolan that has shown great performance in cases of alkali aggregate reaction (AAR), chloride ingress, and carbonation (Lee 2004). In the case of sulfate attack, the deterioration depends on the type of sulfate. Khatib and Wild (1998) show that a minimum of 20% metakaolin is needed to produce durable concrete when exposed to sodium sulfate. In magnesium sulfate solutions, the opposite is true. Lee (2004)

showed that an increase of metakaolin increased expansions and deterioration on mortars and pastes.

2.5.4 Physical sulfate attack

There have been only limited studies on methods of preventing physical sulfate attack. Folliard and Sandberg (1994) reported that low w/cm concrete mixtures are quite effective in preventing physical sulfate attack, especially when SCMs are used. They also showed that air-entrainment is helpful in reducing but not eliminating physical sulfate attack. With time, it was shown that air-entrained voids ultimately become filled with salts, and they are not longer accessible to the salt solution as it increases in volume.

2.6 Characterization of sulfate exposure conditions

Various methods of preventing sulfate attack have been discussed in this chapter, with a wealth of data available from various laboratory studies. Ideally, the level of protection against sulfate attack should be matched to the specific exposure conditions in which the subject concrete will be cast. An example of this approach of selecting mitigation measures based on severity of exposure is shown in Table 2-2 (after ACI 201-2R-01 2001) To establish this link, it is essential to accurately assess exposure conditions by either analyzing the local groundwater or soil sample, each of which are discussed next.

Table 2-2: Sulfate exposure classification for water-soluble sulfates in soil or sulfates in water (ACI 2001)

Severity of potential exposure	Water-soluble sulfate (SO ₄) in soil, percent by mass	Sulfate (SO ₄) in water, ppm	(w/cm) by mass, max.	Cementitious-material requirements
Class 0 exposure	0.00 to 0.10	0 to 150	No special requirements for sulfate resistance	No special requirements for sulfate resistance
Class 1 exposure	>0.10 and <0.20	>150 and <1500	0.50	C 150 Type II or Equivalent
Class 2 exposure	0.20 to <2.0	1500 to <10,000	0.45	C 150 Type V or Equivalent
Class 3 exposure	2.0 or greater	10,000 or greater or greater	0.40	C 150 Type V plus pozzolan or slag

2.6.1 Water samples

The measurement of sulfates from groundwater from a new construction site is fairly straightforward and essentially without controversy. The water can directly be analyzed for sulfate content using widely available analytical methods or diluted to be read by an instrument that measures sulfates.

2.6.2 Soil samples

Since not all sites have groundwater present for sampling, soil samples must be taken to analyze the amount of sulfates. A few issues arise when sampling soil. First, there is no clear consensus or guidance on how many samples to extract and evaluate from a given site. Within a single site, a large variability of sulfate concentrations is quite common. This variation in sulfate content impacts not only sampling regimes but also the actual sulfate resistance of concrete ultimately cast on that site. For example, a foundation in

Italy exhibited severe deterioration from sulfate attack on only certain piers, due to local variations in sulfate content (Tulliani 2002). The flow of groundwater can move sulfates throughout the soil or even the natural soils in different areas can contain different amounts of sulfates. Rainfall and drainage may also affect the locations and concentrations of sulfate within a given site. A statistical number of samples should be taken and measured; however, this increases the cost of testing, and as stated previously, no definitive guidance exists on how to properly sample soils from a given site.

The second major problem that occurs with sulfates and soils is the analytical techniques needed to measure the sulfates. There are two methods of measuring sulfates from a given soil sample -- either water soluble or acid soluble sulfate determination. Acid soluble determination is fairly rare and somewhat complex, and in addition, this method can trigger the release of sulfates from soils that would otherwise not be released under realistic field conditions. Water soluble sulfate testing is more common; however there are many versions of this test and they all provide different results, mostly due to variations in the extraction ratio.

For water-soluble sulfate determination, the extraction ratio can easily change the results of a sulfate concentration from a given sample, especially when the soil contains gypsum. The extraction ratio is the mass of water per mass of soil. There is no clear consensus on what extraction ratio should be used and values range in practice from as low as 1:1 to as high as 20:1. Sodium and magnesium sulfate are very soluble and are not impacted much

by changes in extraction ratio, as even lower extraction ratios (i.e., 1:1 or 2:1) tend to extract most of the sulfates from the subject soil. Gypsum-based soils, however, are highly impacted by varying extraction ratios as increases in extraction ratios yield proportionally higher sulfate contents. Because the sulfate concentration generated from soil analysis is directly linked to levels of sulfate protection, this is clearly a key issue, especially in Texas, where gypsum is the primary sulfate form. For gypsum-bearing soils, higher extraction ratios tend to result in classifying the soil as a higher degree of severity, thereby requiring more stringent preventive measures.

2.7 Structures suffering from sulfate attack

Cases of sulfate attack in field structures are fairly uncommon, mainly because most agencies have already adopted specifications and guidelines aimed at preventing deterioration. Even when sulfate attack does occur, it is not clear how damaging the distress can be in the long term, but Mehta (2000) has suggested that the “threat” of structural failure due to sulfate attack is less than that for other distress mechanisms, such as corrosion or alkali-aggregate reaction. One major issue is that there is a general lack of correlation between accelerated laboratory test methods and actual field performance, which is discussed next.

2.8 Test methods and specifications

There exists a general lack of correlation between the performance of concrete subjected to standard test methods and concrete subjected to realistic field conditions (Santhanam et al. 2001). Two current ASTM test methods for assessing sulfate attack are ASTM C 1012 and ASTM C 452. ASTM C 452 is a test method for the potential expansion of

portland cement mortars exposed to sulfate. In this standard, gypsum is added to the cement prior to mixing to produce 7% SO₃ by mass of cement and gypsum. The additional gypsum allows for ettringite formation to occur internally without the need for external sulfates to enter the specimens. Mortars are then placed in limewater and measured for expansion. This test method is not very common since it is intended only to be used as a test for portland cement, it has limited applicability to more varied systems, such as mixtures containing SCMs.

ASTM C 1012 is one of the most common tests used in practice and is often included in specifications and guidelines. The test involves casting mortar bars, typically containing a high-C₃A cement (with or without SCMs) and standard Ottawa sand, allowing the mixture to reach a minimum strength of 2850 PSI (20 MPa), and then immersing the specimens in 5% sodium sulfate solution for up to 18 months. This is the most common test method for determining sulfate resistance and is the test method chosen for equivalent testing in ACI 201.2R. One concern with this test is that the pH of the sulfate solution will change with time, as will the pH of the pore solution (due to leaching). To minimize this pH effect, the sulfate solution is required to be replaced each time a measurement is conducted. However, at intervals of longer measurements periods, the pH may change considerably, thereby affecting the progression of sulfate attack. Mehta (1974) proposed a test set-up that automatically adjusts the pH of the soak solution to minimize this effect, but the complexity of this approach has hindered its use in standard test methods.

Both of the aforementioned test methods deal with the chemical process of sulfate attack and do not adequately assess the physical component of sulfate attack that may occur in the field. As mentioned in Section 2.2.2, PCA showed that physical salt damage was the predominant damage in their exposure site in Sacramento (Stark 2002). An important finding from this exposure site is that more testing needs to be conducted with specimens in the field or simulated outdoor testing in the laboratory evaluate both physical and chemical attack.

Bellmann and Stark (2006) suggested that test methods that use a high sulfate concentration do not accurately reflect field observations. High sulfate concentrations in laboratory testing results in gypsum formation, whereas ettringite (or sometimes thaumasite) formation is favored under realistic field conditions.

The overall approach to defining severity of exposure and then matching this to a level of protection was previously shown in Table 2-2 and is typical of standard practice in North America and elsewhere. This table results in a situation where concrete placed in a higher severity of classification requires a lower C_3A content of the portland cement, a lower w/cm ratio, and sometimes the use of suitable SCMs. In lieu of this prescriptive approach, performance testing, typically using ASTM C 1012, is often employed to determine if a proposed combination of materials will provide comparable sulfate resistance. For example, an equivalent and acceptable approach to producing concrete

for Class 3 exposure could consist of Type I cement with 30% Class F fly ash, with an 18-month expansion (ASTM C 1012) value of less than 0.1%.

2.9 Research needs

The topic of sulfate attack is still misunderstood. Research is still needed to understand basic mechanisms of sulfate attack and to provide more sound technical guidance on achieving sulfate resistance in field applications. Some of the outstanding research needs include the following, some of which were addressed in the research described later in this dissertation:

- Suitable methods of measuring sulfate content in soils, especially when gypsum-based soils are encountered.
- Possible severity of sulfate attack when concrete is exposed to gypsum-based soils.
- Guidance on how to evaluate physical sulfate attack and how to ensure long-term durability with regard to this mechanism.
- Role of fly ash chemistry and mineralogy on sulfate resistance, especially when considering the use of Class C fly ash in sulfate-rich environments.

Chapter 3. Evaluation of the Sulfate Resistance of Mortars Containing High-Calcium Fly Ashes

3.1 Introduction

The importance of high-calcium fly ashes and fly ash mineralogy is quite evident as shown in previous work, and it is quite clear that relying upon bulk chemistry and oxide analysis does not suffice when attempting to predict the response in a sulfate environment. The characteristics of the glassy or amorphous phase of high-calcium fly ash are particularly important and relevant to sulfate resistance (Dunstan 1980; Mehta 1993). Fly ashes containing gehlenite in the glassy phase generally yielded poor sulfate resistance, whereas fly ashes more comprised of mullite generally performed better in a sulfate environment (Dunstan 1980).

Although certain Class C fly ashes can adversely impact sulfate resistance, Shashiprakash and Thomas (2001) showed that incorporating relatively small dosages of silica fume can substantially improve the sulfate resistance of concrete containing high-calcium fly ash. This approach is quite attractive in regions where Class C fly ash is the only type of fly ash available, as is the case in select portions of Texas. Research is needed to quantify the dosages of silica fume, or other highly-active pozzolans such as ultra-fine fly ash (UFFA), that are required to produce sulfate resistant in concrete containing high-calcium fly ash.

3.1.1 Research significance

Past research has shown that certain Class C fly ashes exhibit poor sulfate resistance when incorporated in mortar or concrete and subjected to accelerated laboratory testing.

The practical relevance of this is especially critical in regions where high-calcium ash is the only type of fly ash available. Research is needed to identify what specific characteristics of high-calcium fly ash impact sulfate resistance, from a chemical and mineralogical perspective, and guidance is needed on how to incorporate high-calcium fly ash in concrete in sulfate-rich environments. The research described in this chapter is aimed at achieving these objectives.

3.2 Experimental methods

3.2.1 Materials

A wide range of materials were chosen for this study to evaluate the performance of Class C fly ash in a sulfate environment. ASTM C 1012 was selected as the standard testing procedure for this research, not because it is deemed to be the best test or the test most linked to field performance, but rather because it is the test most commonly used, specified, and included in national and international guidelines (such as ACI 201.2R-01 (2001)). As per ASTM C 1012, all mortar mixtures were cast with ASTM C 778 Ottawa graded sand. A Type I cement, designated herein as C1, with a C_3A content of 11%, was used for all mixtures. Table 3-1 provides the composition of the Type I cement. As per the guidance in ACI 201.2R, a portland cement with a minimum of 8% C_3A must be used to evaluate the performance of cement/supplementary cementing combinations.

Table 3-1: Chemical data for the portland cements used in this study

Chemical Data	C1	C2*	C5*
SiO ₂ (%)	20.12	19.38	20.55
Al ₂ O ₃ (%)	5.21	4.79	4.19
Fe ₂ O ₃ (%)	1.93	3.17	5.32
CaO (%)	63.78	65.24	63.36
SO ₃ (%)	3.4	2.43	3.81
MgO (%)	1.56	1.44	0.83
Na ₂ O (%)	0.78	0.16	0.32
C ₃ A (%)	11	7.4	2.11

* C2 and C5 were not evaluated in this chapter
but are included in research described in Chapter 4

A range of Class C fly ashes, with CaO contents from 2 to 30%, were included in this investigation. Table 3-2 details the chemical analyses of the 8 Class C fly ashes used in the mortar mixtures. Other SCMs were also included in this study, which were tested separately or in conjunction with the various fly ashes in ternary blends. Specific information regarding these other SCMs is included in Table 3-3.

Table 3-2: Chemical analysis of fly ashes tested in the study

CHEMICAL TESTS	FA-1	FA-2	FA-3	FA-4	FA-5	FA-6	FA-7	FA-8	FA-9*
Silicon Dioxide (SiO ₂), %	38.57	41.32	33.14	34.47	33.35	36.36	37.16	30.76	48.48
Aluminum Oxide (Al ₂ O ₃), %	18.84	19.25	18.12	20.35	18.74	17.44	20.55	17.75	25.01
Iron Oxide (Fe ₂ O ₃), %	6.69	6.48	6.65	5.65	6.69	6.08	6.06	5.98	3.56
Sum of SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , %	64.1	67.05	57.91	60.47	58.78	59.88	63.77	54.49	77.05
Calcium Oxide (CaO), %	23.54	21.58	27.49	26.5	27.3	25.68	24.76	28.98	15.92
Magnesium Oxide (MgO), %	4.76	4.43	5.45	4.7	5.83	6.15	4.29	6.55	2.5
Sulfur Trioxide (SO ₃), %	1.43	1.25	2.71	1.71	1.85	2.03	1.23	3.64	0.72
Sodium Oxide (Na ₂ O), %	1.71	1.43	1.91	1.76	1.93	1.9	1.63	2.15	0.3
Potassium Oxide (K ₂ O), %	0.65	0.78	0.3	0.46	0.38	0.46	0.45	0.3	0.71
Total Alkalies (as Na ₂ O), %	2.14	1.94	2.11	2.06	2.18	2.2	1.93	2.35	0.77
PHYSICAL TESTS	FA-1	FA-2	FA-3	FA-4	FA-5	FA-6	FA-7	FA-8	FA-9
Loss on Ignition, %	0.28	0.16	0.4	0.25	0.21	0.58	0.13	0.44	0.55

* FA9 was not evaluated in this chapter but is included in research described in Chapter 4

Table 3-3: Chemical analysis of other SCMs tested in the study

Chemical Tests	Silica Fume (SF)	UFFA	Slag
SiO ₂ (%)	93.17	50.65	35.91
Al ₂ O ₃ (%)	--	26.64	11.98
Fe ₂ O ₃ (%)	2.1	4.66	0.94
CaO (%)	0.8	10.85	44.1
MgO (%)	0.3	2.23	8.9
SO ₃ (%)	0.2	1	1.63

3.2.2 ASTM C 1012 test procedure

ASTM C 1012 is an accelerated test procedure that exposes mortar specimens to a 5% sodium sulfate solution, with length change being the primary index. Some of the key features of this test method are described next.

As per ASTM C 1012, a standard mortar mixture is cast with 1 part portland cement to 2.75 parts sand. For the control portland cement mixture, the w/cm is fixed at 0.485, and for mixtures incorporating SCMs, water is added to obtain a flow of ± 5 of that of the control portland cement mixture. The mortar bars have dimensions of 1 in X 1 in X 11.25 in (25 mm X 25 mm X 286 mm) with stainless steel gauge studs embedded into the ends for length measurements. Nine mortar cubes (2 in x 2 in or 50 mm x 50 mm) are also cast from each mixture. After casting the mortar bars and cubes, they are sealed and placed into a 95 °F (35 °C) water bath for 23 ± 0.5 hours. After curing, the specimens are demolded and two of the cubes are tested for strength. Once the compressive strength of the cubes has reached 2850psi \pm 100psi (20MPa \pm 0.70 MPa), the bars are then placed into a 5% sodium sulfate solution (352 moles of Na₂SO₄ per m³). Appendix A provides the mortar strengths from each of the mixtures. Otherwise, the bars and cubes are placed into a saturated limewater bath until strength is achieved. Upon immersion in the sulfate

solution, expansion measurements are taken every 1, 2, 3, 4, 8, 13, 15 weeks and 4, 6, 9, 12, 18 months thereafter.

3.2.3 X-ray diffraction

Samples for x-ray diffraction (XRD) were taken from mortar bars at 18 months after storage in sodium sulfate solutions. A single mortar bar was tested from each mixture. The mortar bars that did not fully deteriorate were broken in half with one section used for XRD and the second section for SEM. The detail of the SEM procedures is in section 3.2.4. The bars that had fully deteriorated had a sample carefully removed with most of the entire cross-section preserved. A 2 in (51mm) section near the center of the mortar bar was crushed with a mortar and pestle to pass through a #325 sieve (45 microns). The majority of the sample passed through the sieve; however, sand particles did not successfully pass through the sieve. Once the sample passed through the sieve, it was placed into vials and stored under vacuum until tested.

The samples were front loaded onto the sample holders and placed in the Siemens D500 diffractometer, which scanned each sample from 5° - 65° 2θ . A semi-quantitative analysis was used to determine the phases within the sample that included ettringite, gypsum, portlandite, quartz, and calcite. The analysis is not a full quantitative analysis since an internal standard was not placed within each sample. When an internal standard is used at a given weight percent, the amounts of all phases can be calculated. A semi-quantitative analysis allows only the determination of relative amounts of crystalline phases present. Rietveld analysis through the use of Topas (Bruker) software was used to

determine and provide general information on which phases were forming within each sample. Rietveld analysis is a non-linear least-squares technique that refines x-ray scans to profile fittings for certain crystalline phases. It continues to refine the scan until it best fits the scan. This technique was used to provide a general indication of which phases were forming within each sample.

A quantitative XRD analysis did occur for a few samples. The XRD samples for section 3.3.3 did have 10% rutile as an internal standard to provide a full quantitative Rietveld analysis.

3.2.4 Scanning electron microscopy

Mortars were imaged and analyzed with the use of a scanning electron microscope after 18 months of storage. The second half of the broken bar from section 3.2.4 was taken and sliced 0.24 in. (6mm) with a Buehler Isomet 1000 precision saw with ethanol as the lubricant. The sample was then placed under vacuum for at least 24 hours prior to epoxy impregnation with a two part epoxy resin from Logitech. The epoxy was allowed to cure at least 24 hours at 73 °F (23 °C) prior to grinding. The sample was then grinded with #180, 400, 800, 1200 grit sandpaper on a Buehler Ecomet 6 grinder-polisher. The progression towards finer grit sandpaper depended on scratches on the surface of the specimen. The time spent on each size depended on the amount of scratches. Typically, it took 15 minutes per grit size. After grinding the same instrument, the samples were polished with 3, 1, and ¼ micrometer diamond paste. The samples were polished with an automated Buehler Automet 2000 powerhead. The 3 and 1 micrometer diamond pastes

were used for 1 hour each followed by the $\frac{1}{4}$ micrometer diamond paste for 1.5 hours. After polishing, the sample is cleaned with ethanol and stored under vacuum until analyzed under the SEM.

The samples were placed into a Hitachi 3200N variable pressure SEM with a Robinson detector used for imaging. The SEM uses a tungsten filament. The accelerating voltage used was 20kv. Energy dispersive spectroscopy (EDS) was used to analyze phases within the sample. An Oxford ENCA system was used to analyze the phase contents within each sample.

3.3 Experimental results and discussion

This comprehensive experimental program focuses on a range of fly ashes, used in varying dosages in mortar mixtures tested according to ASTM C 1012. First a discussion section provides details on the current expansion limits set by ACI 201.2R-01. After discussing the results of tests performed on these fly ashes, the results of tests performed on mortar mixtures containing ternary blends (Class C fly ash plus additional SCM) are presented.

3.3.1 Expansion limits

Expansion limits (and immersion times at which expansion limits are applied) vary considerably from one agency/source to another and also depending on the severity of sulfate exposure. In this dissertation, expansion limits from ACI 201.2R-01 are nominally used to compare and evaluate the performance of mortars exposed to sulfate solutions. Table 2-2 in the previous chapter, from ACI 201.2R-01, shows the four classes

of exposure, increasing in order of severity as one progresses downward in the table. The severity is determined based on the sulfate concentration in either the groundwater or soil. As discussed previously in this dissertation and as will be discussed in more detail later in this chapter, there are several unresolved issues when measuring sulfates in soil, especially when gypsiferous soils are encountered. As one moves from the less severe to more severe exposure classes, more stringent prescriptive guidelines are provided, which include lower w/cm, the use of sulfate-resistant cements, and the use of SCMs. The last column in Table 2-2 shows the different cementitious requirements for each of the exposure classes. A Type II or Type V portland cement (as per ASTM C 150) is specified in Class 1-3 exposures, but “equivalent” materials are allowed for these exposure classes, with equivalency based on ASTM C 1012 test results, as described next.

As shown in Table 2-2, “equivalent” cementitious materials can be used in lieu of Type II or Type V cements, which is particularly important for Type V equivalency as there exist very few Type V cements in the United States. Equivalency is judged based on ASTM C 1012 testing, with various expansion limits and test durations, depending on the specific exposure class. An equivalent for a Type II cement in Class 1 exposure would be any type of ASTM C 150 or C 1157 cement with fly ash, silica fume or slag that yields an expansion less than 0.10% after 6 months. An equivalent for Type V cement in Class 2 exposure has two criteria. The first criterion requires the expansion to be less than 0.05% percent after six months, provided that these materials were previously qualified by performance testing. If the materials were not previously qualified, an expansion limit of

0.10% after one year is specified. For Class 3 exposure, an ASTM C 150 Type V or ASTM C 1157 Type HS cement must be used with a suitable dosage of SCM to achieve an expansion less than 0.10% after 18 months of testing using ASTM C 1012.

3.3.2 Evaluation of Class C fly ash

3.3.2.1 Expansions

A comprehensive testing program involving 8 fly ashes and other SCMs was performed, and for convenience, Tables 3-5 and 3-6 summarizes the key data, including the dosages of SCMs used for FA1 and FA2. The data for FA3-FA8 are provided in Appendix B. For conciseness, the expansion values at 6, 12, and 18 months are included in the table as these test ages correspond to age-specific criteria set forth in ACI 201.2R for “equivalent” sulfate resistance. Expansion values that are in bold font indicate expansions in excess of 0.1%, which is a typical expansion limit for the different test ages, depending on the exposure class in ACI 201.2R. The “X” designation in the table represents mortars that had deteriorated and were not measurable. This section discusses only the expansion results for control mixtures (without fly ash) and mixtures containing fly ash; discussion on the behavior of mixtures containing ternary blends (portland cement, Class C fly, and either silica fume or ultra-fine fly ash) is provided in section 3.2.

Table 3-4: Expansion measurements from FA1 in ASTM C 1012 Testing

FA1	Ternary	6 Month	9 Month	12 Month	18 Month
20%		0.043	0.100	0.134	0.900
20%	3% SF	0.060	0.074	0.192	X
20%	5% SF	0.028	0.042	0.074	0.261
20%	6% UFFA	0.037	0.045	0.079	0.244
20%	9% UFFA	0.037	0.038	0.053	0.099
20%	20% Slag	0.028	0.040	0.062	0.106
20%	25% Slag	0.027	0.038	0.052	0.056
25%		0.041	0.092	0.340	X
25%	3% SF	0.036	0.062	0.132	0.395
25%	5% SF	0.027	0.045	0.079	0.194
25%	6% UFFA	0.036	0.044	0.048	0.065
25%	9% UFFA	0.037	0.051	0.069	0.084
25%	20% Slag	0.036	0.054	0.088	0.107
25%	25% Slag	0.039	0.056	0.076	0.091
30%		0.072	0.085	0.229	X
30%	3% SF	0.034	0.058	0.199	0.621
30%	5% SF	0.034	0.051	0.074	0.138
30%	6% UFFA	0.038	0.053	0.077	0.094
30%	9% UFFA	0.028	0.041	0.052	0.057
35%		0.060	0.113	0.398	X
35%	3% SF	0.039	0.062	0.106	0.213
35%	5% SF	0.039	0.047	0.056	0.095
35%	6% UFFA	0.041	0.066	0.084	0.083
35%	9% UFFA	0.038	0.069	0.094	0.097
40%		0.118	0.257	0.511	X
40%	3% SF	0.045	0.072	0.072	0.090
40%	5% SF	0.027	0.046	0.052	0.073
40%	6% UFFA	0.044	0.057	0.073	0.077
40%	9% UFFA	0.040	0.057	0.075	0.071

Table 3-5: Expansion measurements from FA2 in ASTM C 1012 Testing

FA2	Ternary	6 Month	9 Month	12 Month	18 Month
20%		0.055	0.117	0.359	0.995
20%	3% SF	0.039	0.055	0.075	0.201
20%	5% SF	0.035	0.052	0.074	0.162
20%	6% UFFA	0.024	0.031	0.040	0.069
20%	9% UFFA	0.034	0.042	0.054	0.080
20%	20% Slag	0.038	0.058	0.089	0.133
20%	25% Slag	0.048	0.063	0.077	0.085
25%		0.070	0.130	0.470	X
25%	3% SF	0.028	0.037	0.047	0.103
25%	5% SF	0.032	0.039	0.057	0.073
25%	6% UFFA	0.058	0.068	0.080	0.094
25%	9% UFFA	0.069	0.075	0.099	0.090
25%	20% Slag	0.046	0.064	0.090	0.136
25%	25% Slag	0.047	0.037	0.085	0.237
30%		0.051	0.073	0.098	0.191
30%	3% SF	0.060	0.077	0.092	0.124
30%	5% SF	0.072	0.079	0.087	0.100
30%	6% UFFA	0.053	0.067	0.098	0.110
30%	9% UFFA	0.064	0.063	0.075	0.105
35%		0.046	0.070	0.108	0.161
35%	3% SF	0.042	0.062	0.083	0.135
35%	5% SF	0.026	0.049	0.077	0.087
35%	6% UFFA	0.064	0.070	0.088	0.100
35%	9% UFFA	0.064	0.072	0.088	0.109
40%		0.054	0.074	0.075	0.102
40%	3% SF	0.032	0.037	0.048	0.057
40%	5% SF	0.065	0.080	0.091	0.092
40%	6% UFFA	0.061	0.066	0.080	0.099
40%	9% UFFA	0.067	0.080	0.098	0.144

Before discussing the results of testing on mixtures containing fly ash, it is worth discussing the results of the control mixture. The high-C₃A portland cement (C₃A=11%) (C1) used throughout this research program was selected as it conforms to the requirements set forth in ACI 201-2R, specifically it had a C₃A content greater than 8%. Given the high C₃A content of this cement, it would be expected to exhibit poor sulfate resistance in an aggressive test such as ASTM C 1012. In fact, it does expand

considerably (0.55% after one year and expansions so excessive that measurements were not possible at 18 months due to cracking), but interestingly, significant expansion does not occur until after six months of testing. Expansion rapidly increased shortly after six months, with expansion tripling between six and nine months of testing. The practical relevance of the timing of this expansions should not be overlooked – this cement expanded less than 0.1% after six months, which is less than the expansion limit specified in ACI 201.2R (for determining equivalency for a Type II cement in Class I exposure). In current deliberations within ACI (both in ACI 201 and ACI 318), there have been overtures towards moving towards short-term expansion limits, specifically six-month expansion criteria, in lieu of long-term expansion limits (18-month limits) (Hooton 2007). However, if this highly-reactive cement does not begin to expand considerably until after six months of testing, it certainly cannot be used to evaluate SCMs using a six-month expansion limit. This cement was tested on three different occasions during the course of this project, with similar behavior, and based on discussions with other researchers who are active in sulfate-related research; it is quite common for other high- C_3A cements to exhibit minimal expansions up to six months of testing, with large increases in expansion soon thereafter.

With regard to mixtures containing Class C fly ash, almost all mixtures exhibited faster deterioration and often higher expansions compared to the control specimens (note some mixtures showed little expansion before completely deteriorating, as discussed later in this section). To supplement the tabular representation of the expansion results provided

in Table 3-4 and 3-5, some of the key results are shown graphically next to highlight key trends in behavior.

Figure 3-1 shows the behavior of mortar containing fly ash FA1. This mixture begins to expand earlier than the control, and the onset of expansion occurs earlier as the dosage of fly ash is increased. Only the mixture containing 20% FA1 (by mass replacement of portland cement) was intact at the end of the 18 month test; all other mixtures with higher dosages of FA1 deteriorated prior to this time and subsequent measurements were not possible. The increased storage duration of the mortar bars for 18 months shows that 20% FA1 lasts for that period unlike the other replacements; however, it has the highest ultimate expansion compared to the other replacement levels at one year. Increasing the dosage of FA1 tended to increase the expansions. In fact, the mixture containing 40% FA1 “failed” the aforementioned 0.1% expansion limit at 6 months. The increasing replacement dosages of Class C fly ash deteriorated the mortar bars at faster rates due to greater amounts of reactive phases placed into the system. Similar findings by Tikalsky and Carrasquillo (1993) showed a decrease in sulfate resistance with Class C fly ash.

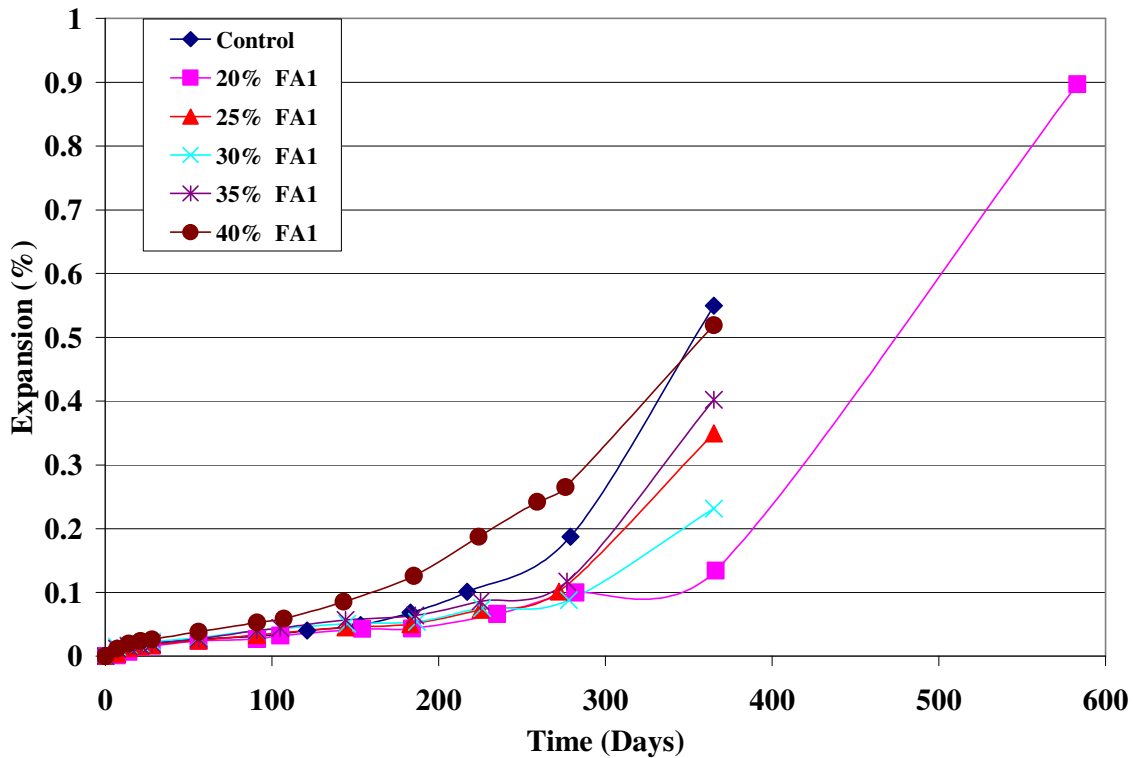


Figure 3-1: Expansions of FA1 at different replacement dosages

All but one of the other Class C fly ashes tested in this program performed similarly to FA1, with increasing fly ash dosages leading to increasing deterioration. The only exception was FA2, which had similar bulk chemistry to FA1, but performed quite differently in ASTM C 1012 testing, as shown in Figure 3-2. Increasing the dosage of FA2 did not result in an increase in expansion, and in fact, after six months, all of the mixtures containing FA2 showed exhibited expansions less than 0.1%. After one year, mixtures containing 20 and 25% FA2 expanded more than the nominal 0.1% expansion limit, mixtures containing 30 and 35% FA2 were approximately at this expansion limit, and the mixture containing 40% FA2 was below this expansion limit. After 18 months, all the mixtures containing FA2 expanded greater than 0.1%.

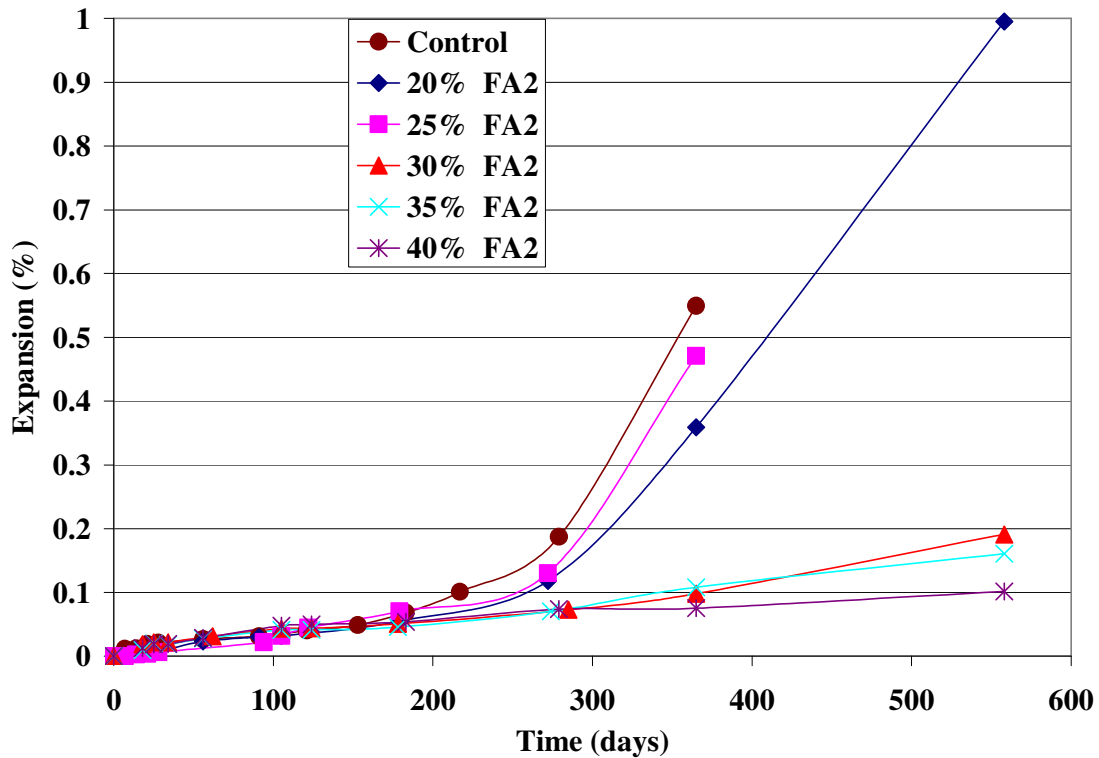


Figure 3-2: Expansions of FA3 at different replacement dosages

Interestingly, the mode of failure of mortar bars containing FA2 was quite similar to that of control specimens specifically high expansions were observed without bulk disintegration of the specimens. Microstructural observations of the mortar bars containing FA2, after exposure to sulfate solution, are described later in section 3.4.1.3.

As previously described, mortar containing fly ashes FA3-FA8 all showed similar behavior to FA1, with increasing deterioration of specimens observed, especially at higher fly ash dosages. In fact, most of the mixtures containing these fly ashes showed significant deterioration without observed expansions, or the specimens completely deteriorated from one measurement age to the next, making it impossible to correlate

failure to a level of expansion. Figure 3-3 illustrates the expansions observed for mortars containing FA8 in which deterioration occurred after minimal times exposed to sulfate solution and without actually passing the nominal 0.1% expansion threshold. Figure 3-4 shows a photograph of mortar bars containing 40% FA8 after only 56 days immersion in sodium sulfate solution in the ASTM C 1012 test. The bars have completely deteriorated, yet expansion was not detected prior to failure. The deterioration of mortar containing FA2 (as well as most of the other high-calcium ashes in this study) is also quite interesting as the mode of failure seems to change as the percent replacement of fly ash for portland cement increases. At lower replacement levels the bars would increase in expansion and break eventually; however at higher replacement levels the bars deteriorate so quickly that they would fail prior to significant expansion. Clearly, this creates yet another interesting challenge when using ASTM C 1012. The technical viability of using expansion limits when testing certain Class C fly ashes clearly comes into question here as the dramatic deterioration occurs without measured increases in expansion. More discussion on the mechanisms responsible for this behavior and the practical implications of such behavior is provided later in this chapter.

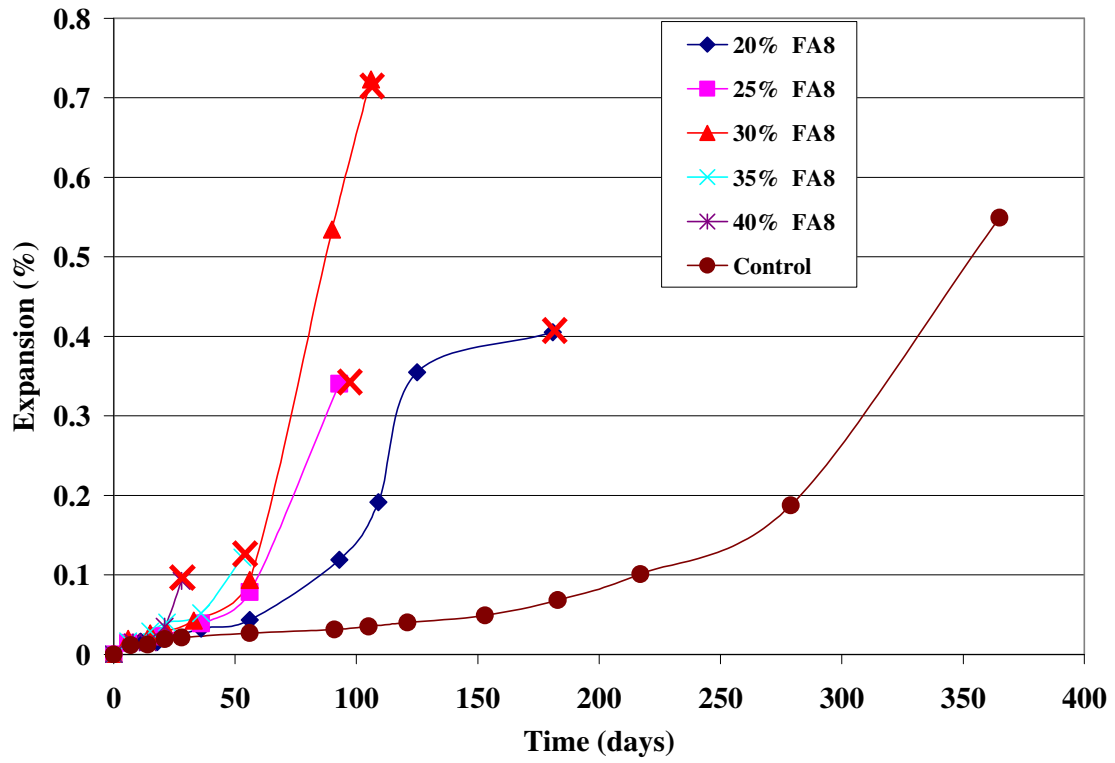


Figure 3-3: Expansion of FA8 fly ash at different replacements



Figure 3-4: Mortar Mixture with 40% FA8 after 56 days in ASTM C 1012 testing

Although the sulfate resistance of most of the Class C fly ashes studied in this program was quite poor, options were identified for improving the durability of mortar or concrete containing these types of ashes. The incorporation of an additional SCM in ternary blends helped to improve the sulfate resistance, as described later in this chapter, and parallel research at the University of New Brunswick showed that the use of higher replacement levels of these ashes (i.e., greater than 60%) actually improved sulfate resistance, as did the addition of small amounts of gypsum (i.e., 0.5% by mass) to mortar mixtures containing these problematic high-calcium ashes. Discussions on the use of high volumes of Class C fly ash or the addition of gypsum are not described herein but will be published at a later date.

3.3.1.2 X-Ray diffraction

X-ray diffraction (XRD) analysis was used to analyze the composition of mortars after 18 months of storage in sodium sulfate solution. Because of the relatively small size of the mortar bars, the entire cross section of a given bar was cut and crushed and subsequently analyzed by XRD. As such, the average composition of a given mortar bar was analyzed, generating data/information on the impact of sulfate attack on bulk or general behavior. As discussed in Chapter 4, detailed evaluations were performed on concrete prisms as a function of depth or distance from sulfate-rich environment, and such analyses provide a more quantitative assessment of the progressive attack that occurs when concrete is exposed to external sulfates. Nevertheless, the data generated from XRD analyses of mortar bars provide an insightful means of determining what hydration products are being attacked and what reaction products are being formed. Furthermore, by applying

advanced semi-quantitative XRD techniques, specifically Rietveld analysis, it is possible to measure the relative amounts of hydration or reaction products present within a given specimen.

Table 3-6 provides semi-quantitative Rietveld analysis of mortar bars containing Class C fly ash after 18 months of sulfate exposure (ASTM C 1012). For mortar mixture 25% FA2 after 12 months, the bars had expanded by 0.47%; however all the bars had broken and were not measurable at 18 months. Semi-quantitative analysis of these specimens identified ettringite as the primary constituent. Similar results were found for mortar bars containing the other Class C fly ashes after 18 months of testing. These large amounts of ettringite forming within the bars are possibly too high due to the ratio of cement to sand in the prepared mortar bar. The amount of ettringite formation from the initial amount of cement in the mortar bar could not be greater than the percentage of sand. This high amount of ettringite could have contributed to the full deterioration of these mortar bars that fell apart within the storage container. These deteriorated bars were removed from the storage container and not hammered due to the bars had broken into small pieces. Although the classic symptoms of sulfate attack were observed in mortar bars containing each of the Class C fly ashes, specifically the presence of ettringite and gypsum and the general reduction in portlandite and monosulfate concentration, it was not possible to distinguish major differences between the different fly ash-containing mortars or to elucidate major differences for a given fly ash as the dosage of fly ash was varied. The inability to differentiate between different fly ashes and dosages was likely due to the fact

that the specimens had undergone such high levels of distress prior to analyses and/or the method of analyzing the entire cross-section of a given mortar bar does not allow for detailed quantification of distress. More detailed evaluations of concrete affected by sulfate attack are described in Chapter 4, where concrete prisms, because of their larger size, were analyzed as a function of distance from the sulfate solution using profile grinding and subsequent XRD analysis.

Table 3-6: Semi-quantitative Rietveld analysis of select mortar mixtures at 18 months

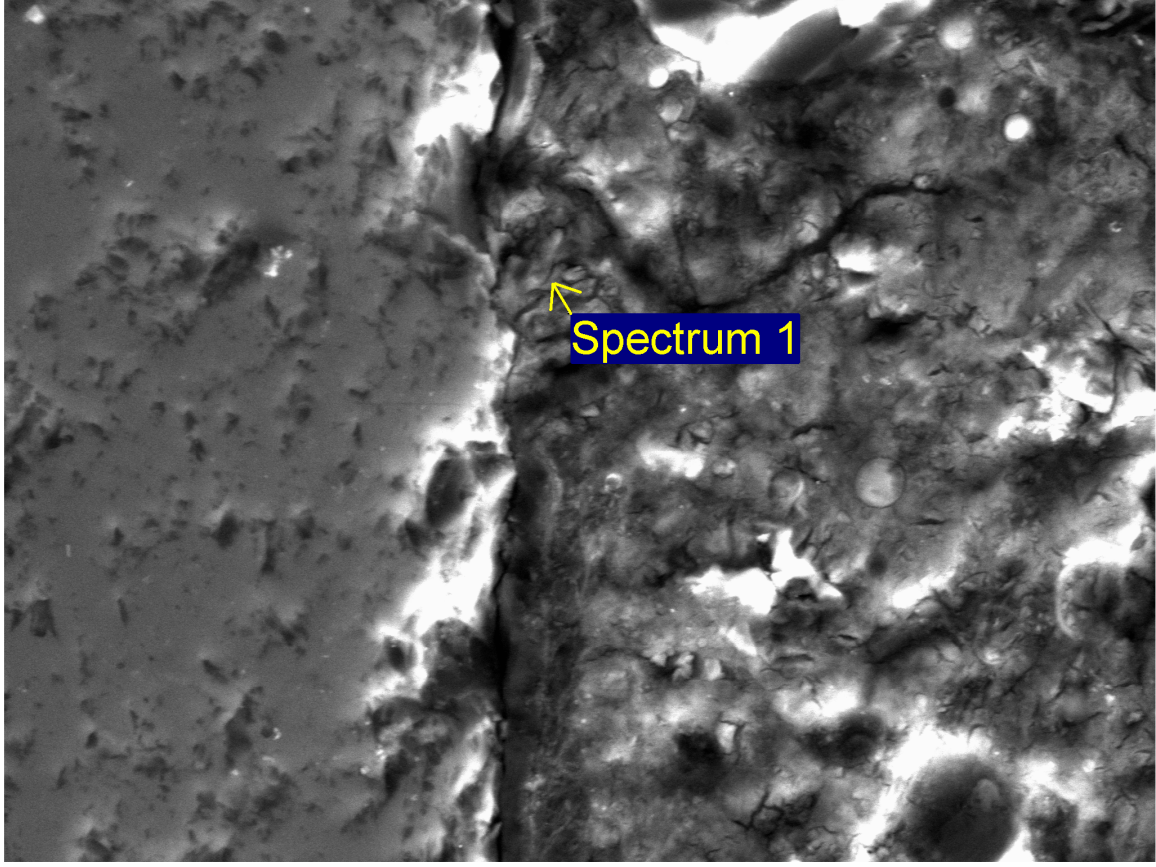
Mixture	Ettringite (%)	Gypsum (%)	Monosulfate (%)	Portlandite (%)
20% FA2	48.13	8.62	0.02	0.38
25% FA2	64.59	5.02	0.09	0.55
20% FA3	48.72	5.13	0.14	0.66
25% FA3	32.81	7.85	1.41	3.33
30% FA3	50.66	2.1	0.06	0.06
30% FA4	49.12	3.28	0.42	0.59
25% FA6	45.92	3.35	0.95	3.83
30% FA6	41.64	1.52	1.38	5.39
35% FA6	29.17	3.47	5.1	6.4

3.3.1.3 Scanning electron microscopy

In order to better understand the mechanisms occurring with Class C fly ash and sulfate attack, scanning electron images with energy dispersive spectroscopy (EDS) were taken for analysis. Figure 3-5 is a SEM image of 25% FA2 after 18 months of storage in sodium sulfate solution. Throughout the sample, ettringite pockets are found in the paste. Ettringite was more prevalent in the paste than around the aggregates. The selected area in the image was chosen for EDS analysis. EDS provides the chemical analysis of this area comprising with amounts of Ca, S, and Al in this region and EDS confirms that these

pockets are ettringite. Small amounts of gypsum throughout the sample were identified with EDS. With expansion initiating several months before the analysis of these specimens, it is possible that gypsum may have formed earlier and subsequently converted to ettringite.

Comparing FA1 and FA2 at lower replacements, 20% FA2 had expanded early compared to 20% FA1 which expanded after 1 year. Figure 3-6 is a SEM image of 20% FA1 after 18 months of storage in sodium sulfate. There are many large bands of gypsum that surround many of the aggregates in the system. There was more gypsum observed around aggregates and very little ettringite was detected within the paste. The EDS spectrum shows large amounts of calcium (Ca) and sulfur (S), reflecting gypsum in the system. In parts of the mortar bars, it is evident that gypsum could be converting to ettringite. The late expansion of 20% FA1 is noticed from the conversion of gypsum to ettringite in the sample. At 20% FA1 replacement there is less reactive calcium aluminates than compared to 40% which may suggest attack is occurring more on the calcium hydroxide in the 20% FA1 mortar bars and could contribute to the later formation of ettringite from its conversion from gypsum. Figure 3-7 shows this possible conversion in an area of ettringite and gypsum formed in the same area. Gypsum and ettringite are in this same area as seen in the EDS spectrum.



50µm

Electron Image 1

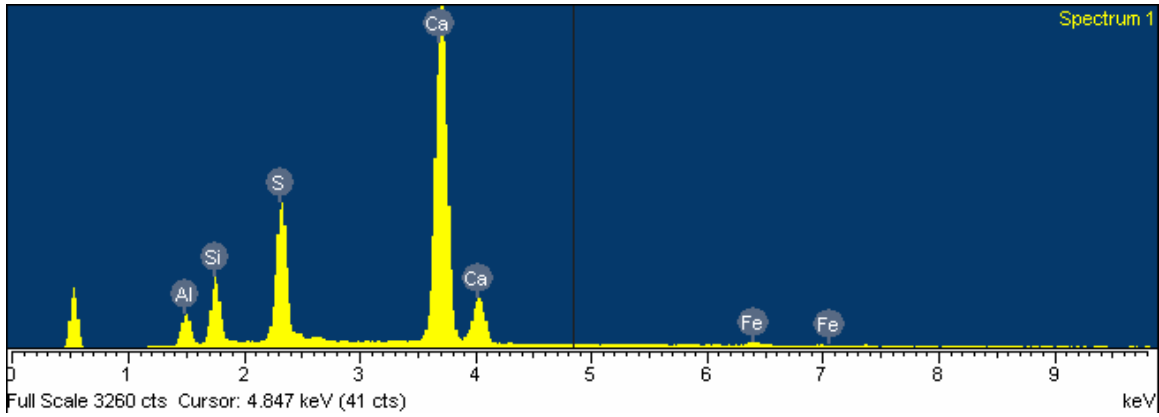


Figure 3-5: SEM image and EDS spectrum of 25% FA2 after 18 months storage in sodium sulfate solution showing ettringite pockets.

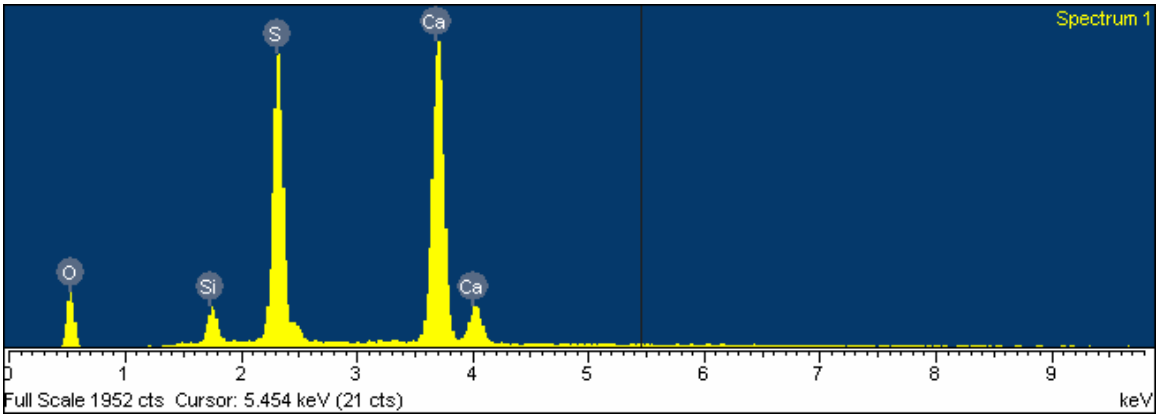
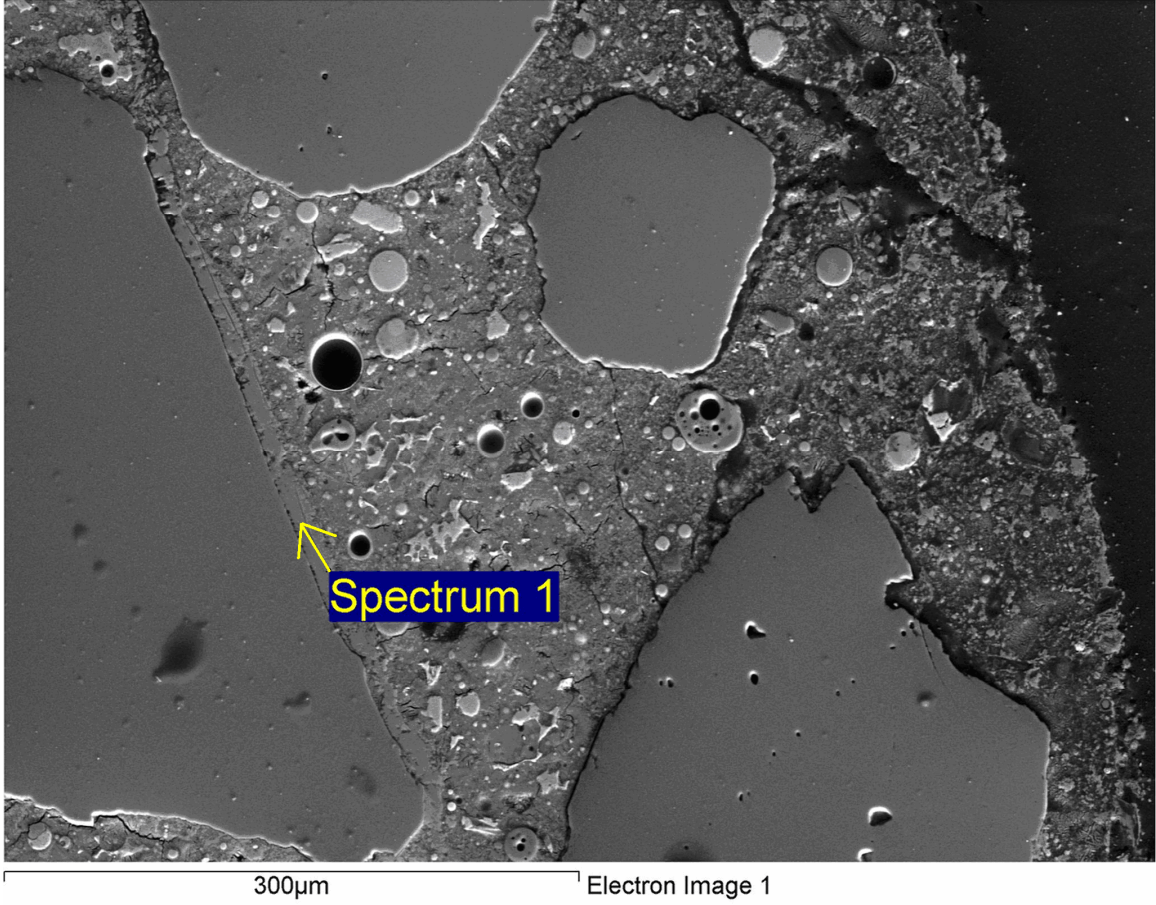


Figure 3-6: SEM image and EDS spectrum of 20% FA1 after 18 months of storage showing gypsum formation around aggregates

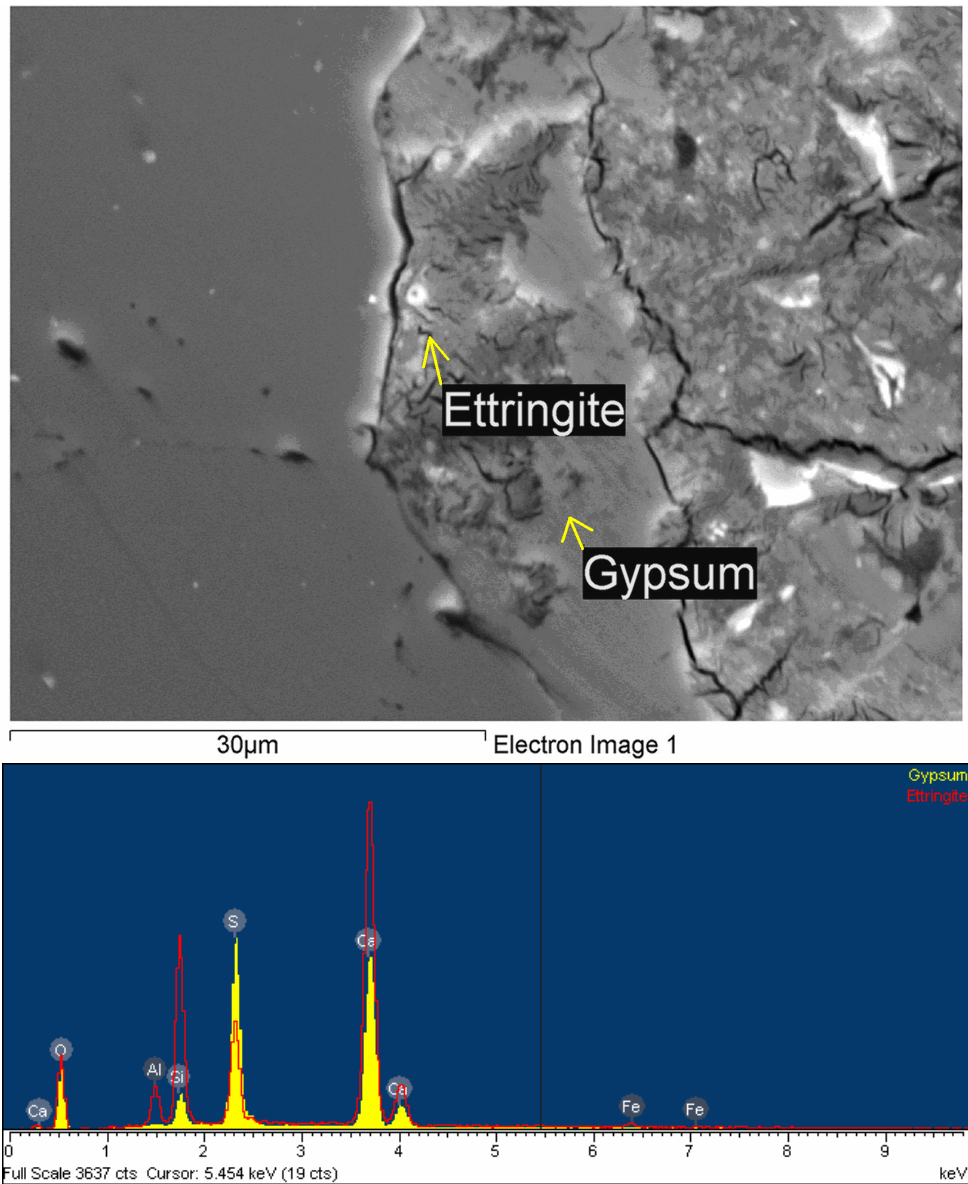


Figure 3-7: SEM image and EDS spectrum of 20% FA1 mortar after 18 months storage in sodium sulfate showing possible conversion of gypsum into ettringite.

At the higher end of the replacement dosages, 40% FA1 and 35% FA2 were analyzed to determine the differences between the two fly ash responses. Figure 3-8 and 3-9 show SEM and EDS analyses of 40% FA1 and 35% FA2. In the SEM images of 40% FA1, there are many cracks throughout the hydrated paste. Ettringite formation is visible

throughout the paste, with small amounts of gypsum near aggregates. The EDS spectrum confirms the small area of gypsum occurring near the aggregate. In comparison, 35% FA2 has gypsum formation lining aggregates and very small amounts of ettringite. Gypsum deposits are found lining aggregates and in some cases branching into the paste and connecting to other aggregates. The bands are similar to ettringite filled cracks often observed in delayed ettringite formation, but in this case the cracks are filled with gypsum. The gypsum bands that form around the aggregates have not converted to ettringite possibly due to aluminates from monosulfoaluminate not being available. In addition, the FA2 may not present any reactive calcium aluminates that may react at later times to react with gypsum to form ettringite. There are a few small areas that have ettringite filled voids within the sample. The bulk chemistries of these two ashes were quite similar, but subsequent quantification of the glassy phases showed distinct differences in composition, as described later in this chapter.

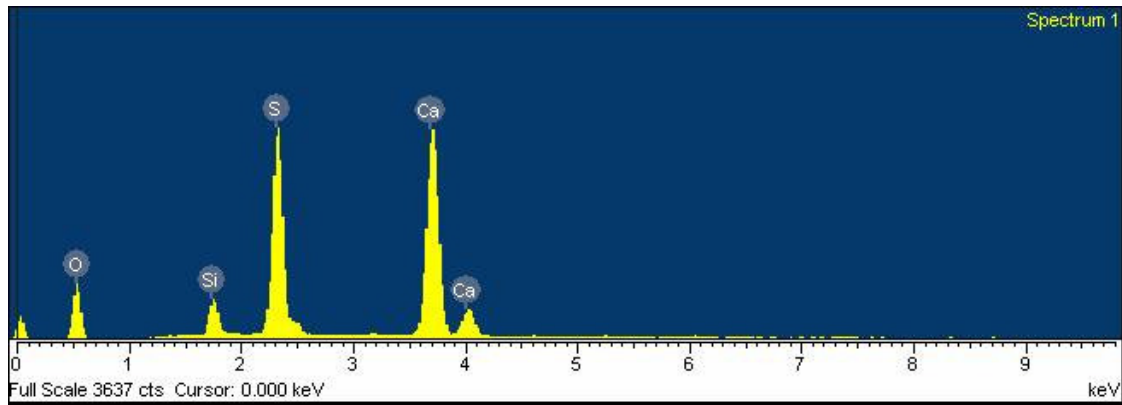
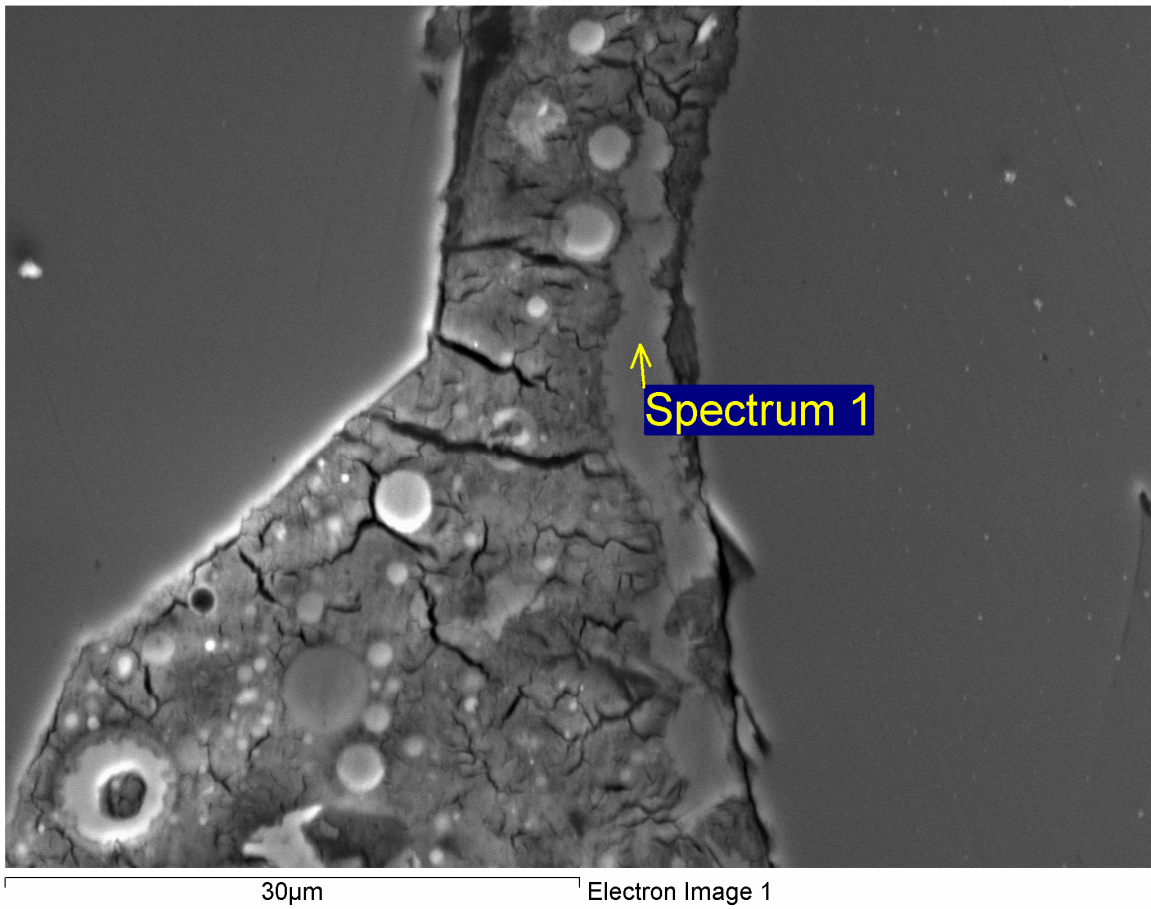


Figure 3-8: SEM image and EDS spectrum analysis of 40% FA1 after 18 months in sodium sulfate solution ettringite and gypsum formations.

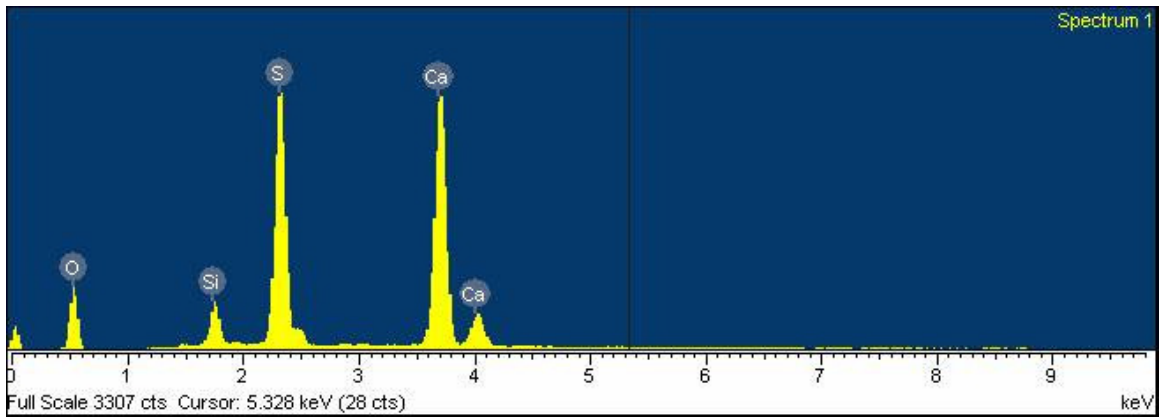
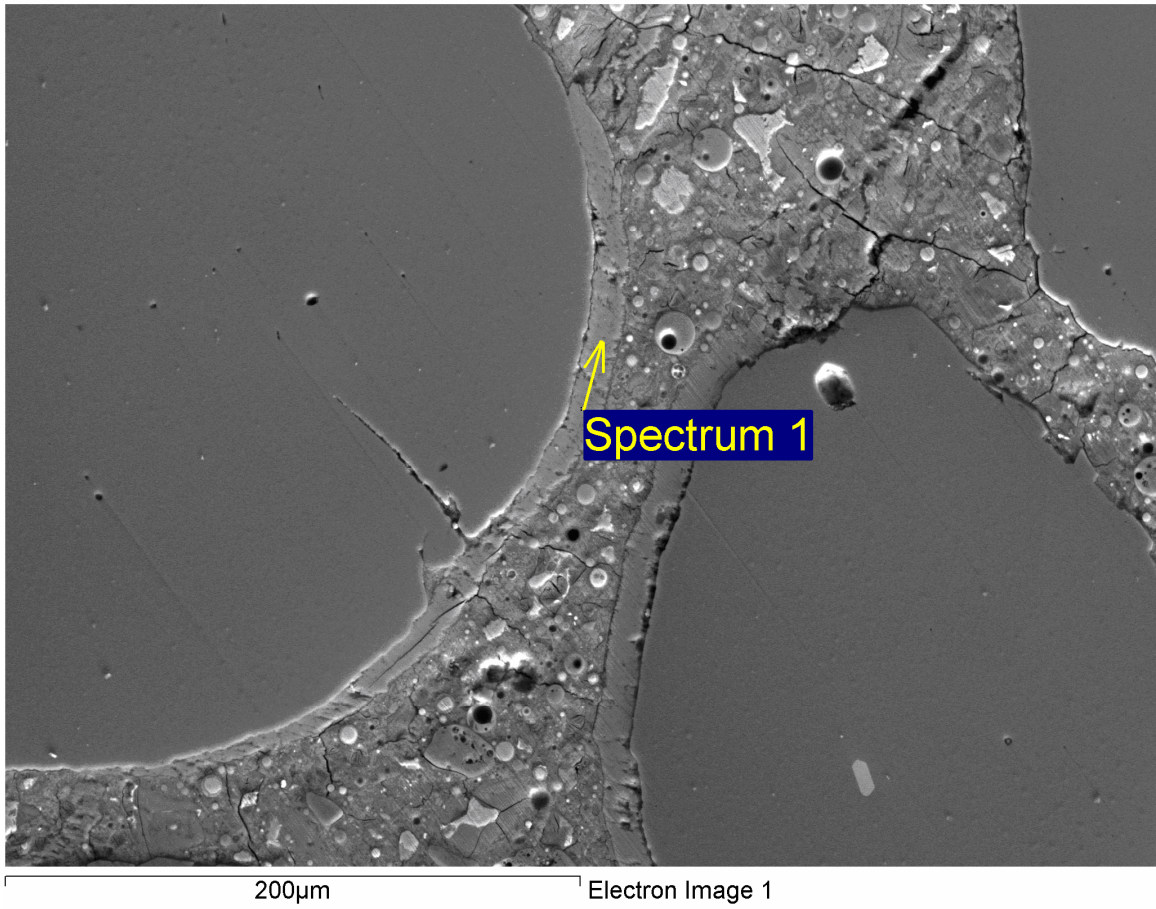


Figure 3-9: SEM image and EDS spectrum analyses of 35% FA2 after 18 months of storage in sodium sulfate showing gypsum formation around aggregates

3.3.2 Ternary blends

This section describes the results of ASTM C 1012 testing performed on mortar mixtures containing ternary blends of Class C fly ash plus an additional SCM (silica fume, ultra fine fly ash (UFFA), or GGBFS) For convenience and to allow for direct comparison between the performance of ternary blends and mixtures containing only Class C fly ash, the expansion data were previously included in Table 3-4. The majority of testing reported herein involved ternary blends including FA1, FA2, or FA3.

3.3.3.1 Expansions

Twenty four ternary blends were made with FA1, FA2 and FA3 at replacements between 20 and 40%. At all replacement levels, 3 and 5% silica fume, and 6 and 9% UFFA were used as a ternary blends. At 20 and 25% Class C fly ash replacements, 20 and 25% slag replacements were used. Replacement dosages of 30% Class C fly ash did not include slag as part of the ternary blend.

When adding either silica fume or ultra-fine fly ash to mortar containing FA1, significant improvements in sulfate resistance were realized. All of these ternary blends reduced expansions at six months below 0.1% expansion criteria at 6 months, and the majority satisfied the aforementioned requirements for Class 2 equivalent sulfate resistance, as per ASTM C 1012. At 18 months, ternary blends at the lower replacement levels of Class C fly ash performed worse than those at higher replacement dosages. In almost all cases,

ternary blends with 6 and 9% UFFA exhibited excellent sulfate resistance. A surprising trend noticed was an increase in protection of ternary blends as the replacement levels of FA1 increased, which was the opposite when FA1 was used separately (without silica fume or ultra-fine fly ash). Figures 3-10 and 3-11 provide the ternary blends for 20 and 40% FA1. The decrease in expansion with ternary blends at higher replacement dosages may be related to reductions in permeability, which slow down and reduce the ingress of sulfate solution into the bars. GGBFS performed well in a ternary blend with either 20 or 25% FA1 with 25% GGBFS. The performance of GGBFS is substantial as it usually takes at least a 50% replacement dosage to control sulfate attack. The addition of Class C fly ash and GGBFS provides a combination that removes nearly 50% of the cement.

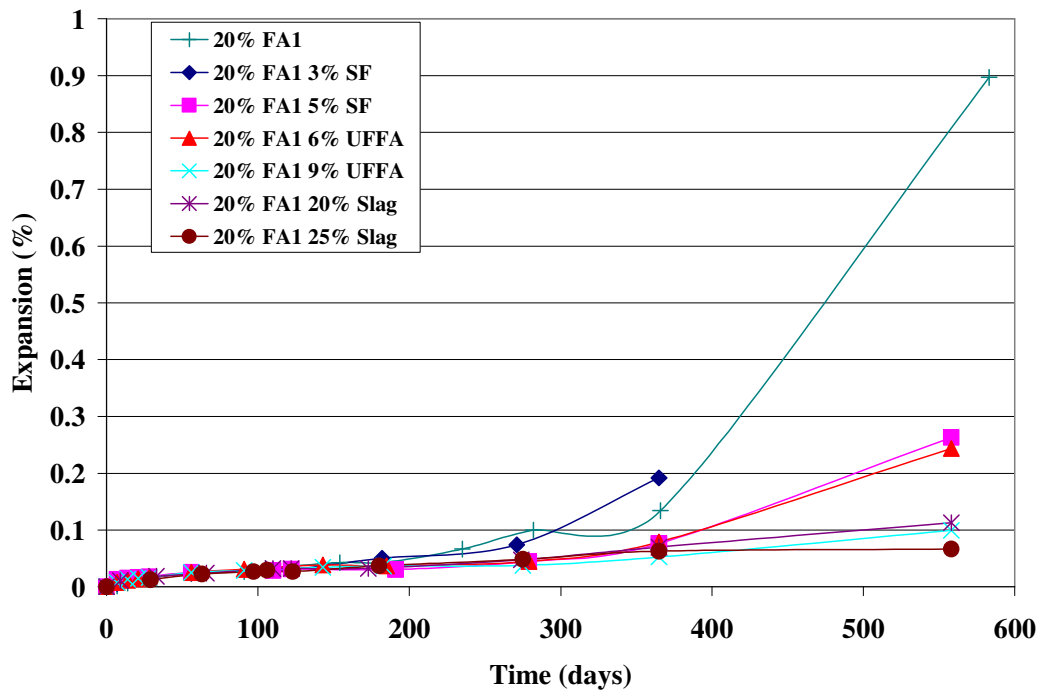


Figure 3-10: Mortar mixtures with 20% FA1 and ternary blends

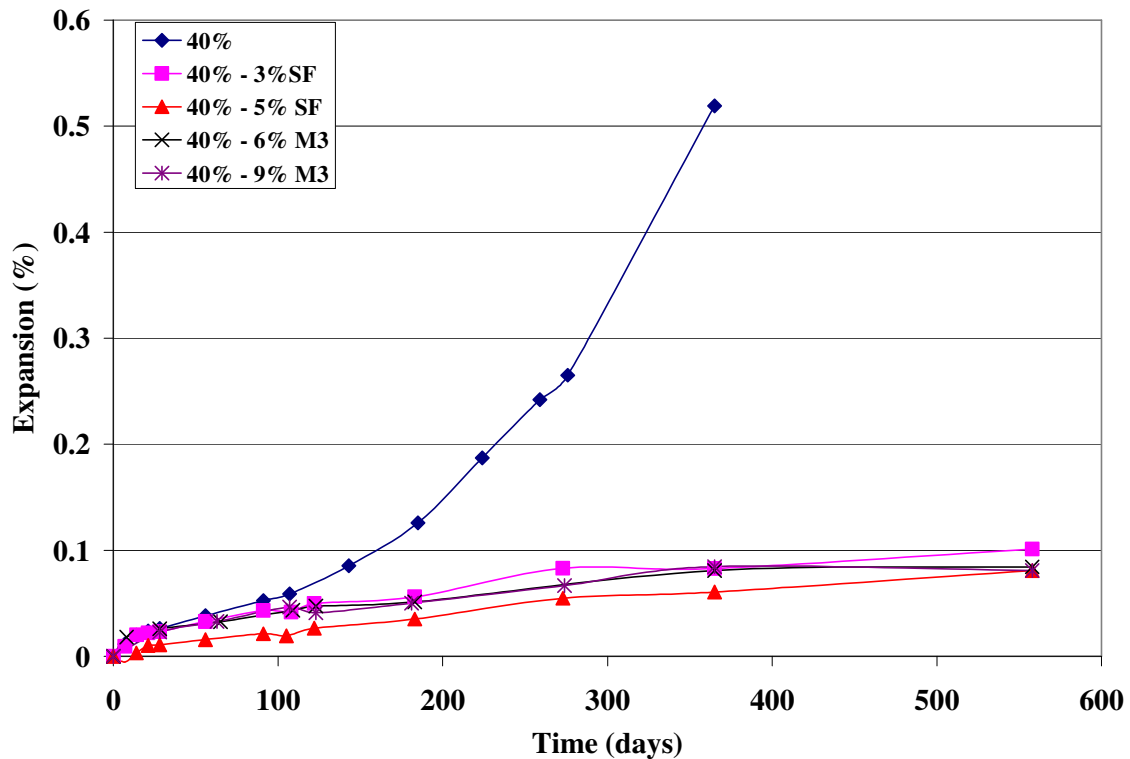


Figure 3-11: Mortar mixtures with 40% FA1 and ternary blends

Ternary blends with FA2 performed well at 6 months and at 1 year. All the ternary blends passed the 6 month criteria of 0.1% expansion; however, at 1 year three mixtures containing UFFA barely failed at 0.1%. At 18 months, the performance of ternary blends declined slightly. Many of the mixtures that failed had expansions close to 0.1% expansion. Although the sulfate resistance was improved through the use of ternary blends, FA2 did not respond as well as FA1, and it was difficult to reduce expansions to meet the criteria set forth for Class 3 exposure, as per ACI 201.2R.

Ternary blends cast with FA3, a fly ash that failed rapidly when tested by itself, performed similarly to ternary blends containing FA1 in that as the replacement levels of Class C fly ash increased, the performance of ternary blends improved. Silica fume at a 3% dosage in ternary blends did not perform well at any replacement level, but did perform better than only using FA3. In all cases, UFFA performed better than silica fume. Mortars with 40% FA3 disintegrated after 6 months while all the ternary blends were still intact and measurable at 18 months. Slag did not perform as well in ternary blends with FA3.

3.3.2.2 X-Ray diffraction

X-ray diffraction analyses were performed on a wide range of mortar specimens containing ternary blends, with samples scanned from 5° to $65^{\circ} 2\theta$, at a 0.01° step size per 2 seconds. Semi-quantitative Rietveld analysis was conducted on all samples as described in section 3.2.3. As previously described in Section 3.4.1.2, abundant amounts of ettringite were detected in mixtures containing Class C fly ash after exposure to sulfate solution. Ettringite concentrations in mixtures containing only Class C fly ash were found to range between 30 and 65% of the total specimen mass in deteriorated specimens. When sulfate resistance was achieved through the use of ternary blends, the composition of the mortar bars after testing in ASTM C 1012 changed significantly. Table 3-7 provides semi-quantitative results from ternary blends with FA1 and FA2. For example, 25% FA2 with 9% UFFA, expanded only 0.09% at 18 months, meeting all

expansion limits set forth by ACI 201.2R, even for the most severe exposure class. Semi-quantitative Rietveld analysis yielded an ettringite content of 26%, which is far less than the 65% shown in Table 3-6. The gypsum content was the same between mortars; however only trace amounts of monosulfate and portlandite were found in 25% FA2 mortars. All of the monosulfate and calcium hydroxide had converted to ettringite in the 25% FA2 bars. The ternary blends show greater monosulfate and portlandite content after 18 months. The silica fume, UFFA, and slag create less permeable system. In addition these SCMs create a greater pozzolanic reactivity that does not allow growth of deleterious products to form in the transition zone around aggregates.

Table 3-7: Semi-quantitative Rietveld analysis of ternary blends with FA1 and FA2

Mixture	Ettringite (%)	Gypsum (%)	Monosulfate (%)	Portlandite (%)
25% FA1 3% SF	43.51	5.83	1.41	5.24
25% FA1 20% Slag	39.08	6.46	1.53	3.35
25% FA1 25% Slag	25.85	12.43	4.2	1.05
30% FA1 3% SF	65.7	6.36	0.32	0.57
30% FA1 5% SF	44.88	4.6	0.97	2.67
30% FA1 9% UFFA	23.15	5.04	3.15	3.44
35% FA1 5% SF	54.64	5.08	1.11	2.37
35% FA1 6% UFFA	34.33	5.93	0.94	1.73
35% FA1 9% UFFA	37.5	6.5	3.46	2.74
20% FA2 3% SF	26.07	7.14	4.75	7.09
20% FA2 5% SF	35.26	8.84	1.86	5.17
20% FA2 6% UFFA	28.22	5.98	4.33	7.16
20% FA2 9% UFFA	40.29	7.27	3.15	3.45
20% FA2 20% Slag	34.44	6.26	4.17	3.59
20% FA2 25% Slag	25.32	8.55	4.16	3.73
25% FA2 6% UFFA	25.18	6.57	4.11	5.64
25% FA2 9% UFFA	26.17	6.31	3.98	4.09
25% FA2 3%SF	30.66	8.08	7.21	5.89
25% FA2 5%SF	33.41	10.12	0.22	0.11
25% FA2 20% Slag	41.28	7.14	1.3	0.43
25% FA2 25% slag	38.69	5.4	0.93	0.01

3.3.2.3 Scanning electron microscopy

Figure 3-12 shows an SEM image and EDS spectrum of 40% FA1 with 5% SF. In the image, a long band of gypsum runs along the sample's edge. This band runs along the entire sample along the edge of the sample nearest to the sodium sulfate solution. The Ca and S in the EDS spectrum confirm the gypsum band in the image. In comparison with 40% FA1 in Figure 3-8, there is much less ettringite in the paste and around aggregates. Semi-quantitative XRD results show only 0.8% monosulfate in the 40% FA1 with 5% SF sample which suggests that gypsum has not converted to ettringite. Ternary blends with 6 and 9% UFFA also did well in suppressing expansion, even at 18 months. The use of these ternary blends significantly reduces the permeability of mortar, minimizing the ingress of sulfates and preventing chemical alterations of the matrix. This physical effect is also accompanied by the chemical effect of the pozzolanic reaction, resulting in lower CH contents and concomitant reductions in attack on this vulnerable phase.

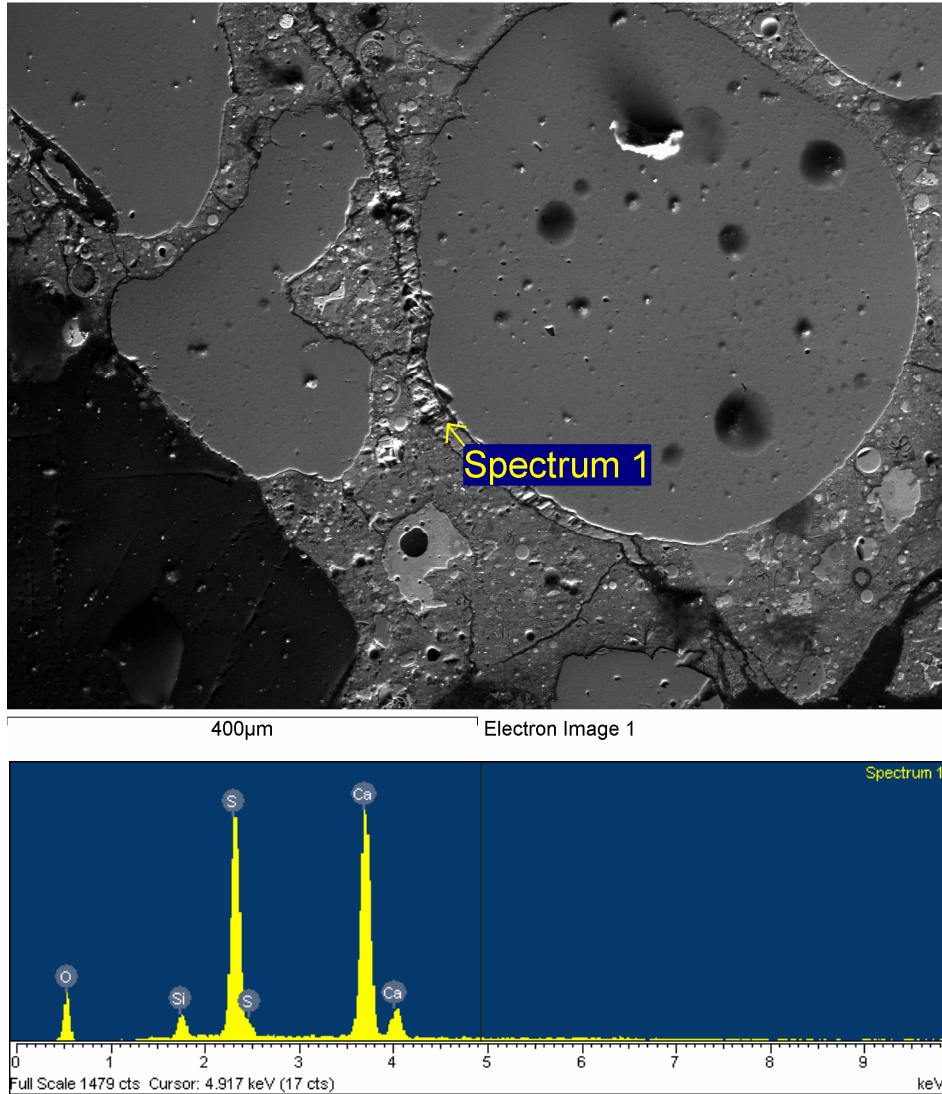


Figure 3-12: SEM image and EDS spectrum of 40% FA1 with 5% SF after 18 months of storage in sodium sulfate storage showing a gypsum band along the samples edge and around aggregates

3.3.3 Fly ash investigation

The bulk chemical compositions of the Class C fly ashes used in this study were provided in Table 3-1. However, as previously described, fly ashes with similar chemical compositions exhibited starkly different behaviors when tested using ASTM C 1012. As such, it is necessary to go beyond chemical composition and to try to better quantify the

mineralogy of fly ash, including both the crystalline and amorphous phases. Figure 3-13 shows the XRD quantitative Rietveld analyses for FA1, FA2, and FA8. FA1 and FA2 showed similar crystalline phase compositions, and these were quite different from the crystalline composition of FA8.

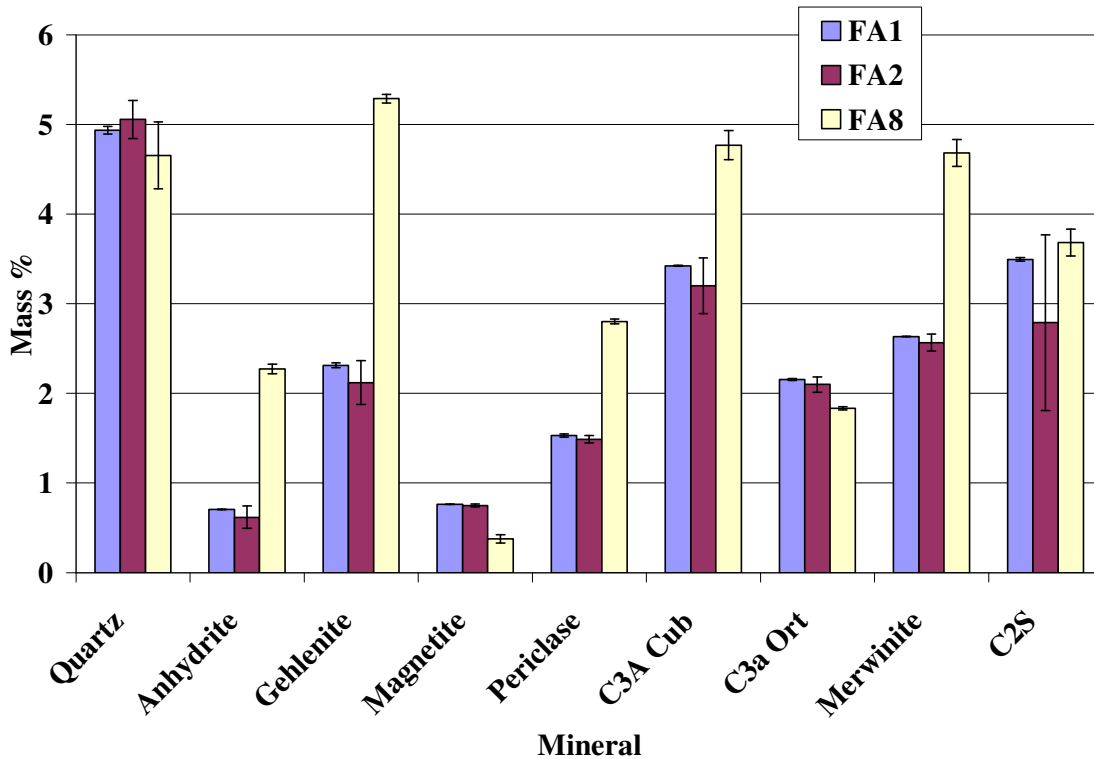


Figure 3-13: Quantitative XRD Rietveld analyses for FA1, FA2, and FA8.

As previously described in Section 3.3.1, FA1 and FA2 exhibited drastically different behavior in ASTM C 1012 testing, despite similarities in crystalline compositions, suggesting strongly that one must evaluate the amorphous or glassy phases to determine if the differences in behavior can be elucidated. FA8, which was one of the worst

performers in ASTM C 1012, was found to have significant differences in its crystalline content and composition, when compared to FA1 and FA2.

A detailed evaluation of the amorphous or glassy phases is currently underway through the use of scanning electron microscopy to analyze the bulk and glassy phases of the ashes. The chemical analysis of the glassy phases are then plotted onto a calcia-alumina-silica ternary phase diagram. A correlation between the composition of the reactive glassy phases and the sulfate resistance of Class C fly ashes has been found and will be reported in future publications. Fly ashes that exhibited the worst sulfate resistance in ASTM C 1012 testing show a tendency towards containing more calcium aluminates in the glassy phase. This is especially evident for FA8, which exhibited the most significant deterioration in ASTM C 1012. Research at the University of New Brunswick has linked the composition of the glassy phase to early hydration products and ultimately to the mechanism of failure when mortar containing Class C fly ash is exposed to sulfate solutions (Raj and Drimalas 2007)

3.4 Summary

This chapter summarized a comprehensive study in which a wide range of high-calcium fly ashes were evaluated to determine their sulfate resistance when tested according to ASTM C 1012. All tests were conducted for 18 months (except for those specimens that failed prior to this age) in order to generate that can be used as inputs for selecting preventive measures for ensuring sulfate resistance as per ACI 201.2R. The following are significant findings from this chapter

High-calcium fly ashes evaluated in this study showed poor sulfate resistance with a decrease in performance as the replacement dosages increased. The addition of reactive phases caused the mortars to deteriorate.

- The formation of ettringite was determined to cause the deteriorating expansions occurring in the mortar bars. Calcium hydroxide and monosulfate were depleted in these systems to form gypsum and ettringite.
- The incorporation of a second SCM (silica fume, UFFA, or GGBFS) helped to restore sulfate resistance. This can allow agencies to use ternary blends in areas that may not be able to use Class C fly ash in sulfate prone areas. The use of these second SCMs in the mixtures created a less permeable system which slowed down the progression of attack. The increased pozzolanic activity from the additional SCMs helped prevent further deterioration.
- Mechanistic studies using XRD and SEM identified the key modes of failure, such as ettringite formation, being greater in specimens with only Class C fly ash. Monosulfate and portlandite was also depleted from attack in these same mortar bars.
- Lastly, detailed evaluations of the mineralogy of Class C fly ashes were performed using Rietveld analyses for the crystalline phases and SEM (and EDS) analyses for the glassy phases, and work at UNB has found a link between the mineralogy of the glassy phase and sulfate resistance. The glassy phase has more reactive calcium aluminates which tend to destruct the mortars

containing these fly ashes. The fly ashes that behave worse in sulfate environments tend to have more of these reactive calcium aluminates.

Chapter 4. Evaluation of Concrete Prisms in Various Sulfate Solutions including Outdoor Exposure Site Testing

4.1 Introduction

ASTM C 1012 is the most common test method used to predict sulfate attack and it is specified in many guidelines for the evaluation of external sulfate attack. However, there is a lack of correlation between standard test methods and concrete subjected to sulfate-bearing soils in-situ. The research described in this chapter aims to help bridge the gap between laboratory and field performance of concrete subjected to external sulfates. Before describing this work, a brief background is presented on some past work aimed at addressing this same linkage between the laboratory and the field.

Based on the recent findings of laboratory and field evaluations, there seems to be a disconnect between the performance of concrete exposed to external sulfates in the laboratory (where specimens are stored in sulfate solutions at constant temperature) and concrete exposed to realistic field conditions, where evaporation fronts and concentration gradients exist and where temperature fluctuations are commonplace. To attempt to understand these key differences in behavior and to attempt to better correlate standard laboratory tests with field performance, a comprehensive research program was initiated at the Concrete Durability Center (CDC) at the University of Texas at Austin, including the development of an outdoor sulfate exposure site and the evaluation of concrete mixtures subjected to different sulfate solutions at this outdoor site and in parallel laboratory tests. Mechanistic work is also presented that aimed to identify the cause and

extent of distress of the various concrete specimens exposed to the different test conditions.

4.2 Experimental methods

4.2.1 Materials

4.2.1.1 Aggregates

A crushed limestone coarse aggregate and a manufactured limestone sand were used in all concrete mixtures. These aggregates were procured from central Texas sources, and prior testing at the CDC found these aggregates to be non-reactive with regard to alkali-silica reaction (ASR). It was deemed important to select aggregates not susceptible to ASR to ensure that any damage occurring either in the laboratory or in the outdoor exposure site could be attributed solely to sulfate-induced distress. For the mortar mixtures described in this chapter, as per ASTM C 1012, a standard graded ASTM C 778 Ottawa sand was used for all mixtures.

4.2.1.2 Cement

Three portland cements were used in this research, all obtained from sources within Texas. A Type I cement (C1), a moderate sulfate resistant Type I/II cement (C2) and a sulfate resistant Type V cement (C5) were used for both the laboratory evaluations and the outdoor exposure site testing. Table 3-1 in Chapter 3 provides the chemical composition of the cements. The C_3A contents for the three cements were 3%, 7%, and 11%, respectively.

4.2.1.3 Supplementary cementing materials

One source each of Class C fly ash and Class F fly ash (as per ASTM C 618) and one source of silica fume, conforming to ASTM C 1240, were used in the concrete mixtures evaluated in the outdoor sulfate trenches. Tables 3-2 and 3-3 in Chapter 3 provide the chemical compositions of the SCMs. The aforementioned Class C fly ash (FA1) was shown to exhibit poor sulfate resistance when testing using ASTM C 1012, as described in Chapter 3. The Class F fly ash (FA9) has been shown in previous work to exhibit good sulfate resistance and is included herein to allow for comparisons of Class C fly ash (and ternary blends) to a fly ash source with known sulfate resistance. For convenience, this chapter refers to these ashes as “Class C fly ash” and “Class F fly ash” when referring to FA1 and FA 9, respectively.

4.2.2 Outdoor sulfate exposure site design and test procedure

The development of an outdoor sulfate exposure site began in 2005 at the Concrete Durability Center (CDC) in Austin, Texas. Figure 4-1 shows the outdoor sulfate exposure site. The design of this site was based loosely on the PCA site in Sacramento, but various modifications were employed to evaluate a more comprehensive range of exposure conditions and test parameters. Detailed information on the key features of this site in Austin, Texas is presented next.



Figure 4-1: Outdoor sulfate exposure site located in Austin, TX. From left to right, the trenches contain calcium sulfate, sodium sulfate and magnesium sulfate.

4.2.2.1 Exposure site design

The exposure site consists of three 13 ft x 16 ft (4 m x 5 m) trenches, each having a depth of 18 in (450 mm). After excavation, a 0.045 in (1.14 mm) ethylene propylene diene terpolymer (EPDM) pond liner made by Firestone was placed for confinement of sulfates in each trench. A sandy loam used for residential foundations in Austin, Texas was used as the fill material in the trenches, filled to a depth of 8 in (200 mm). Testing of this loam confirmed sulfates were not present. Sulfate solutions (sodium, magnesium and calcium) were then added to each of the three trenches. The trench containing sodium sulfate was filled with solution to obtain a concentration of 5% sodium sulfate, which matches the sulfate concentration used in ASTM C 1012. For comparison, the PCA site (Stark 1989) contained a 10% sodium sulfate solution, but this concentration was deemed to be too aggressive and not indicative of realistic soils. The other two trenches for the current

study were matched to the total sulfate concentration contained in the sodium sulfate trench, but contained calcium sulfate and magnesium sulfate. The sulfate solutions were initially kept at a height 3 in (75 mm) above the soil. The trenches were subsequently monitored and allowed to evaporate until the solutions just reached the soil level and were then filled with water. As such, the concentrations of sulfates in the trenches are at a minimum when the levels are at their highest (and initial) level and at a maximum when the water has evaporated to the point where the solution reaches the soil level.

For the magnesium and sodium sulfate trenches, the high solubility of these salts allowed for easy filling of the trenches. For example, for the sodium sulfate trench, anhydrous sodium sulfate was simply dissolved in water and added to the trench to yield a concentration of 5% sodium sulfate in the water-filled pores of the soil. A similar approach was followed for magnesium sulfate, but in this case, the *sulfate ion* concentration was matched to that of the sodium sulfate trench, thereby allowing for a more direct comparison between the two trenches. For the gypsum trench, the limited solubility of gypsum did not allow for complete dissolution of the calcium sulfate into water. Rather gypsum was added to water until it precipitated out of solution (1440 ppm), and additional gypsum powder was added to the soil to reach the target concentration (same sulfate ion concentration as sodium sulfate trench) and mixed thoroughly. This, in essence, is what is encountered in heavily concentrated gypsum soils, and it helps to explain why high extraction ratios tend to result in higher values of gypsum in the extracted solution.

4.2.2.2 Concrete prism testing regime

Thirty concrete mixtures, each comprised of 24 concrete prisms, were cast for placement in the outdoor sulfate exposure site. Details of these concrete mixtures are provided later in this chapter. Concrete prisms with dimensions of 3 in x 3 in x 11.25 in (75 mm x 75 mm x 285 mm) were selected, rather than larger prisms used at the PCA exposure site, to allow for expansion measurements, mass loss, and dynamic modulus testing in standard laboratory equipment at the CDC. The prisms were demolded 24 hours after casting. After demolding, the prisms were cured in a fog room (73 °F (23 °C), 100% RH) for 28 days. At 28 days of age the prisms were placed in either the outdoor exposure site or in a modified ASTM C 1012 testing regime.

Figure 4-2 shows the testing program and the disposition of the 24 concrete prisms per mixture. A total of 15 prisms were stored in the sulfate exposure site, either completely submerged or stored vertically with 6 in (150 mm) of the prism submerged in the sulfate-bearing soil. The other 9 prisms were placed in a modified ASTM C 1012 storage condition in solutions containing calcium, sodium, or magnesium sulfate (matched to the same concentration as trenches containing same solution). Because larger prisms were used than those typically used in ASTM C 1012, larger storage containers with the appropriate ratio of the volume of sulfate-bearing solution to volume of concrete were necessary. To address the issue of the limited solubility of gypsum, solutions were prepared with the target sulfate concentration (to match the sulfate ion concentration of the 5% sodium sulfate solution), resulting in large amounts of sulfate precipitating out of solution. The specimens stored in this solution were elevated off of the bottom of the

container at a height sufficiently high to prevent the bars from being in contact with the precipitant. As such, the bars were stored in a solution surrounded by saturated gypsum solution but the bars were not in intimate or direct contact with “solid” gypsum.

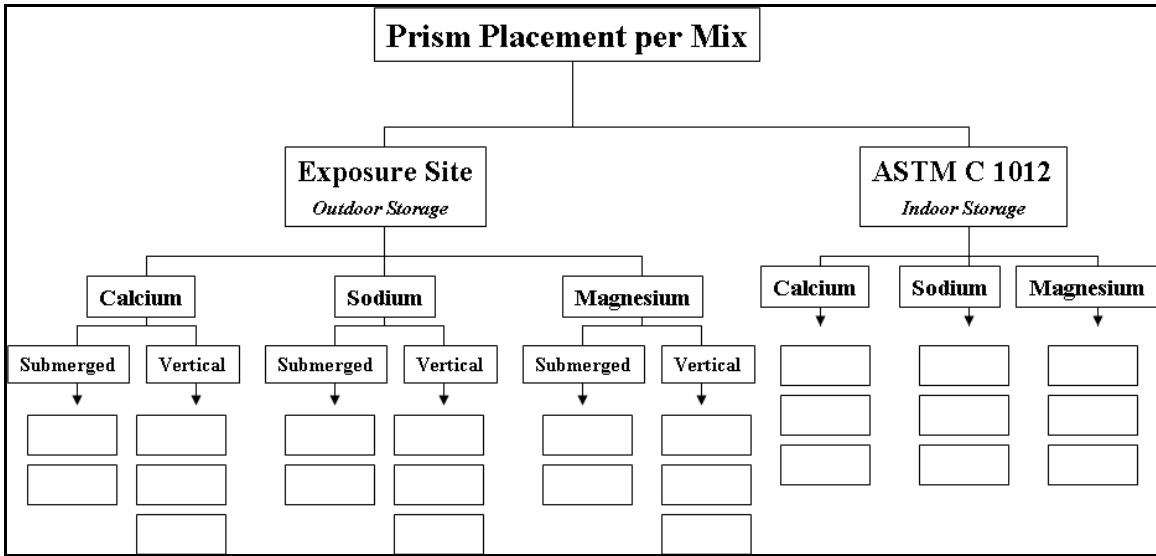


Figure 4-2: The placement of prisms from each mixture into the outdoor exposure site or in the modified ASTM C 1012 testing.

The concrete prisms were strategically placed in the outdoor sulfate exposure sites to provide multiple storage conditions per mixture. Figure 4-3 shows how each mixture was placed in the respective sulfate trench. From each mixture in each trench, two prisms were placed below the soil level, roughly 2 in (51 mm) above the bottom of the trench, and three prisms were placed vertically. The vertical prisms were halfway submerged to provide the following three areas of exposure: submerged (in sulfate solution below grade), soil/solution interface zone (wetting/drying zone), and non-contact zone (above solution but subject to wicking action for some salts).

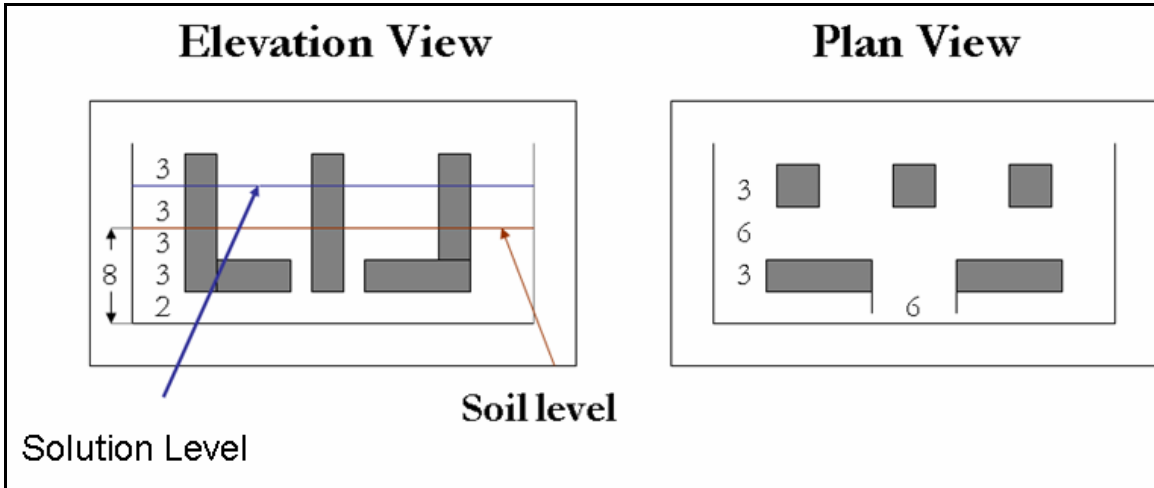


Figure 4-3: Placement of prisms in each outdoor exposure trench. The units are in inches.

Prisms in each trench were measured (for mass change, length change, and dynamic modulus as per resonant frequency) after the following durations of exposure: 1, 2, 3, 4, 6, 9, 12, and 18 months. The prisms were removed from the exposure site one day prior to each measurement. Once removed from the exposure site, the prisms were wrapped with moist towels and placed in a temperature and humidity controlled environment at 73 °F (23 °C) and a RH < 50% to ensure that thermal or moisture effects would not substantially impact the properties measured.

The remaining nine prisms from each mixture were placed in a modified ASTM C 1012 storage condition as noted above. Measurements on these prisms were taken at the same intervals of those in the exposure site. The sulfate solution was changed at each measurement period to a new solution. Each mixture was stored in its own container in a

temperature controlled environment of 73 °F (23 °C). The prisms were elevated from the bottom of the container to reduce friction and raise the prisms that were in gypsum solutions above the super saturated gypsum.

4.2.3 Mortar bar testing using ASTM C 1012

Mortar bars comprised of the same materials tested in the outdoor exposure site and in concrete prism testing (modified ASTM C 1012 storage condition) were also tested in accordance with ASTM C 1012. This procedure is provided in detail in section 3.2.2. Typically ASTM C 1012 only subjects mortar specimens to 5% sodium sulfate. However, to allow for comparisons with the concrete prisms previously described, mortar bars were also placed in calcium and magnesium sulfate solutions with sulfate concentrations equal to that in the 5% sodium sulfate solution.

4.2.4 Sulfate profiling

Concrete prisms tested as per the modified version of ASTM C 1012 were removed at 18 months and progressively milled to a depth of 0.12 in (3 mm) to generate concrete powder samples to be analyzed by x-ray diffraction for the presence of hydration products and potentially detrimental reaction products from sulfate attack. For comparison, concrete prisms stored vertically at the outdoor exposure site were removed for milling and subsequent profile analysis. Figure 4.4 shows the process of how concrete cubes were cut from the prisms for milling. Each vertical prism was cut into 3 zones with a wet saw. Each zone has two concrete specimens removed, a 3 in (75 mm) cube cut for milling and a smaller slice for scanning electron microscopy. The specimens were cut into cubes to mill between saw cuts to have a one dimensional entrance of

sulfates. The cubes were placed on a lathe that was attached to a drill press. The drill press allowed for vertical movement which determined the depth of the mill. The lathe moved the specimen horizontally through the diamond tipped bit that turned the concrete into a powder. A 1 in (25 mm) wide path was used for milling and the samples were milled every 0.12 in (3 mm) to a depth of 0.48 in (12 mm) and analyzed by either XRD or SEM as described in sections 3.2.3 and 3.2.4. For convenience, units of mm will be used when sulfate milling is discussed. Once the powder was collected it was sieved through the No. 325 (45 micron) sieve and steps followed in 3.2.3 were followed for preparation of the powder for the SEM.

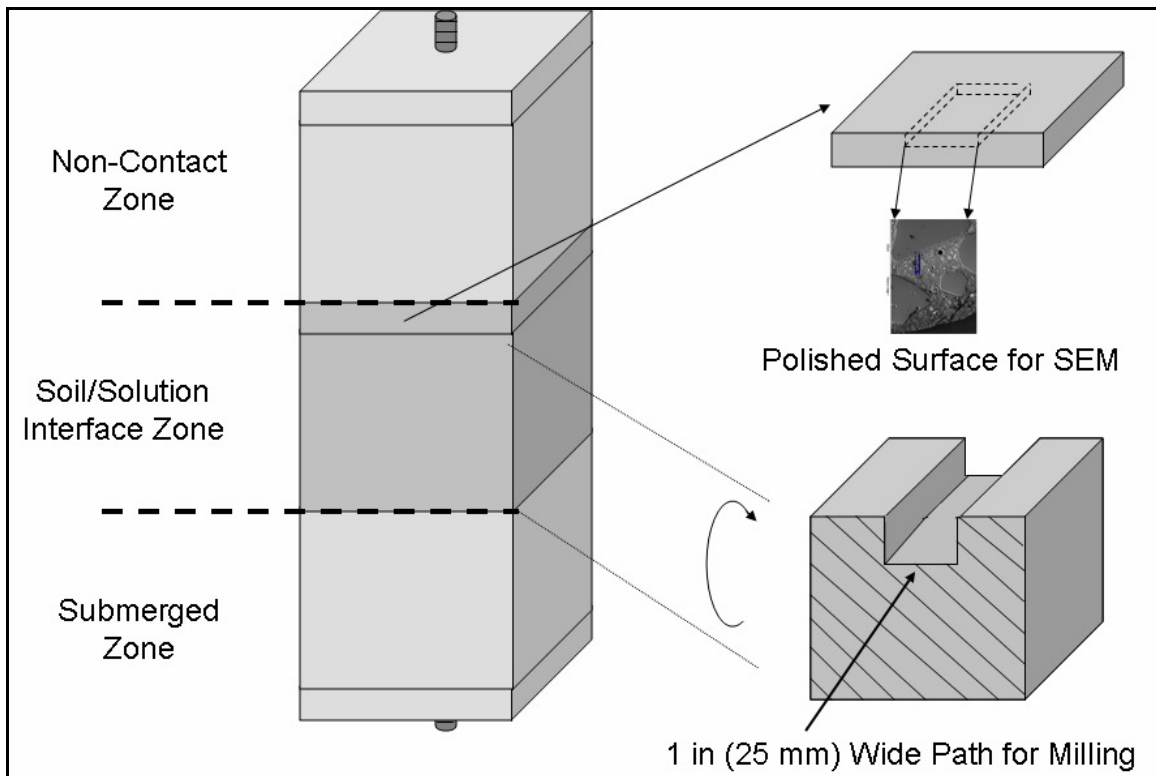


Figure 4-4: Prisms were cut into 3 in (75mm) cubes to allow for milling for sulfates. Slices were also removed for SEM analysis.

4.2.5 Physical sulfate attack testing

In addition to the concrete and mortar testing program previously described, a test procedure modified from Folliard and Sandberg (1994) was employed for evaluating physical sulfate attack. Mortar mixtures were cast into discs measuring 2 in (50 mm) in diameter and 1 in (25 mm) thick. Twenty-four hours after casting the discs were demolded and placed into solutions containing 10, 20, 30% sodium sulfate and 10, 20, 30% magnesium sulfate. Eight mortar mixtures were made with Type I and Type V cement at either 0.4 or 0.7 w/cm. Corresponding air-entrained mixtures were also cast. The mortar disks in the containers were enclosed with a lid and were subjected to 150 temperature cycles, as shown in Figure 4-5.

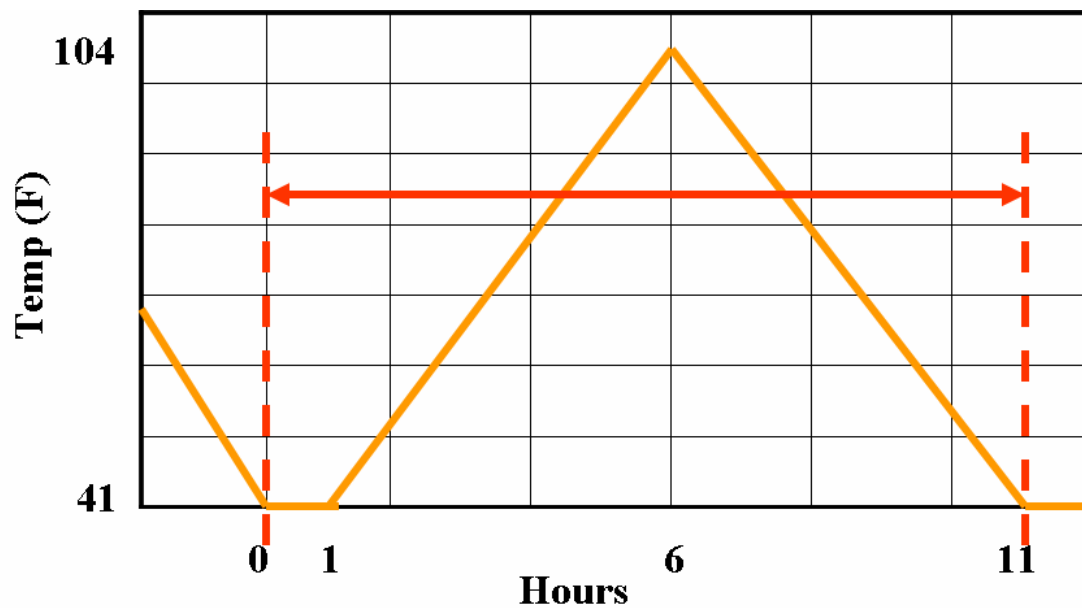


Figure 4-5: Temperature Cycle for mortars subjected to physical sulfate attack.

This temperature cycling, which takes 11 hours for a single cycle, was selected because Folliard and Sandberg reported that this cycle triggers the most damaging transition between thenardite and mirabilite, resulting in the most significant concrete deterioration. The samples were removed at different cycle periods and weighed to measure if any mass changes occurred.

4.4 Results and discussion

This section summarizes the results of laboratory and outdoor testing related to external sulfate attack. It is divided into four sub-sections with each of the first three providing results from each type of sulfate condition, and the fourth section comparing mixtures from all three sulfate conditions. Calcium sulfate is discussed in the first section followed by sodium sulfate and then magnesium sulfate. Within each section the following are discussed: effects of cement composition, w/cm, supplementary cementing materials, and the comparison of concrete prisms to mortar bars. Semi-quantitative Rietveld analyses were used to understand the mechanisms occurring in the specimens. Figure 4-6 provides the mixture designation for the mixtures discussed in this chapter. For example, the designation in Figure 4-6 is for a mixture with Type I/II cement, 20% Class C fly ash at a w/cm of 0.4. If this mixture did not contain SCMs, the designation would be C2-4.

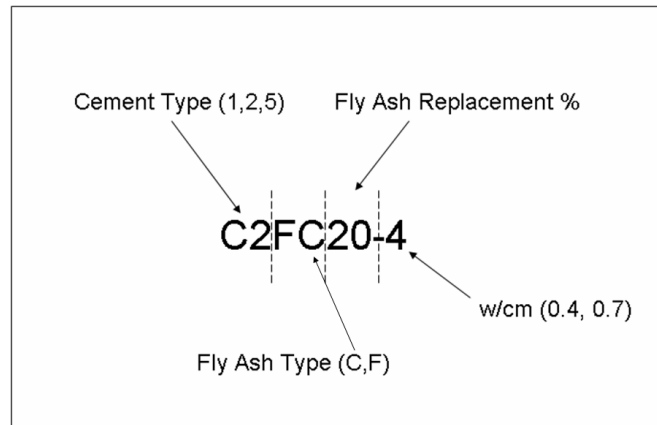


Figure 4-6: Mixture designations used throughout this chapter.

4.4.1 Calcium sulfate

4.4.1.1 Cement composition and w/cm

Expansions and mass change

Mixtures containing Type I cement (without SCMs) were the only ones to show any expansion in calcium sulfate conditions. These were not significant expansions greater than 0.1%. Table 4-1 provides the expansion and mass change for these mixtures. Mixtures C1-4 and C1-7 exhibited expansions of 0.05% and 0.09% at 18 months, respectively, in the modified ASTM C 1012 indoor testing. However, these mixtures exhibited very little mass loss compared to the submerged and vertically placed prisms in the outdoor calcium sulfate exposure site. Interestingly, these prisms that exhibited mass loss outdoors did not show any appreciable expansion. In a visual inspection of the prisms at 18 months, the indoor prisms showed minor cracking along the sides. The prisms placed in the outdoor exposure site showed deterioration below the soil level which leads to the mass loss.

Table 4-1: Expansion and mass change data from mixtures placed in calcium sulfate conditions

Mixture ID	Age (Months)	Calcium Sulfate 1012		Calcium Submerged		Calcium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1-4	3	-0.01	0.48	0.01	0.39	-0.01	0.07
C1-4	6	0.01	0.54	0.01	-0.19	0.00	-0.01
C1-4	9	0.02	0.71	0.01	-0.35	-0.01	-0.05
C1-4	12	0.02	0.63	0.02	-0.59	0.00	-0.28
C1-4	18	0.05	0.43	0.02	-1.44	0.01	-0.28
C1-7	3	0.00	0.27	0.00	0.03	0.00	-0.12
C1-7	6	0.01	0.32	0.00	-1.15	0.00	-0.33
C1-7	9	0.02	0.37	0.01	-1.70	0.01	-0.64
C1-7	12	0.05	0.29	0.02	-1.83	0.01	-0.64
C1-7	18	0.09	0.40	0.03	-3.72	0.00	-0.68
C2-4	3	0.01	0.18	-0.02	0.40	-0.01	-0.09
C2-4	6	-0.01	0.26	0.00	0.42	0.01	-0.02
C2-4	9	0.00	0.25	0.01	0.18	0.02	-0.02
C2-4	12	0.00	0.25	0.00	0.15	0.00	0.01
C2-4	18	-0.01	0.23	-0.02	0.17	0.00	0.07
C2-7	3	0.00	0.22	0.00	-0.06	-0.01	-0.09
C2-7	6	-0.01	0.27	0.00	-0.42	-0.01	-0.15
C2-7	9	0.00	0.31	0.01	-0.56	0.00	-0.25
C2-7	12	0.01	0.39	-0.01	-0.73	-0.01	-0.28
C2-7	18	0.00	0.35	0.01	-1.85	-0.01	-0.84
C5-4	3	0.01	0.36	-0.01	0.26	0.00	-0.07
C5-4	6	0.01	0.40	-0.01	0.30	0.00	0.06
C5-4	9	0.01	0.39	0.00	0.26	0.00	0.07
C5-4	12	0.02	0.36	0.00	0.27	-0.01	-0.12
C5-4	18	0.02	0.30	0.01	0.27	0.00	0.05
C5-7	3	0.01	0.40	0.01	0.01	0.01	0.05
C5-7	6	0.01	0.39	0.01	0.01	0.01	0.11
C5-7	9	0.01	0.65	0.02	0.01	0.01	0.13
C5-7	12	0.01	0.28	0.01	0.01	0.01	0.12
C5-7	18	0.02	0.37	0.02	0.02	0.02	0.15

Figure 4-7 shows a vertical prism from mixture C1-4. This vertically placed prism exhibiting deterioration occurring below the soil level. The deterioration that is occurring on these prisms is significant. Many debates do occur if whether gypsum causes damage

to concrete structures. There is not an increase in expansion which many might not consider as damage, but if the concrete is deteriorating on the outside this is considered as damage. The low solubility of gypsum is probably preventing the sulfates from entering at a higher rate as seen with sodium and magnesium sulfates. Prisms containing Type I/II and Type V cements did not expand at either 0.4 or 0.7 w/cm in any calcium sulfate condition. From mixtures containing Type I/II cement, only prisms cast from mixture C2-7 showed any appreciable mass loss.

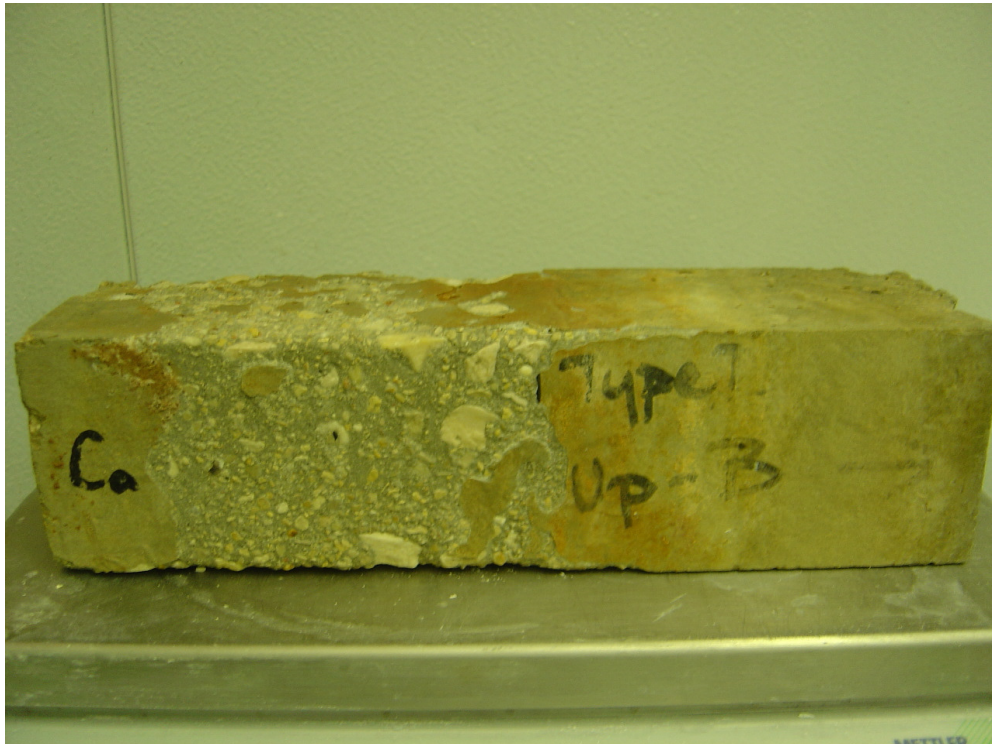


Figure 4-7: Concrete prism with a 0.4 w/cm placed vertically in the outdoor calcium sulfate exposure site. In this photograph, the left side shows the portion of the prism that was below the soil level.

Sulfate profiling

Figure 4-8 depicts the semi-quantitative x-ray Rietveld analyses from the milling of concrete prisms at 0.4 w/cm in the indoor modified ASTM C 1012 testing after 18 months of storage. Semi-quantitative analyses are compared separately between w/cm as the cement content in the mixture can change the amount of hydration products formed. This could lead to different amounts of ettringite/gypsum formed and a dissimilar amount of calcium hydroxide depleted. In the outer 3 mm of the prism, ettringite formation was similar between each of the cement types. It is not uncommon to see this ettringite formation with Type V cement, Mehta (1993) mentions that sulfate resistant cements do not stop sulfate attack since calcium hydroxide can still be attacked. Further into the prisms, ettringite formation decreased. The gypsum content in the outer layer showed an increase from Type I to Type V cements. These results provide a general indication of the phases forming since the samples did not have an internal standard.

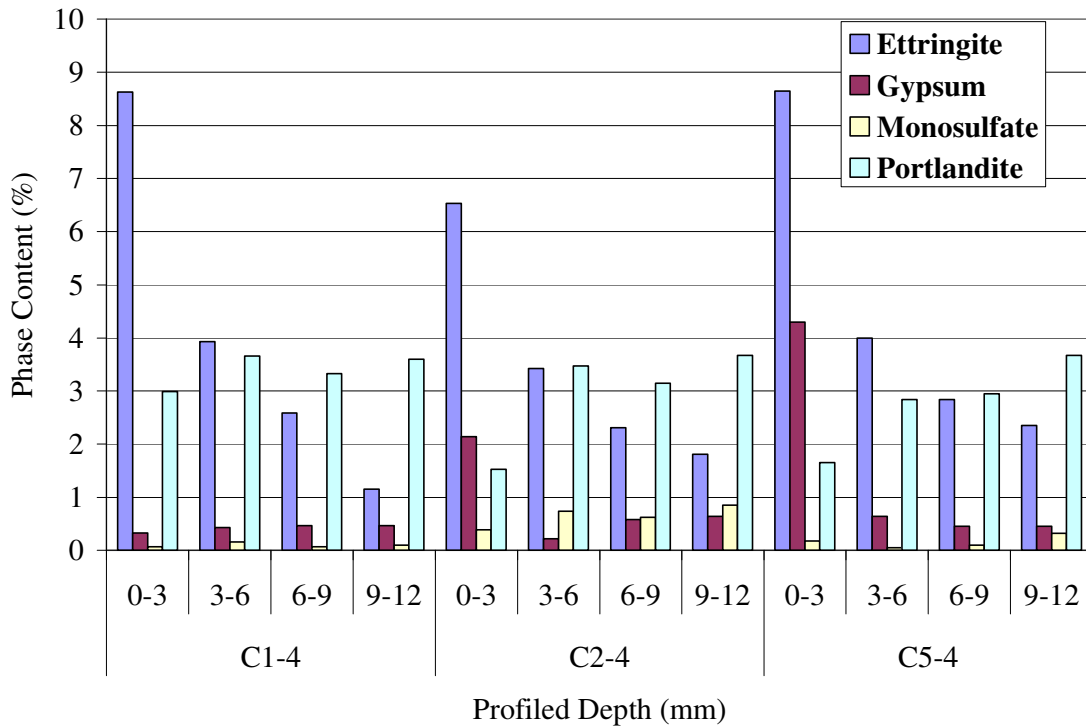


Figure 4-8: Semi-quantitative Rietveld analysis showing differences in cement types for prisms at 0.4 w/cm, placed indoors in calcium sulfate.

Figure 4-9 depicts the quantitative x-ray analyses from the milling of concrete prisms at 0.7 w/cm in the modified ASTM C 1012 testing after 18 months of storage. Similar to the 0.4 w/cm prisms, ettringite formation occurred with these mixtures as well; however, these lower quality mixtures allowed for further penetration of solution into the concrete, allowing for ettringite to form further into the concrete. In addition, greater gypsum formation was shown in the outer layer of the concrete.

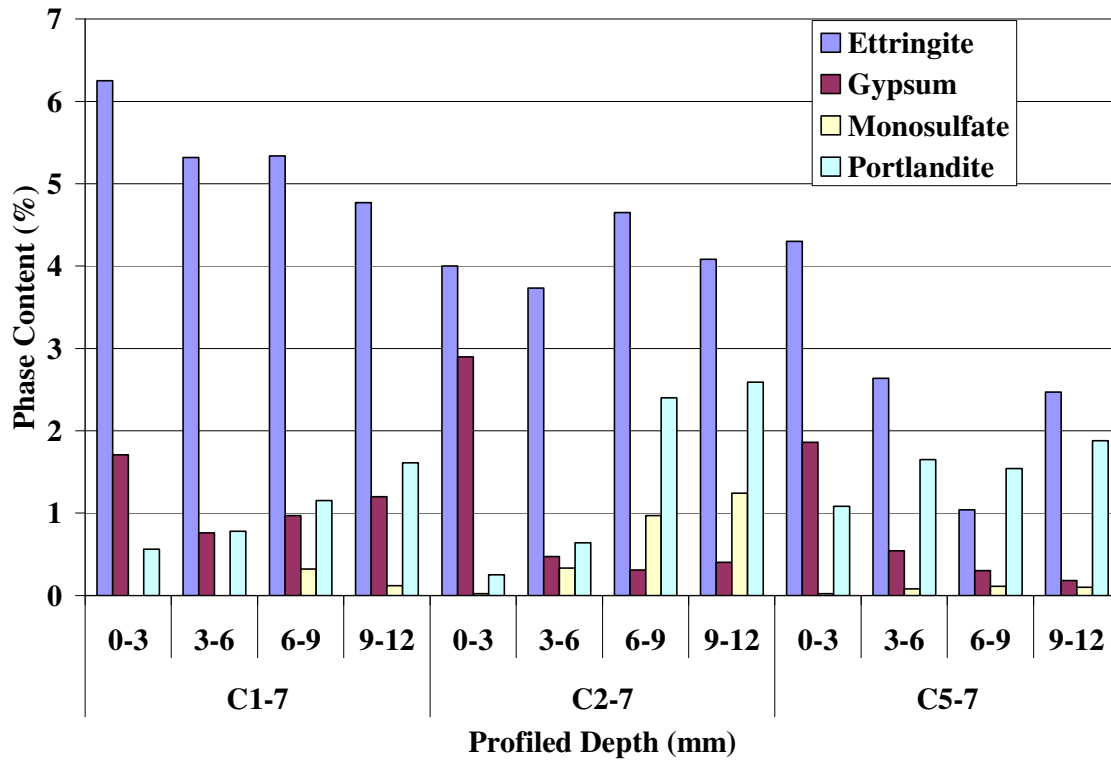


Figure 4-9: Quantitative analysis showing differences in cement types for prisms at 0.7 w/cm placed indoors in calcium sulfate.

4.4.1.2 Supplementary cementing materials

Expansions and mass change

Concrete mixtures containing either Class C or Class F fly ash did not increase in expansion in any of the calcium sulfate conditions. Table 4-2 shows the expansion and mass change data from mixtures containing Type I and Type I/II cement with Class C fly ashes.

Table 4-2: Expansion and mass change data from mixtures with Class C fly ash placed in calcium sulfate conditions

Mixture ID	Age (Months)	Calcium Sulfate 1012		Calcium Submerged		Calcium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1FC20-4	3	0.00	0.00	-0.01	0.19	0.00	0.04
C1FC20-4	6	0.00	0.00	0.00	0.26	0.01	0.11
C1FC20-4	9	0.00	0.00	0.00	0.27	0.02	0.12
C1FC20-4	12	0.00	0.00	0.02	0.27	0.01	0.01
C1FC20-4	18	0.00	0.00	0.03	0.19	0.04	0.10
C1FC20-7	3	0.00	0.29	-0.01	0.19	0.00	0.04
C1FC20-7	6	0.01	0.36	0.00	0.26	0.01	0.11
C1FC20-7	9	0.03	0.44	0.01	0.27	0.02	0.12
C1FC20-7	12	0.03	0.52	0.02	0.27	0.01	0.01
C1FC20-7	18	0.07	0.60	0.03	0.18	0.04	0.11
C1FC40-4	3	0.02	0.05	0.01	0.12	0.01	0.12
C1FC40-4	6	0.03	0.28	0.01	0.05	-0.01	0.03
C1FC40-4	9	0.03	0.11	0.01	0.03	0.01	0.05
C1FC40-4	12	0.04	-0.05	0.03	-0.05	0.01	-0.17
C1FC40-4	18	0.08	0.19	0.05	-0.22	0.03	-0.19
C1FC40-7	3	0.03	0.23	0.00	0.04	0.00	-0.07
C1FC40-7	6	0.03	0.21	-0.01	0.12	0.00	0.00
C1FC40-7	9	0.05	0.37	-0.06	0.12	-0.02	-0.07
C1FC40-7	12	0.03	0.32	-0.04	0.08	0.00	-0.19
C1FC40-7	18	0.05	0.37	-0.04	0.05	0.01	-0.22
C2FC20-4	3	0.01	0.17	0.00	0.20	0.00	0.01
C2FC20-4	6	0.01	0.17	0.01	0.22	0.00	-0.03
C2FC20-4	9	0.01	0.35	0.01	0.30	-0.01	-0.04
C2FC20-4	12	0.00	0.27	0.02	0.30	0.01	0.03
C2FC20-4	18	0.01	0.27	0.01	0.26	0.00	0.07
C2FC20-7	3	0.03	0.42	0.00	-0.40	0.00	-0.07
C2FC20-7	6	0.03	0.37	0.01	-0.64	0.01	-0.20
C2FC20-7	9	0.02	0.50	0.02	-1.00	0.01	-0.34
C2FC20-7	12	0.04	0.13	0.03	-2.00	0.02	-0.26
C2FC20-7	18	0.02	-0.51	0.04	-3.10	-0.01	-0.33
C2FC40-4	3	0.04	0.20	0.00	-0.04	-0.01	0.07
C2FC40-4	6	0.04	0.31	0.00	0.03	-0.01	0.10
C2FC40-4	9	0.03	0.34	0.00	0.09	-0.02	-0.11
C2FC40-4	12	0.06	0.44	0.00	0.02	-0.02	0.05
C2FC40-4	18	0.07	0.48	-0.03	0.04	-0.04	0.06
C2FC40-7	3	0.01	0.29	0.01	0.05	0.01	0.00
C2FC40-7	6	0.01	0.33	0.00	0.19	0.00	0.06
C2FC40-7	9	0.01	0.44	0.01	0.22	0.01	-0.13
C2FC40-7	12	0.03	0.73	0.00	0.15	0.00	0.01
C2FC40-7	18	0.03	0.76	0.00	0.12	0.00	0.02

In many cases, including mixtures with Class C fly ash, the expansions were less than the controls shown in section 4.3.1.1. However, after 18 months of exposure the prisms did show signs of deteriorations similar to Figure 4-7. Mixtures with Type V cement and Class C fly ashes, and mixtures with all three cements with ternary blends and Class F fly ash are shown in Appendix C.

Sulfate profiling

Figure 4-10 provides semi-quantitative XRD Rietveld analyses on prisms with Class C fly ash at 0.4 w/cm placed indoors in calcium sulfate. Similar to mixtures without SCMs, ettringite formation was the greatest in the outer layer and decreased with increasing depth into the concrete. The difference in calcium hydroxide content between mixtures containing 20 and 40% Class C fly is likely due to the diluting effect of replacing additional portland cement with fly ash and perhaps due to increased pozzolanic activity with increasing fly ash dosage.

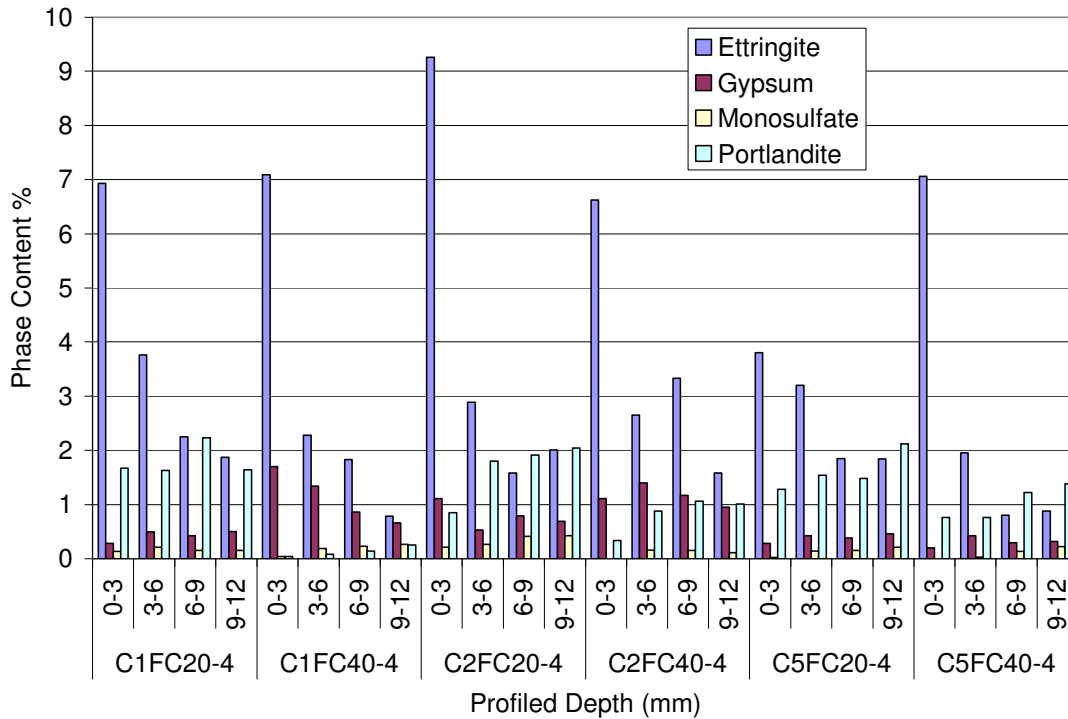


Figure 4-10: Semi-quantitative XRD analysis of profiled prisms containing Class C fly ash at a 0.4 w/cm

Figure 4-11 shows the semi-quantitative XRD analysis of prisms at 0.7 w/cm in the modified ASTM C 1012 calcium sulfate solutions. The progression of attack into concrete containing SCMs does not penetrate as deep as the control mixtures at the same w/cm. C5FC40-7 had less ettringite formation than C5FC20-7, which suggests that decreased permeability may reduce penetration of sulfates in prisms containing fly ash.

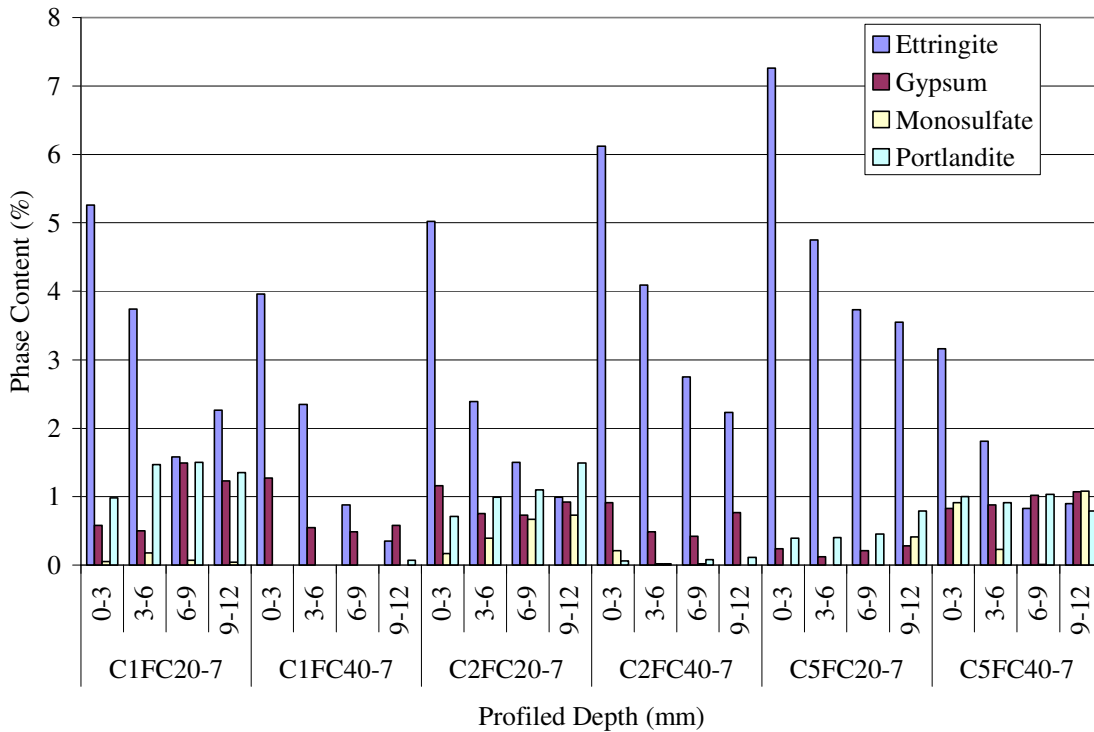


Figure 4-11: Quantitative XRD analysis of profiled prisms containing Class C fly ash at a 0.4 w/cm to determine phase content at different milled depths

4.4.1.3 Mortar and concrete comparisons

Modified ASTM C 1012 testing of mortars containing Type I/II and Type V cements and immersed in calcium sulfate solution was performed to compare with concrete prisms subjected to the same testing regime. Table 4-3 summarizes the expansions of these mixtures, as well as similar mixtures containing Class C fly ash. Mixtures that are bolded have failed the commonly applied 0.1% expansion criteria. Both control mixtures had similar expansion values at 18 months. The Type I/II control mixture (C2) had an expansion of 0.07% and the Type V control mixture (C5) had an expansion of 0.06% at 18 months. These mortar mixtures expanded more than concrete prisms containing the

same blend of cementitious materials and at approximately the same w/cm ratio (as previously detailed in Table 4-2). This increase in expansion may be due to the higher paste content of the mortar mixtures or may also be size-related, as the concrete prisms have large cross sections, making it more difficult for gypsum to reach the interior core of the specimens. Mortars containing 20% Class C fly ash showed very little expansion, but mortars containing 40% Class C fly ash expanded beyond 0.1% within 6 months in calcium sulfate condition. Similar concrete mixtures did not expand at either 0.4 or 0.7 w/cm at 18 months. The reasons for this difference in behavior may be similar to those discussed above (e.g., paste content, specimen size, etc.). It is interesting to note that mortar containing these “sulfate resistant” cements still expanded when higher dosages of Class C fly were used, highlighting the key role that fly ash mineralogy plays in expansion and distress in sulfate environments.

Table 4-3: Comparison between mortar bars and concrete prisms evaluated using calcium sulfate solution in ASTM C 1012 storage conditions

Age (Months)	Mixture	Concrete* Expansion (%)	Mortar** Expansion (%)	Mixture	Concrete* Expansion (%)	Mortar** Expansion (%)
3	Type I/II Cement	0.01	0.02	Type V Cement	0.01	0.02
6		-0.01	0.02		0.01	0.03
9		0.00	0.04		0.02	0.03
12		0.00	0.05		0.02	0.04
18		-0.01	0.07		0.02	0.06
3	Type I/II Cement 20% FA1	0.01	0.02	Type V Cement 20% FA1	0.04	0.02
6		0.01	0.03		0.03	0.03
9		0.01	0.04		0.06	0.04
12		0.00	0.06		0.07	0.04
18		0.01	0.09		0.05	0.04
3	Type I/II Cement 40% FA1	0.04	0.02	Type V Cement 40% FA1	0.03	0.03
6		0.04	0.06		0.02	0.1
9		0.03	0.14		0.07	0.21
12		0.06	0.24		0.06	0.29
18		0.07	0.36		0.06	TBM

* w/cm = 0.40 ; ** w/cm = 0.43 – 0.485 (based on meeting target flow value)

4.4.2 Sodium sulfate

4.4.2.1 Cement composition and w/cm

Expansion and mass change

The concrete prisms in sodium sulfate conditions did not perform as well as their counterparts in calcium sulfate. Expansion measurements were taken for 18 months or until they were not measurable due to deterioration. Table 4-4 gives the expansion and mass change data for prisms placed into either the outdoor sodium sulfate exposure site or placed in modified ASTM C 1012 storage conditions containing sodium sulfate solutions in the laboratory. Mixtures containing Type I cement performed worse than mixtures containing Type I/II cement. Mixtures containing Type V cement did not show any significant expansions in any sodium sulfate storage condition. Mixture C1-4 performed well for 12 months, but expanded to 1.08% at 18 months in indoor testing. In outdoor testing, the same mixture failed at 9 months in the submerged conditions and failed at 12 months in the vertical condition. The outdoor prisms stored in sodium sulfate are also affected by physical sulfate attack, explaining why deterioration was more rapid and severe.

Table 4-4: Expansion and mass change data for mixtures without SCMs, exposed to sodium sulfate solution

Mixture ID	Age (months)	Sodium Sulfate 1012		Sodium Submerged		Sodium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1-4	3	0.00	0.21	0.02	0.02	0.02	-0.06
C1-4	6	0.03	0.48	0.03	0.02	0.02	-0.18
C1-4	9	0.04	0.79	0.10	0.05	0.05	-1.38
C1-4	12	0.07	1.10	0.43	0.43	0.43	-2.21
C1-4	18	1.08	-3.67	Broken	Broken	Broken	Broken
C1-7	3	0.02	0.32	0.06	0.24	0.07	-0.37
C1-7	6	0.10	0.53	0.52	0.71	0.23	-0.46
C1-7	9	0.20	0.72	1.20	1.21	0.54	-0.52
C1-7	12	0.28	0.86	1.40	1.44	0.69	-0.67
C1-7	18	0.36	1.05	1.82	0.65	1.13	-1.08
C2-4	3	0.00	-0.09	0.00	-0.09	0.01	-0.12
C2-4	6	0.01	-0.06	0.01	0.21	0.01	0.05
C2-4	9	0.01	0.00	0.01	0.29	0.01	0.04
C2-4	12	0.01	0.12	0.03	0.35	0.01	0.10
C2-4	18	0.01	0.21	0.11	0.12	0.04	0.04
C2-7	3	-0.02	0.20	0.01	0.17	-0.01	-0.15
C2-7	6	0.02	0.23	0.02	0.17	0.01	-0.14
C2-7	9	0.03	0.27	0.05	0.36	0.03	-0.20
C2-7	12	0.07	0.43	0.08	0.38	0.06	-0.20
C2-7	18	0.11	0.46	0.21	0.55	0.12	-0.14
C5-4	3	0.00	0.00	0.00	0.04	0.00	-0.17
C5-4	6	0.01	-0.01	0.01	0.12	0.01	-0.07
C5-4	9	0.03	-0.02	0.01	0.20	0.01	-0.15
C5-4	12	0.02	0.03	0.00	0.29	0.00	-0.07
C5-4	18	0.03	0.05	0.01	0.35	0.01	-0.04
C5-7	3	0.00	0.23	0.02	0.31	0.01	-0.17
C5-7	6	0.02	0.24	0.03	0.40	0.01	-0.17
C5-7	9	0.02	0.23	0.04	0.46	0.00	-0.30
C5-7	12	0.02	0.27	0.04	0.56	0.00	-0.25
C5-7	18	0.03	0.32	0.06	0.57	0.04	-0.13

In the outdoor sulfate exposure site, mixture C1-7 expanded more than 0.1% after 6 months and more than 1% after 18 months. Despite this excessive expansion, the prisms were still intact and measurable after 18 months. Mixture C1-4 exceeded the 0.1%

expansion threshold at 9 months (submerged) and 12 months (vertical) and the prisms were completely deteriorated and immeasurable at 18 months. Interestingly, the higher w/cm prisms tended to gain mass and show expansion, yet did not deteriorate to the level of mixtures at 0.4 w/cm. It is possible that the higher w/cm mixtures were able to accommodate expansive products, such as ettringite, more within the more porous matrix, resulting in a mass gain as more sulfate solution enters the system. Figure 4-12 shows an image of a submerged prism from mixture C1-7 in the outdoor sulfate site after 18 months of exposure. While the bar appears to be in good condition, it has expanded by 1.8%. However, at this time it is unclear as to why this increase in mass and significant expansion does not result in cracking or deterioration as seen in the lower w/cm concretes. A possible conclusion is the porosity allows for ettringite formation to form within these areas.

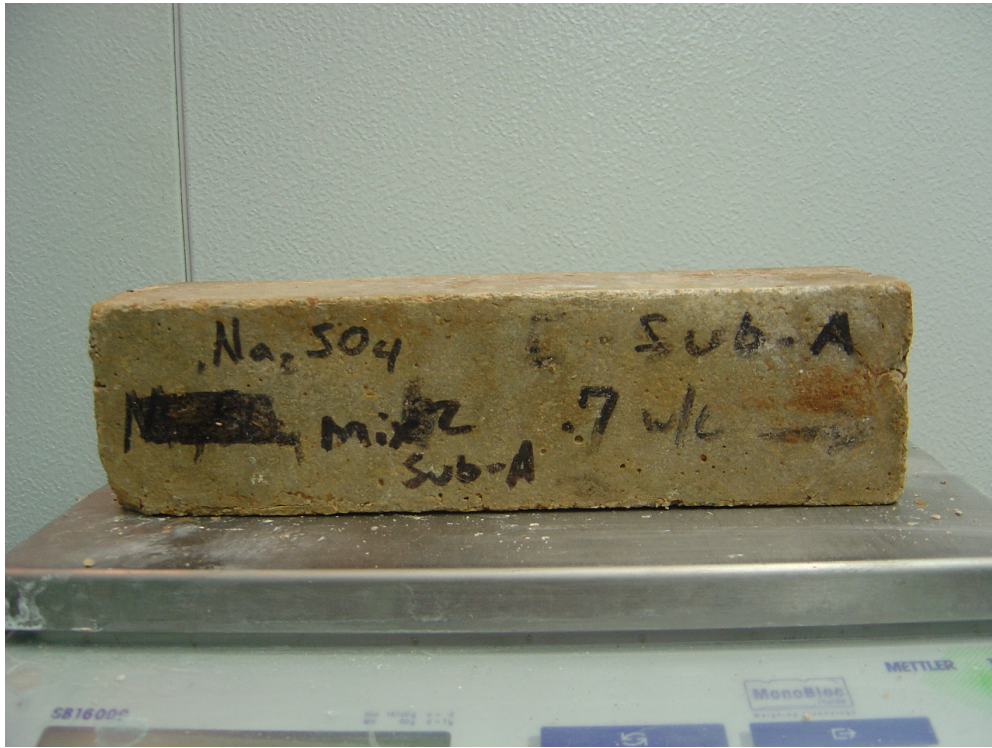


Figure 4-12: C1-7 prism submerged in the outdoor sodium sulfate exposure site after 18 months

Mixture C2-7 failed the 0.1% expansion criteria at 18 months in all exposure conditions, while the lower w/cm mixture, C2-4, failed the 0.1% criteria at 18 months only in the submerged specimens stored outdoors. There are no significant mass changes associated with any of these prisms. However, vertically placed prisms containing either Type I/II or Type V cements did show signs of deterioration occurring in the section exposed to the atmosphere (no-contact with soil zone). Figure 4-13 shows a prism from mixture C5-7 placed vertically after 18 months of exposure in the sodium sulfate exposure site. The top of the prism (right part in the picture) does have visible paste loss. This may be attributed to physical sulfate attack and is discussed in more detail later in this chapter.

Similar distress was found at the PCA (2002) exposure site in Sacramento, California which they contributed to physical sulfate attack.



Figure 4-13: Mixture C5-7 after 18 months of outdoor exposure to sodium sulfate. This prism was placed vertically, with the section on the left fully submerged below sulfate-saturated soil.

Sulfate profiling

Figure 4-14 shows the semi-quantitative XRD analyses of concrete prisms with various cement types subjected to modified ASTM C 1012 storage conditions after 18 months. It should again be noted that the values in Figure 4-14 do not reflect the actual amounts of these phases in the sample, but are reported in order to be able to determine relative values of phases and trends. Ettringite content is higher in the C1-4 prisms, compared to prisms comprised of the Type I/II and V cements. This is expected due to the higher C_3A content of the Type I cement (C1). Also, the additional ettringite formation in mixture C1-4 may be the consequence of the depletion of calcium hydroxide, leading to the

formation of calcium monosulfoaluminate. This then combines with gypsum to form ettringite. Mixtures with Type I/II and Type V cement show no signs of chemical alteration or deterioration.

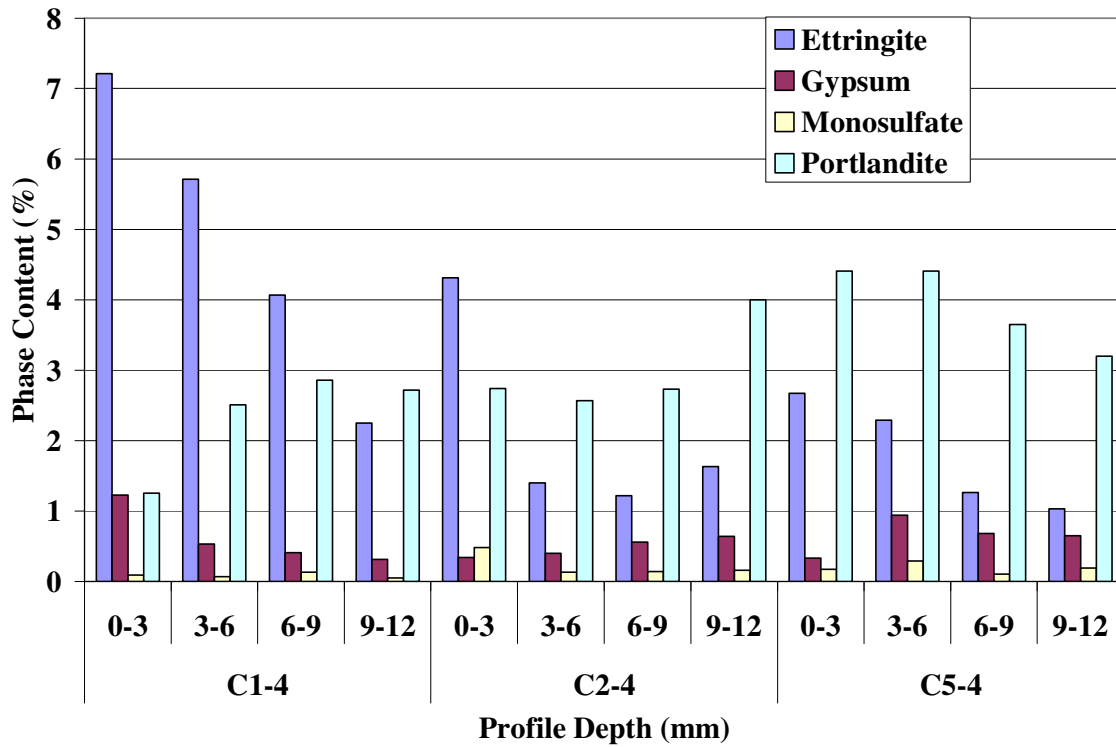


Figure 4-14: Semi-quantitative XRD Rietveld analyses of concrete prisms at 0.4 w/cm, placed indoors in sodium sulfate solutions after 18 months

In Figure 4-15, the semi-quantitative XRD analyses for concrete prisms at a 0.7 w/cm subjected to modified ASTM C 1012 storage conditions are presented. Mixture C1-7 shows the most ettringite formation in the outer layer of the prism. A slight decrease in the amount of ettringite occurs as a function of distance into the prism. Gypsum formation is low in mixture C1-7 in all the layers compared to mixtures C2-7 and C5-7. Mixtures with Type I/II and Type V cement do not show a decreasing amount of

ettringite formation with distance from the surface, perhaps suggesting that the all reaction products that can lead to ettringite formation have been consumed.

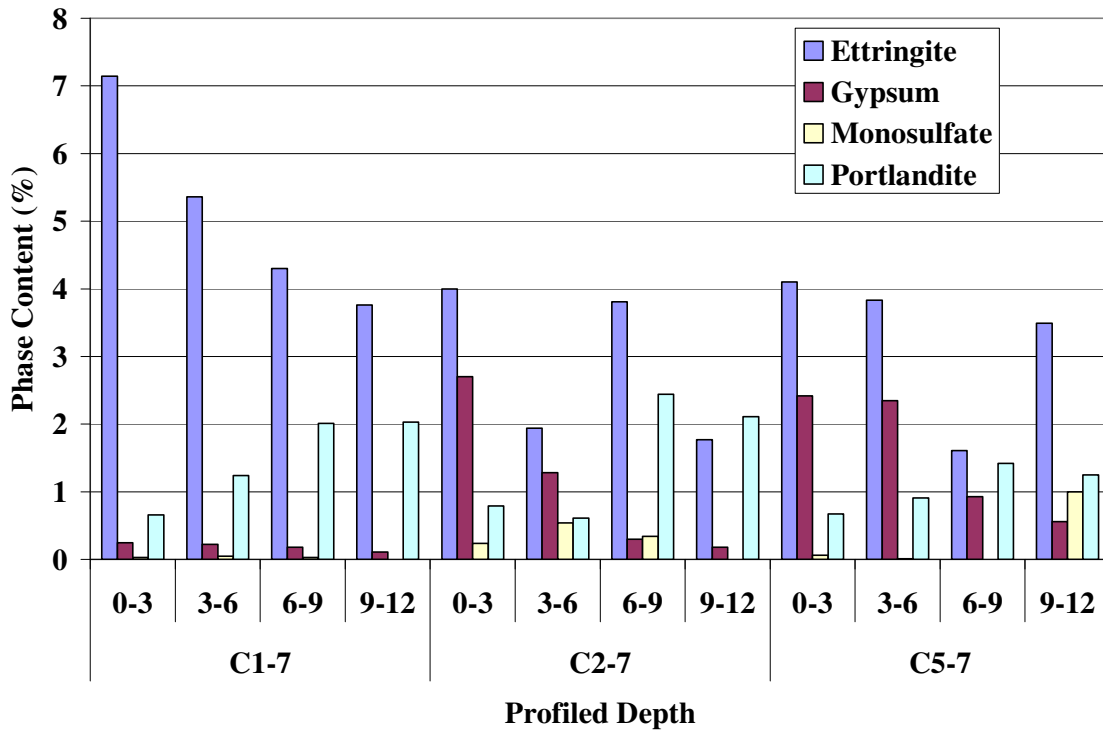


Figure 4-15: Semi-quantitative XRD Rietveld analysis of concrete prisms at 0.7 w/cm, placed indoors in sodium sulfate solutions after 18 months

Semi-quantitative XRD analyses were also performed on prisms in the outdoor sulfate exposure site. Figure 4-16 presents the semi-quantitative XRD analyses of Type V mixtures in the submerged and non-contact zones. The gypsum formation in the outdoor submerged conditions is greater than the prisms from the same mixture in the modified ASTM C 1012 testing. This may be attributed to the average higher temperature for the

outdoor site, compared to the indoor testing environment. Higher temperatures tend to increase rates of ionic movement and accelerate chemical reactions. The portion of the beams in the “non-contact” zone show very little alterations or excessive amounts of gypsum; this may be attributed to the fact that gypsum shows very little propensity for wicking, in contrast to sodium sulfate, which tends to wick considerably in the vertical direction.

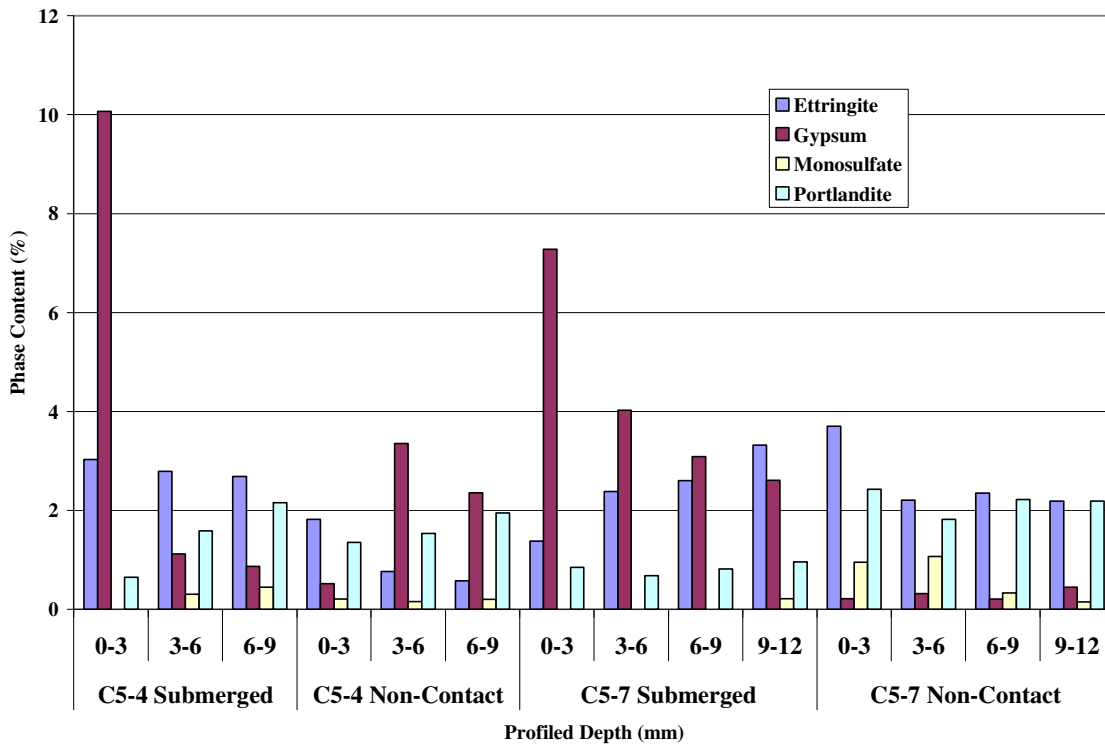


Figure 4-16: Semi-quantitative XRD analysis from mixtures containing sulfate resistant cement at in the outdoor sulfate exposure site

4.4.2.3 Supplementary cementing materials
Expansion and mass change

This section summarizes the measured expansions and mass changes for concrete mixtures containing SCMs (with a primary focus on Class C fly ash). The use of Class C fly ash will be discussed first followed by mixtures containing Class F fly ash. Table 4-5 shows the expansion and mass change data for mixtures containing Type I cement and Class C fly ash. Mixtures with lower w/cm (0.4) performed substantially better than mixtures with higher w/cm ratio. For example, mixture C1FC20-7 failed the 0.1% expansion criteria at 3 months while mixture C1FC20-4 failed at 1 year for the submerged conditions and 18 months for the other two conditions. Mass loss was significant during the expansion of these prisms, with a mass loss of greater than 1% for prisms that expanded greater than 0.1%. The addition of Class C fly ash showed more deterioration (but not expansion) compared to the control specimens. An increasing replacement dosage of Class C fly ash was found to generally cause more deterioration in mortar bars tested using ASTM C 1012, as described in Chapter 3. However, for the concrete mixtures shown in Table 4-5, mixtures with 20% Class C fly ash (C1FC20-4 and C1FC20-7) performed worse than those containing 40% Class C fly ash (C1FC40-4 and C1FC40-7). One possible explanation is that higher fly ash contents tend to reduce permeability more than lower fly ash contents, and this effect may be even more important for larger, concrete specimens and for specimens exposed to temperature variations and wetting and drying cycles.

Table 4-5: Expansion and mass change data for concrete with Type I cement and Class C fly ash, exposed to sodium sulfate solution

Mixture ID	Age (months)	Sodium Sulfate 1012		Sodium Submerged		Sodium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1FC20-4	3	0.01	0.09	0.01	-0.08	0.01	-0.09
C1FC20-4	6	0.02	-0.02	0.02	-1.24	0.02	-0.32
C1FC20-4	9	0.02	-0.49	0.03	-3.18	0.02	-0.64
C1FC20-4	12	0.05	-1.58	0.23	-3.81	0.07	-1.34
C1FC20-4	18	Broken	Broken	Broken	Broken	Broken	Broken
C1FC20-7	3	0.25	-0.28	0.50	-5.31	0.40	-1.55
C1FC20-7	6	Broken	Broken	Broken	Broken	Broken	Broken
C1FC20-7	9	--	--	--	--	--	--
C1FC20-7	12	--	--	--	--	--	--
C1FC20-7	18	--	--	--	--	--	--
C1FC40-4	3	0.03	0.36	0.00	-0.17	0.00	-0.18
C1FC40-4	6	0.03	-0.53	0.00	-2.35	0.01	-0.93
C1FC40-4	9	0.08	-0.83	0.01	-3.88	0.02	-1.20
C1FC40-4	12	0.12	-1.30	0.03	-3.94	0.07	-1.58
C1FC40-4	18	0.48	-3.30	0.10	-4.43	0.12	-2.47
C1FC40-7	3	0.05	-1.45	0.01	-0.84	0.02	-1.26
C1FC40-7	6	0.18	-2.88	0.09	-7.58	0.11	-4.55
C1FC40-7	9	0.64	-4.08	Broken	-13.97	0.14	-6.23
C1FC40-7	12	Broken	Broken	--	Broken	Broken	Broken
C1FC40-7	18	--	--	--	--	--	--

Mixtures containing Type I/II cement with Class C fly ash are shown in Table 4-6, with expansion and mass change data collected during the 18 month exposure to sodium sulfate conditions. Similar to Type I cement, mixtures with Type I/II cement did not perform well at higher w/cm ratios, and mass loss was observed to occur along with expansion in the prisms. At the lower w/cm ratio of 0.4, mixtures containing Type I/II cement exhibited better sulfate resistance than similar mixtures containing Type I cement.

Table 4-6: Expansion and mass change data for concrete with Type I/II cement and Class C fly ash, exposed to sodium sulfate solution

Mixture ID	Age (months)	Sodium Sulfate 1012		Sodium Submerged		Sodium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C2FC20-4	3	0.01	-0.01	0.00	0.13	-0.01	-0.04
C2FC20-4	6	0.01	0.01	0.01	0.22	0.00	-0.06
C2FC20-4	9	0.02	0.09	0.02	0.37	0.01	-0.01
C2FC20-4	12	0.00	-0.39	0.05	0.28	0.03	-0.02
C2FC20-4	18	0.04	-0.07	0.15	-0.49	0.06	-1.32
C2FC20-7	3	.05`	0.28	0.01	-0.24	0.01	-0.25
C2FC20-7	6	Broken	Broken	Broken	-9.67	0.11	-2.03
C2FC20-7	9	--		--	Broken	Broken	-6.99
C2FC20-7	12	--	--	--	--	--	--
C2FC20-7	18	--	--	--	--	--	--
C2FC40-4	3	0.01	0.03	0.00	-0.20	0.00	-0.12
C2FC40-4	6	0.01	0.08	0.01	-0.96	0.00	-0.22
C2FC40-4	9	0.01	0.14	0.05	-1.54	0.01	-0.29
C2FC40-4	12	0.04	0.24	0.14	-1.57	0.03	-0.31
C2FC40-4	18	0.07	0.30	0.33	-3.01	0.03	-0.51
C2FC40-7	3	0.07	-1.44	0.05	-5.49	0.02	-2.66
C2FC40-7	6	0.24	-0.64	0.21	-31.35	Broken	-8.36
C2FC40-7	9	0.15	-14.28	Broken	Broken	--	Broken
C2FC40-7	12	0.20	-14.36	--	--	--	--
C2FC40-7	18	0.31	-14.56	--	--	--	--

Table 4-7 presents the expansion and mass loss data for the mixtures containing Type V cement with Class C fly ash. Expansion was only observed for mixtures containing 20% Class C fly ash at the higher w/cm ratio of 0.7. After 6 months, prisms from mixture C5FC20-7 placed in the outdoor sulfate conditions expanded past 0.1%. At 9 months, the prisms from the same mixture exceeded this same expansion threshold when tested indoors using ASTM C 1012 storage conditions. Interestingly, all three cements tested with either 20 or 40% Class C fly ash showed greater deterioration at the lower

replacement dosage. Type V cement with Class C fly ash may not be suitable due to the reactive phases in the fly ash as shown in Chapter 3.

Table 4-7: Expansion and mass change data for concrete with Type V cement and Class C fly ash, exposed to sodium sulfate solution

Mixture ID	Age (months)	Sodium Sulfate 1012		Sodium Submerged		Sodium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C5FC20-4	3	0.00	0.11	0.01	0.28	0.01	0.01
C5FC20-4	6	0.02	0.12	0.02	0.37	0.02	0.06
C5FC20-4	9	0.03	0.14	0.03	0.47	0.02	0.03
C5FC20-4	12	0.03	0.19	0.02	0.48	0.02	0.02
C5FC20-4	18	0.02	0.23	0.03	0.54	0.01	0.04
C5FC20-7	3	0.01	0.08	0.05	-0.24	0.03	-0.12
C5FC20-7	6	0.05	0.15	0.23	-0.10	0.10	-0.31
C5FC20-7	9	0.15	0.33	0.49	-0.98	0.27	-1.06
C5FC20-7	12	0.24	0.50	0.67	-1.06	0.42	-1.26
C5FC20-7	18	0.42	0.68	Broken	Broken	0.45	-8.60
C5FC40-4	3	0.00	0.11	0.00	0.12	0.00	-0.08
C5FC40-4	6	0.00	0.19	0.00	0.21	0.00	-0.09
C5FC40-4	9	0.03	0.16	0.01	0.22	0.01	-0.11
C5FC40-4	12	0.03	0.25	-0.01	0.26	0.01	-0.06
C5FC40-4	18	0.05	0.31	0.06	0.28	-0.01	-0.03
C5FC40-7	3	0.00	-0.12	0.00	0.05	0.00	-0.16
C5FC40-7	6	0.02	-0.11	0.01	-0.51	0.00	-0.47
C5FC40-7	9	0.02	-0.03	0.03	-1.80	0.01	-1.04
C5FC40-7	12	0.03	0.06	0.04	-1.91	0.02	-1.21
C5FC40-7	18	0.04	0.12	0.04	-1.88	0.02	-1.29

Table 4-8 shows the expansion and mass change data for ternary blends containing 30% Class C fly ash and 3% silica fume. Ternary blend mixtures at 0.4 w/cm passed the 0.1% expansion criteria for all time periods, whereas mixtures C1FC30SF3-7 and C2FC30SF3-7 failed the expansion criteria at 6 months. These prisms exhibited mass loss but were still cohesive until the 18 month measurements.

Table 4-8: Expansion and mass change data for concrete with ternary SCM blends exposed to sodium sulfate solution

Mixture ID	Age (months)	Sodium Sulfate 1012		Sodium Submerged		Sodium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1FC30S3-4	3	0.02	0.09	0.00	-0.08	0.00	-0.15
C1FC30S3-4	6	0.04	0.19	0.02	-0.18	0.02	-0.15
C1FC30S3-4	9	0.02	0.20	0.02	-0.42	0.02	-0.15
C1FC30S3-4	12	0.04	0.23	0.01	-0.86	0.00	-0.16
C1FC30S3-4	18	0.04	0.25	0.02	-0.82	0.00	-0.16
C1FC30S3-7	3	0.03	-0.53	0.05	-3.66	0.04	-1.37
C1FC30S3-7	6	0.09	-1.23	0.20	-4.76	0.27	-2.25
C1FC30S3-7	9	0.18	-2.83	0.42	-5.16	0.35	-3.08
C1FC30S3-7	12	0.28	-0.53	1.18	-6.75	Broken	-7.36
C1FC30S3-7	18	Broken	Broken	broken	broken	Broken	Broken
C2FC30S3-4	3	0.00	-0.02	0.02	-0.02	0.01	-0.07
C2FC30S3-4	6	0.01	0.01	0.03	-0.08	0.02	-0.14
C2FC30S3-4	9	0.02	-0.07	0.04	-0.03	0.02	-0.14
C2FC30S3-4	12	0.03	0.07	0.05	-0.04	0.03	-0.10
C2FC30S3-4	18	0.03	0.09	0.09	-0.30	0.05	-0.25
C2FC30S3-7	3	0.03	-0.02	0.07	-0.12	0.06	-1.20
C2FC30S3-7	6	0.17	-0.79	0.18	-3.62	0.14	-2.02
C2FC30S3-7	9	0.31	-1.28	0.34	-4.70	0.16	-0.24
C2FC30S3-7	12	0.56	-2.65	0.47	-5.21	0.18	-2.89
C2FC30S3-7	18	Broken	-4.65	0.78	-15.42	Broken	-3.96
C5FC30S3-4	3	0.00	0.10	0.00	-0.06	0.00	-0.10
C5FC30S3-4	6	0.01	0.13	0.00	-0.08	0.00	-0.06
C5FC30S3-4	9	0.00	0.19	0.00	-0.05	0.00	-0.05
C5FC30S3-4	12	0.00	0.19	-0.01	-0.07	-0.01	-0.06
C5FC30S3-4	18	0.01	0.20	-0.01	-0.01	-0.01	-0.04
C5FC30S3-7	3	0.01	0.05	0.00	0.16	0.00	-0.08
C5FC30S3-7	6	0.02	0.42	0.02	0.19	0.01	-0.13
C5FC30S3-7	9	0.02	0.21	0.03	0.20	0.01	-0.14
C5FC30S3-7	12	0.04	0.24	0.03	0.19	0.00	-0.17
C5FC30S3-7	18	0.07	0.45	0.04	0.18	0.01	0.12

Table 4-9 summarizes the expansion and mass change data for mixtures with Class F fly ash in the three sodium sulfate conditions. The use of 20% Class F fly ash suppressed expansion when used with Type V cement at all w/cm ratios and it suppressed expansion

in low w/cm mixtures with Type I and Type I/II cement. Mixtures C1FF20-7 and C2FF20-7 expanded in all three sodium sulfate exposure conditions at 6 months.

Table 4-9: Expansion and Mass Change Data for Concrete with Various Cements (Type I, II, or V) in combination with Class F fly ash and exposed to sodium sulfate solution

Mixture ID	Age (months)	Sodium Sulfate 1012		Sodium Submerged		Sodium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1FF20-4	3	0.01	0.06	0.01	0.06	0.00	-0.12
C1FF20-4	6	0.02	0.15	0.01	0.11	0.00	-0.10
C1FF20-4	9	0.03	0.21	0.02	0.16	0.00	-0.08
C1FF20-4	12	0.03	0.29	0.02	-0.57	-0.01	-0.55
C1FF20-4	18	0.06	0.16	0.02	-0.19	0.00	-0.34
C1FF20-7	3	0.03	0.26	0.03	0.01	0.03	-0.38
C1FF20-7	6	0.08	0.23	0.12	0.03	0.11	-0.82
C1FF20-7	9	0.39	-0.99	0.40	-0.10	0.34	-1.22
C1FF20-7	12	Broken	Broken	Broken	-0.94	Broken	-1.74
C1FF20-7	18	Broken	Broken	Broken	Broken	Broken	-13.57
C2FF20-4	3	0.00	0.00	0.00	-0.01	0.00	-0.08
C2FF20-4	6	0.00	0.00	0.00	0.11	-0.01	-0.12
C2FF20-4	9	0.00	0.06	0.00	0.19	0.01	-0.08
C2FF20-4	12	0.01	0.16	0.01	0.22	0.01	-0.03
C2FF20-4	18	0.00	0.23	0.01	0.27	0.01	0.03
C2FF20-7	3	0.00	0.00	0.00	0.24	-0.02	0.08
C2FF20-7	6	0.02	0.07	0.07	0.42	0.01	-0.03
C2FF20-7	9	0.06	0.15	0.17	0.50	0.08	-0.01
C2FF20-7	12	0.15	0.36	0.25	0.62	0.12	0.04
C2FF20-7	18	0.26	0.49	0.65	0.10	0.47	-0.81
C5FF20-4	3	0.00	0.12	0.00	-0.06	0.00	-0.07
C5FF20-4	6	0.01	0.12	0.00	0.03	0.02	-0.09
C5FF20-4	9	0.02	0.13	0.01	0.13	0.01	-0.04
C5FF20-4	12	0.02	0.14	0.00	0.20	-0.01	0.02
C5FF20-4	18	0.03	0.12	0.01	0.30	-0.01	0.05
C5FF20-7	3	0.01	0.19	0.02	-0.01	0.01	-0.05
C5FF20-7	6	0.01	0.22	0.01	0.01	0.00	-0.16
C5FF20-7	9	0.02	0.23	0.02	0.19	0.03	-0.20
C5FF20-7	12	0.03	0.22	0.03	0.29	0.02	-0.14
C5FF20-7	18	0.06	0.26	0.04	0.31	0.04	-0.15

The mixtures that expanded also lost mass, but the form of deterioration was different. The prisms did not show the same disintegration form of attack as was noticed with the Class C fly ash. The pieces that broke off from the prisms were still solid and the loss of cohesion often observed with Class C fly ash was not observed.

Sulfate Profiling

Figure 4-17 shows the semi-quantitative XRD Rietveld analyses of concrete prisms containing Class C fly ash at 0.4 w/cm placed in the modified ASTM C 1012 indoor sodium sulfate conditions. The outer 0.12in (3mm) layer of the prisms once again shows the highest amount of ettringite formation. Ettringite formation decreased with increasing depth into the specimens. Interestingly, it appears that the prisms containing 20% fly ash show more ettringite than the prisms with 40% Class C fly ash, though this is not certain given that the data do not reflect actual amounts of the phases in the prisms. This observation makes sense, though, since it could correspond to the higher expansions occurring with mixtures containing 20% Class C fly ash. Mixture C1FC20-4 was not shown in Figure 4-17 due to complete deterioration of the prisms.

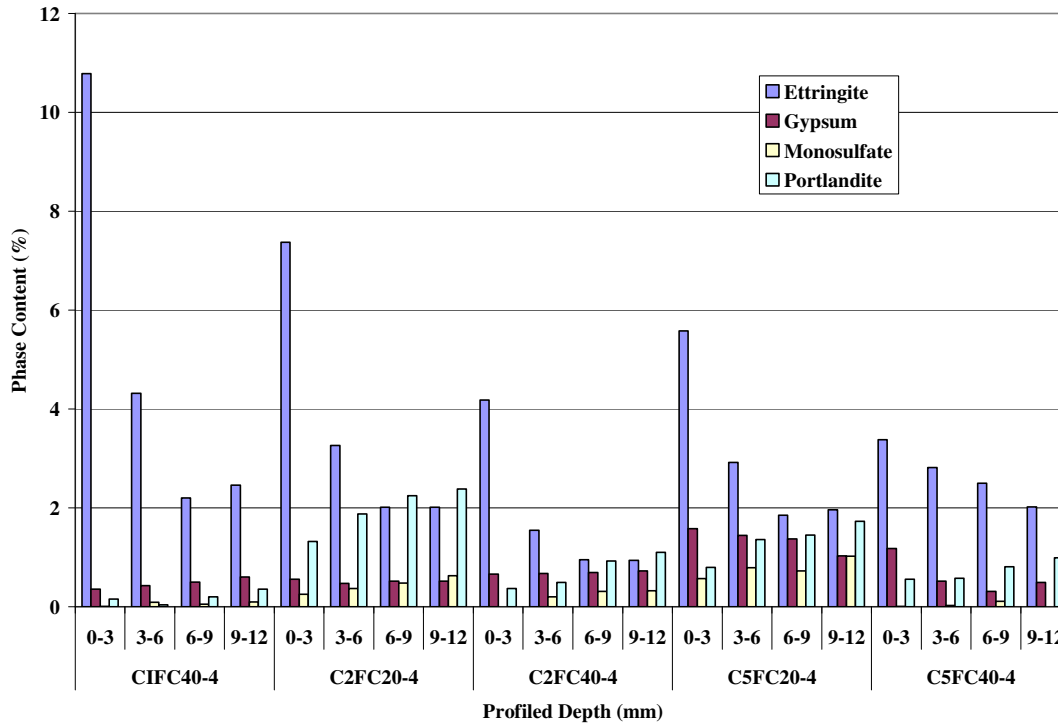


Figure 4-17: Semi-quantitative XRD Analysis of Concrete prisms at 0.4 w/cm placed in sodium sulfate solutions for 18 months

Mixtures C2FC40-7, C5FC20-7, and C5FC40-7 were the only high w/cm ratio mixtures with Class C fly ash to be milled for sulfate profiling. Figure 4-18 presents the phase contents from the milled sections for these three mixtures. Ettringite formation in mixture C5FC20-7 appears to be greater than C5FC40-7, which again corresponds well with expansion data shown in Table 4-7. The ettringite levels decrease after the first layer in all three mixtures. This did not occur with mixtures with high w/cm and without SCMs, once again illustrating the importance of permeability in combating sulfate attack (both chemical and physical forms of distress).

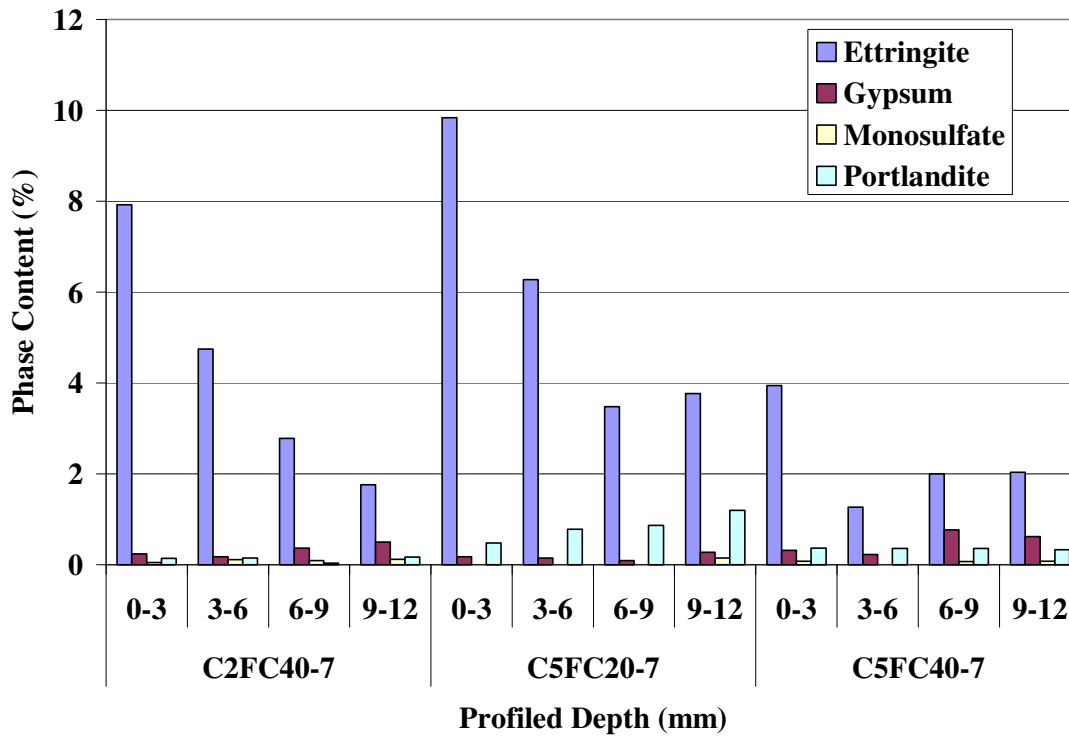


Figure 4-18: Quantitative XRD analysis of prisms at 0.7 w/cm placed tested indoors in sodium sulfate solutions

4.4.3.1 Comparison of mortar to concrete

Several mortar mixtures were tested using ASTM C 1012 that had similar combinations and dosages of cementitious materials, as well as fairly comparable w/cm (0.43 to 0.485) to the concrete mixtures (0.40) tested in sulfate solutions, as previously summarized in Table 4-4. These similar mixtures included control mixtures incorporating Type I, Type I/II, and Type V cements and mixtures containing these cements in combination with either 20 or 40% Class C fly ash. The results of these mortar tests are summarized in Table 4-10, and for convenience, the data from comparable concrete mixtures are also included.

Table 4-10: Comparison between mortar bars and concrete prisms evaluated using sodium sulfate solution in ASTM C 1012 storage

Age (Months)	Mixture	Concrete* Expansion (%)	Mortar** Expansion (%)	Mixture	Concrete* Expansion (%)	Mortar** Expansion (%)
3	Type I Cement	0.00	0.03	Type I/II Cement	0.00	0.04
6		0.03	0.07		0.01	0.04
9		0.04	0.19		0.01	0.08
12		0.07	0.55		0.01	0.11
18		1.08	Broken		0.01	0.32
3	Type I Cement 20% FA1	0.01	0.03	Type I/II Cement 20% FA1	0.01	0.04
6		0.02	0.04		0.01	0.06
9		0.02	0.1		0.02	0.1
12		0.05	0.13		0.00	0.15
18		Broken	0.9		0.04	0.35
3	Type I Cement 40% FA1	0.03	0.04	Type I/II Cement 40% FA1	0.01	0.07
6		0.03	0.12		0.01	0.58
9		0.08	0.26		0.01	Broken
12		0.12	0.51		0.04	Broken
18		0.48	Broken		0.07	Broken
3	Type V Cement	0.00	0.03	Type V Cement 20% FA1	0.00	0.03
6		0.01	0.03		0.02	0.04
9		0.03	0.05		0.03	0.05
12		0.02	0.06		0.03	0.05
18		0.03	0.07		0.02	0.05
3	Type V Cement 40% FA1	0.00	0.06			
6		0.00	0.27			
9		0.03	0.53			
12		0.03	Broken			
18		0.05	Broken			

* w/cm = 0.40

** w/cm = 0.43 – 0.48 (based on meeting target flow value)

As has been the general trend in this experimental program, the expansion and/or deterioration of mortar mixtures has been greater than that observed for similar concrete mixtures. In some cases, there were particularly stark differences in behavior between mortar and concrete exposed to similar sulfate solutions. For example, mortar containing Type V cement and 40% Class C fly ash (FA1) expanded considerably (0.27% at 6

months and 0.53% at 12 months) and were not intact by 12 months. Conversely, a similar concrete mixture (C5FC40-4) expanded by only 0.05% after 18 months. There is a large disconnect between mortar and concrete performance, but as mentioned earlier, the higher paste content and smaller specimen size for the mortar samples may be key factors.

4.4.3 Magnesium sulfate

4.4.3.1 Cement composition and w/cm

Expansions and mass change

Table 4-11 summarizes the expansions and mass changes for mixtures without SCMs in all three magnesium sulfate conditions. Regardless of exposure conditions (ASTM C 1012 or outdoor exposure site), only control mixtures containing Type I cement exhibited significant expansion. Mixtures C1-4 and C1-7 both exhibited expansion under ASTM C 1012 storage conditions. In addition, C1-7 expanded in the submerged placement in the outdoor sulfate exposure site. Prisms that expanded outdoors exhibited mass loss, which was mainly from deterioration of the prisms below the ground level. On the other hand, concrete prisms that expanded under ASTM C 1012 testing conditions gained mass, exhibited large cracks, but were still intact after 18 months of testing.

Table 4-11: Expansion and mass change data for mixtures without SCMs, exposed to magnesium sulfate solution

Mixture ID	Age (months)	Magnesium Sulfate 1012		Magnesium Submerged		Magnesium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1-4	3	0.00	0.52	0.01	0.01	0.01	-0.01
C1-4	6	0.02	0.54	0.01	0.02	0.01	0.06
C1-4	9	0.03	0.79	0.02	0.08	0.02	0.21
C1-4	12	0.04	0.87	0.03	0.13	0.02	0.11
C1-4	18	0.44	1.73	0.05	-0.45	0.02	-0.76
C1-7	3	0.01	0.32	0.01	-0.01	0.00	-0.17
C1-7	6	0.03	0.66	0.02	0.14	0.01	0.04
C1-7	9	0.09	0.79	0.07	0.34	0.02	0.16
C1-7	12	0.18	0.97	0.13	0.38	0.04	-0.15
C1-7	18	0.45	1.29	0.61	-1.58	0.06	-0.73
C2-4	3	0.00	0.15	0.00	-0.01	0.00	-0.15
C2-4	6	0.00	0.23	0.00	-0.02	0.01	-0.06
C2-4	9	-0.01	0.33	0.01	-0.02	0.01	-0.07
C2-4	12	0.00	0.38	0.01	0.00	0.01	-0.04
C2-4	18	0.00	0.45	0.02	0.08	0.01	0.03
C2-7	3	-0.01	0.27	0.00	0.05	-0.02	-0.22
C2-7	6	0.01	0.35	0.00	0.12	-0.01	0.02
C2-7	9	0.01	0.32	0.01	0.23	-0.01	0.06
C2-7	12	0.02	0.29	0.01	0.17	-0.01	-0.02
C2-7	18	0.03	0.28	0.01	0.31	0.01	0.16
C5-4	3	-0.01	0.37	0.00	0.00	-0.01	-0.15
C5-4	6	0.00	0.20	0.01	0.03	0.00	-0.03
C5-4	9	0.01	0.21	0.01	0.02	0.00	-0.02
C5-4	12	0.01	0.24	0.02	0.04	0.00	-0.08
C5-4	18	0.02	0.25	0.03	0.07	0.01	0.14
C5-7	3	0.00	0.46	0.02	0.03	0.01	-0.25
C5-7	6	0.01	0.45	0.02	0.01	0.01	-0.07
C5-7	9	0.01	0.56	0.02	0.05	0.02	-0.10
C5-7	12	0.02	0.50	0.03	0.10	0.01	-0.22
C5-7	18	0.03	0.48	0.03	0.12	0.03	-0.07

Sulfate profiling

Figure 4-19 depicts the XRD results from powders milled at successive depth into the prisms placed in ASTM C 1012 storage conditions in magnesium sulfate solution after 18

months of storage. The three mixtures shown in the Figure 4-20 show a large amount of ettringite in the outer layer followed by an abrupt decrease in ettringite with proximity toward the center of prism. It was originally thought that brucite may have formed due to magnesium sulfate exposure; however, XRD analysis did not confirm this supposition since no brucite was detected. Gypsum and monosulfate formed in large amounts in these layers. Calcium hydroxide was nearly depleted in the outer layer of the C1-4 mixture. Decalcification of C-S-H could potentially be occurring in this sample. Mixture C2-4 exhibited ettringite formation in the outer layer. Mixture C5-4 does not show any significant reaction products forming that would indicate sulfate attack.

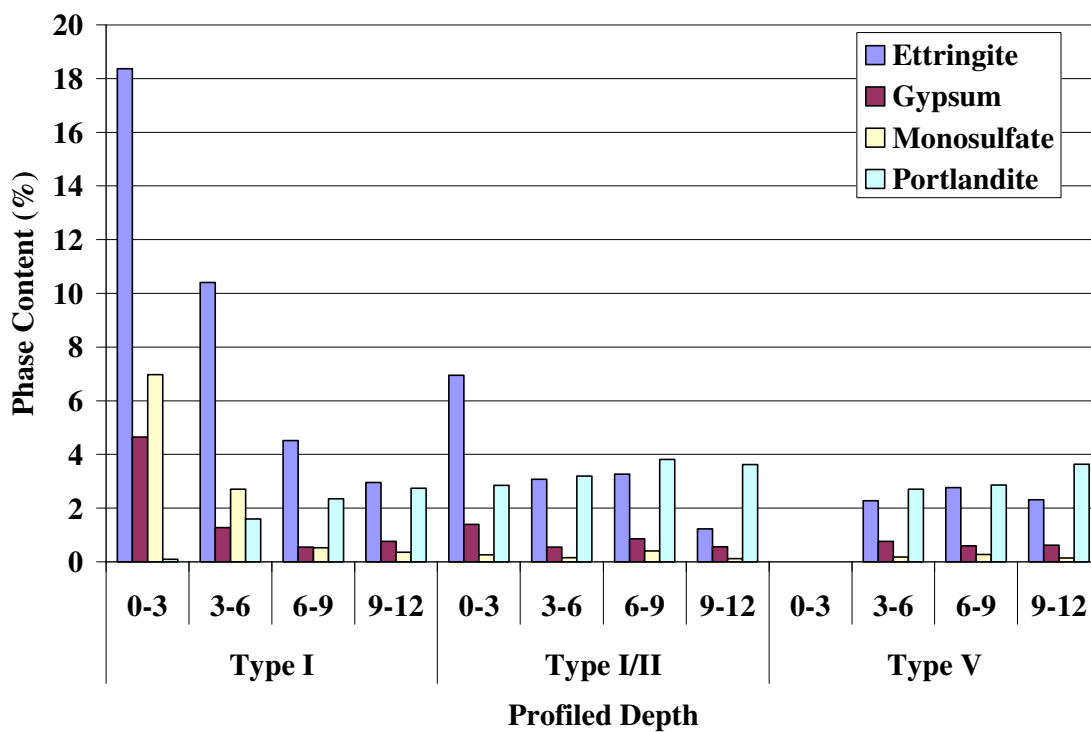


Figure 4-19: Semi-quantitative XRD analysis of concrete prisms at 0.4 w/cm placed in indoor magnesium sulfate conditions

Figure 4-20 shows XRD results for mixtures at 0.7 w/cm in ASTM C 1012 storage conditions in magnesium sulfate. Ettringite is highest in the outer layer but does not decline further into the specimen. Gypsum formation is also greatest in the outer layer but does decrease with increasing depth toward the middle of the prism. Calcium hydroxide is depleted towards the outer layer and increases in content further into the prisms.

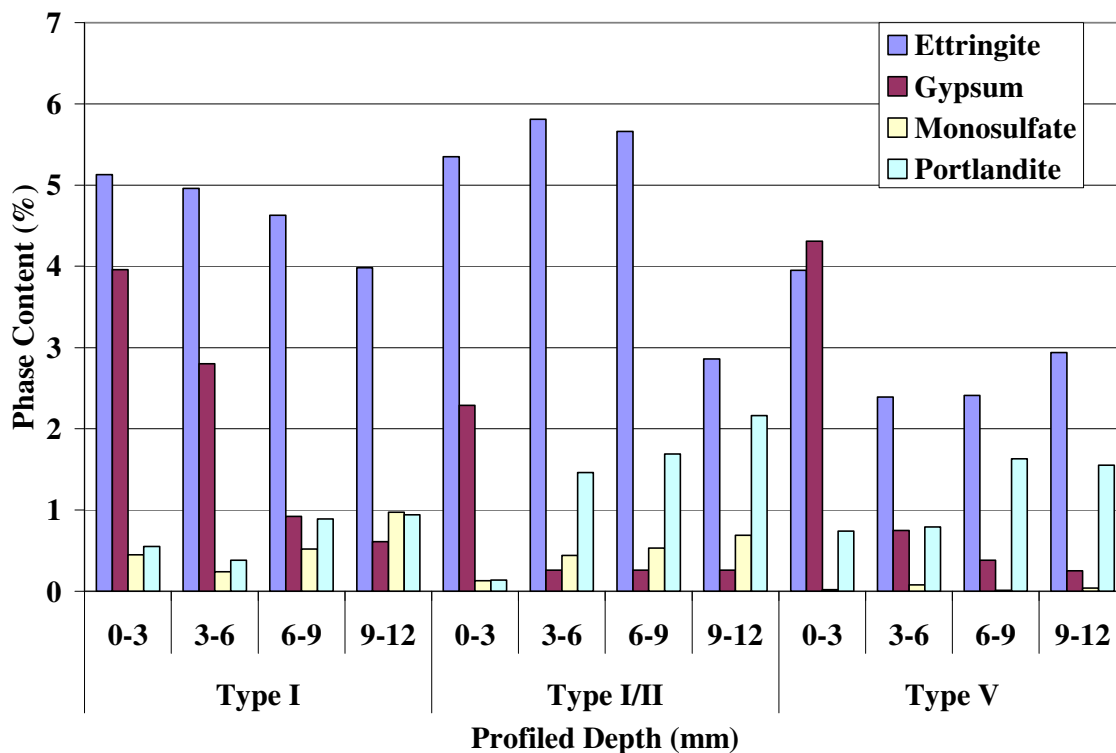


Figure 4-20: Semi-quantitative XRD Rietveld analysis of prisms placed in magnesium sulfate conditions

4.4.3.2 Supplementary cementing materials

Expansions and mass change

Similar to mixtures in sodium sulfate, the addition of 20% Class C fly ash performed worse than a replacement level of 40% Class C fly ash. Table 4-12 provides the expansion and mass change data for mixtures containing Type I cement and SCMs.

Prisms in the indoor controlled environment from mixture C1FC20-7 were not measurable at 12 months due to their length being too long for the comparator. The same mixture in the outdoor environment expanded over 1% and did not fully deteriorate. Large cracks in the prisms and physical damage which occurred during removal from the soil made these bars immeasurable. Prisms that did expand too much for the comparator gained mass until they finally fully deteriorated. Mixtures with 40% Class C fly ash did not fail the 0.1% expansion criterion in any of the three environments.

Table 4-12: Expansion and mass change data for concrete with Type I cement and Class C fly ash, exposed to magnesium sulfate solution

Mixture ID	Age (months)	Magnesium Sulfate 1012		Magnesium Submerged		Magnesium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1FC20-4	3	0.01	0.11	0.00	-0.08	0.00	-0.05
C1FC20-4	6	0.01	0.10	0.01	-0.09	0.01	0.03
C1FC20-4	9	0.02	0.17	0.02	-0.06	0.01	0.07
C1FC20-4	12	0.02	0.21	0.03	0.05	0.02	0.06
C1FC20-4	18	Broken	Broken	0.04	-2.13	0.02	0.15
C1FC20-7	3	0.03	0.34	0.03	0.15	0.02	-0.09
C1FC20-7	6	1.07	1.28	0.29	-6.94	0.10	-2.81
C1FC20-7	9	1.52	2.04	1.06	-7.92	0.36	-11.05
C1FC20-7	12	Too Long	1.22	1.28	Broken	Broken	Broken
C1FC20-7	18	--	2.35	Broken	--	--	--
C1FC40-4	3	0.02	0.25	0.00	0.01	-0.01	-0.12
C1FC40-4	6	0.03	0.30	0.00	0.08	-0.01	-0.10
C1FC40-4	9	0.03	0.38	0.00	0.08	-0.01	-0.09
C1FC40-4	12	0.02	0.21	0.02	0.15	0.01	-0.14
C1FC40-4	18	0.04	0.20	0.02	0.06	0.01	-0.20
C1FC40-7	3	0.02	0.18	0.00	0.06	-0.01	-0.11
C1FC40-7	6	0.03	0.09	0.00	0.23	0.00	-0.14
C1FC40-7	9	0.05	0.27	0.01	0.27	0.00	-0.18
C1FC40-7	12	0.05	0.22	0.03	0.28	0.01	-0.43
C1FC40-7	18	0.09	0.18	0.04	0.19	0.02	-0.35

Mixtures with Type I/II cement and Class C fly ash are shown in Table 4-13, along with expansion and mass change data. Similar to mixtures in magnesium sulfate conditions containing Type I cement, 20% Class C fly ash performed worse than 40% Class C fly ash. Reducing the w/cm was effective in improving sulfate resistance. Lastly, for the indoor testing, using ASTM C 1012 storage conditions, mixture C2FC20-4 exhibited better sulfate resistance than C1FC20-4, illustrating the importance of cement composition.

Table 4-13: Expansion and mass change data for concrete with Type I/II cement and Class C fly ash, exposed to magnesium sulfate solution

Mixture ID	Age (months)	Magnesium Sulfate 1012		Magnesium Submerged		Magnesium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C2FC20-4	3	0.01	0.14	0.00	0.11	-0.01	-0.04
C2FC20-4	6	0.01	0.17	0.00	0.11	-0.01	-0.05
C2FC20-4	9	0.02	0.36	0.01	0.12	0.01	0.04
C2FC20-4	12	0.01	0.32	0.02	0.10	0.02	0.02
C2FC20-4	18	0.00	0.33	0.02	0.18	0.02	0.09
C2FC20-7	3	0.02	0.59	0.00	0.01	0.00	-0.20
C2FC20-7	6	0.03	0.56	0.01	0.17	0.01	-0.24
C2FC20-7	9	0.60	1.01	0.03	0.31	0.06	-0.08
C2FC20-7	12	Broken	1.63	0.11	-0.58	0.12	-0.12
C2FC20-7	18	--	3.14	Broken	Broken	Broken	Broken
C2FC40-4	3	0.00	0.07	-0.01	-0.04	-0.01	-0.07
C2FC40-4	6	0.01	0.19	0.00	0.01	0.00	-0.02
C2FC40-4	9	-0.01	0.33	0.00	0.11	0.00	-0.06
C2FC40-4	12	0.01	0.22	0.00	0.06	0.00	-0.03
C2FC40-4	18	0.02	0.22	0.00	0.11	0.00	-0.02
C2FC40-7	3	0.04	0.26	0.01	0.30	0.01	0.00
C2FC40-7	6	0.18	0.52	0.03	0.29	-0.01	0.10
C2FC40-7	9	0.27	0.67	0.05	0.56	0.00	-0.26
C2FC40-7	12	0.34	0.67	0.05	0.63	0.01	-0.53
C2FC40-7	18	0.41	0.66	0.07	0.52	-0.02	-0.76

All mixtures containing Type V cement and Class C fly ash performed well except for C5FC20-7 which failed the expansion criteria at 12 months in only the modified ASTM C 1012 magnesium sulfate solution. Mixtures with Class C fly ash performed better in magnesium sulfate conditions than those in sodium sulfate. These prisms in magnesium sulfate conditions did not fail in many conditions and did not lose mass.

Ternary blends exhibited good sulfate resistance in all mixtures. Similar to sodium sulfate, the 30% Class C fly ash and 3% silica fume ternary blend performed well. Every mixture passed the expansion criteria up to the 18 month measurements in magnesium sulfate conditions. Mixtures containing 20% Class F fly ash are shown in Table 4-14 with their expansion and mass change data. C1FF20-7 was the only mixture that failed the 0.1% expansion criteria. Class F fly ash was more sulfate-resistant than Class C fly ash in magnesium sulfate solutions.

The prisms in the modified ASTM C 1012 magnesium sulfate solutions failed at 9 months while the outdoor submerged and vertical prisms were broken for the 18 month measurements. This failure was surprising since the bars had not expanded prior to 18 months.

Table 4-14: Expansion and mass change data for concrete with ternary SCM blends exposed to magnesium sulfate solution

Mixture ID	Age (months)	Magnesium Sulfate 1012		Magnesium Submerged		Magnesium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C1FF20-4	3	0.01	-0.24	0.01	-0.02	0.00	-0.08
C1FF20-4	6	0.01	0.27	0.00	0.01	0.00	-0.06
C1FF20-4	9	0.01	0.30	0.01	0.02	0.00	-0.06
C1FF20-4	12	0.03	0.35	0.00	0.07	-0.01	-0.01
C1FF20-4	18	0.02	0.44	0.00	0.10	0.00	0.02
C1FF20-7	3	0.01	0.38	0.02	0.04	0.00	-0.07
C1FF20-7	6	0.03	0.41	0.02	0.09	0.00	-0.05
C1FF20-7	9	0.10	0.51	0.03	0.08	0.01	-0.05
C1FF20-7	12	0.27	0.65	0.02	0.15	0.00	0.10
C1FF20-7	18	broken	broken	Broken	Broken	Broken	Broken
C2FF20-4	3	0.01	0.07	0.00	-0.15	-0.01	-0.07
C2FF20-4	6	0.02	0.10	-0.01	-0.08	0.00	-0.05
C2FF20-4	9	0.02	0.12	0.00	-0.03	0.00	-0.08
C2FF20-4	12	0.03	0.13	0.00	-0.06	0.00	-0.02
C2FF20-4	18	0.03	0.30	0.00	-0.02	0.01	0.05
C2FF20-7	3	-0.02	0.18	0.00	-0.06	0.00	0.03
C2FF20-7	6	-0.01	0.15	0.00	0.03	0.00	-0.02
C2FF20-7	9	0.01	0.22	0.01	0.08	0.00	-0.18
C2FF20-7	12	0.01	0.28	0.02	0.08	0.02	-0.11
C2FF20-7	18	0.06	0.49	0.04	0.20	0.05	0.01
C5FF20-4	3	0.00	0.00	0.00	0.09	0.00	-0.05
C5FF20-4	6	0.00	0.14	0.00	0.04	-0.01	-0.08
C5FF20-4	9	0.01	0.13	0.01	0.09	0.00	-0.12
C5FF20-4	12	0.01	0.13	-0.01	0.17	-0.01	-0.04
C5FF20-4	18	0.01	0.14	-0.01	0.16	-0.01	-0.06
C5FF20-7	3	0.01	0.13	0.01	-0.03	0.00	-0.07
C5FF20-7	6	0.00	0.14	-0.01	-0.13	0.00	-0.06
C5FF20-7	9	0.00	0.11	0.02	-0.06	0.01	-0.18
C5FF20-7	12	0.00	0.12	0.00	0.01	0.00	-0.08
C5FF20-7	18	0.03	0.21	0.01	0.12	0.00	-0.01

Sulfate profiling

Figure 4-21 shows semi-quantitative XRD Rietveld analyses on concrete prisms placed in the modified ASTM C 1012 storage condition in magnesium sulfate. Specifically, this

graph compares the differences between different cements with Class C fly ash at varying replacement levels.

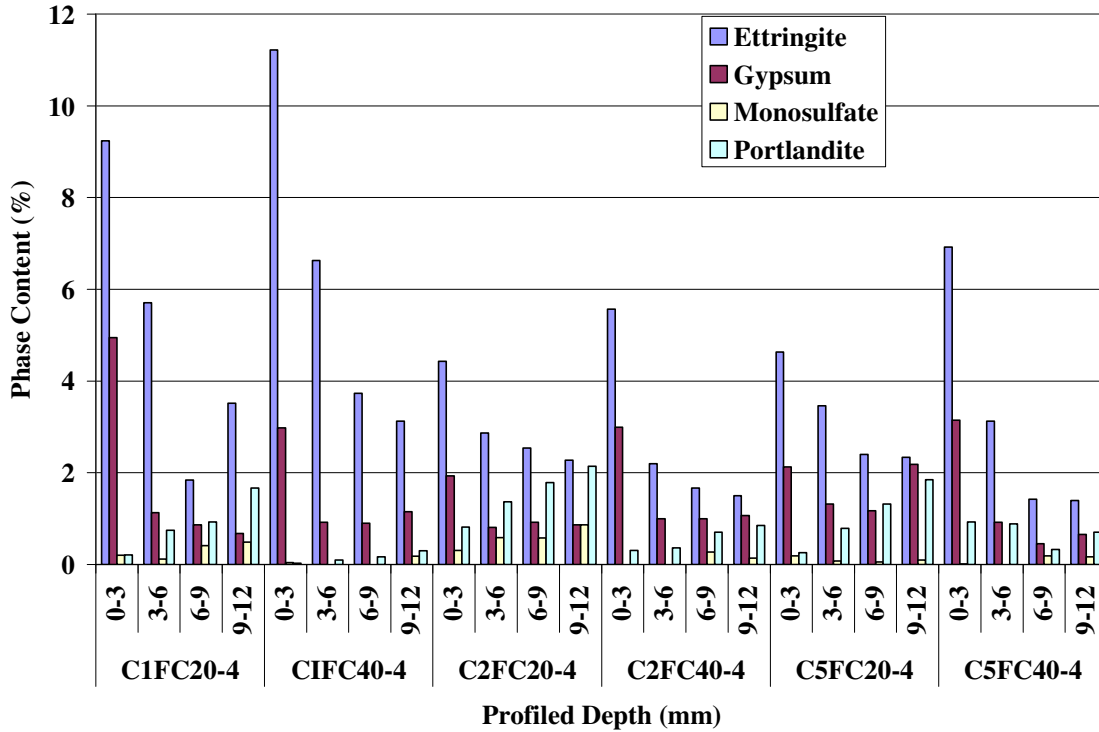


Figure 4-21: Semi-quantitative XRD Rietveld analysis of prisms containing SCMs in indoor magnesium sulfate conditions

Ettringite and gypsum formation were greater in the outer layer of each mixture shown. Both 20% and 40% Class C fly ash replacement resulted in formation of nearly the same amount of ettringite. Portlandite was reduced in mixtures containing higher fly ash replacement due to the pozzolanic reaction occurring with the additional fly ash.

Similarly at higher w/cm of 0.7, Figure 4-22, shows ettringite and gypsum formation are greater in the outer layer. At 40% replacement, a decline in ettringite formation can be

seen as toward the interior of the concrete, owing to the reduced permeability of the mixtures.

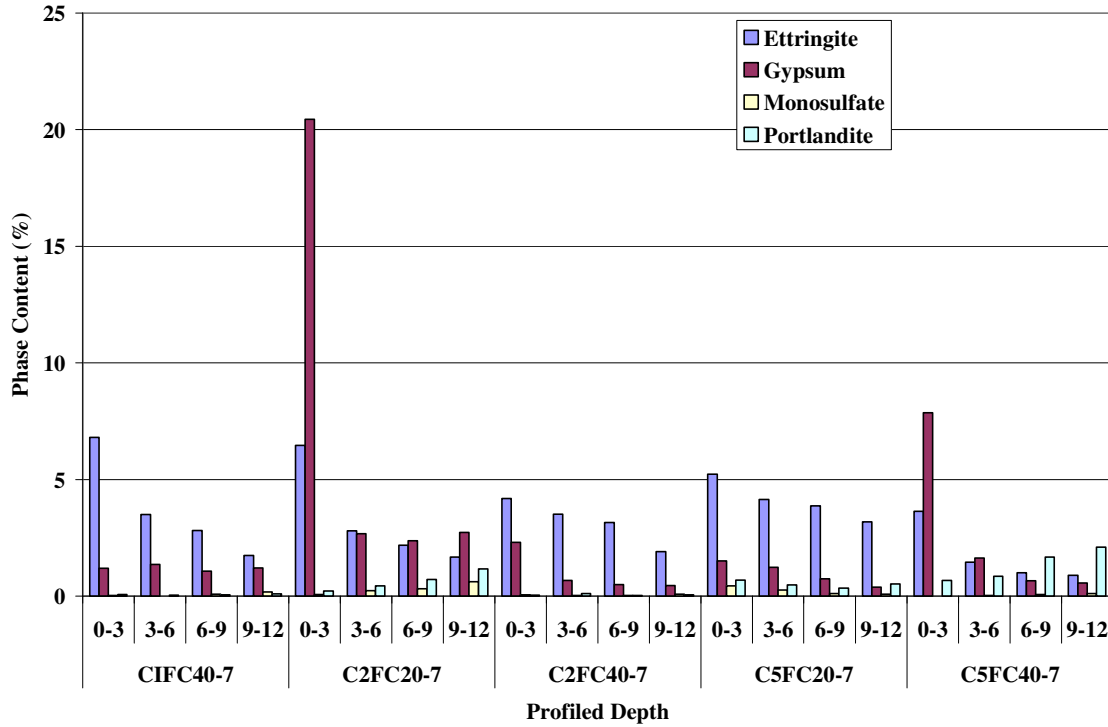


Figure 4-22: Semi-quantitative XRD Rietveld analysis of prisms with SCMs placed indoors in magnesium sulfate solution

4.4.3.3 Comparison between concrete and mortars

Expansion results for Type I/II and Type V control mixtures exposed to magnesium sulfate solution are shown in Table 4-15. Mortars made with similar materials performed worse than companion concrete prisms. Concrete control mixtures did not expand at either w/cm whereas control mortar mixture C2 failed at 18 months. Concrete prisms with Class C fly ash did not fail in any of the comparable mortar mixtures. Mortar mixtures containing Class C fly ash expanded past the expansion limit usually within 6 to 9 months.

Table 4-15: Comparison between mortar bars and concrete prisms evaluated using magnesium sulfate solution in ASTM C 1012 storage conditions

Mixture	Age (Months)	Concrete* Expansion (%)	Mortar** Expansion (%)	Mixture	Concrete* Expansion (%)	Mortar** Expansion (%)
Type I/II Cement	3	0.00	0.03	Type V Cement	-0.01	0.02
	6	0.00	0.04		0.00	0.03
	9	-0.01	0.07		0.01	0.05
	12	0.00	0.09		0.01	0.06
	18	0.00	0.2		0.02	0.09
Type I/II Cement 20% FA1	3	0.01	0.03	Type V Cement 20% FA1	0.00	0.03
	6	0.01	0.04		0.01	0.04
	9	0.02	0.1		0.03	0.05
	12	0.01	0.17		0.03	0.07
	18	0.00	0.38		0.02	0.12
Type I/II Cement 40% FA1	3	0.00	0.04	Type V Cement 40% FA1	0.01	0.05
	6	0.01	0.25		0.03	0.21
	9	-0.01	0.74		0.04	0.44
	12	0.01	Broken		0.03	Broken
	18	0.02	Broken		0.03	Broken

* w/cm = 0.40

** w/cm = 0.43 – 0.48 (based on meeting target flow value)

4.4.2.2 Physical sulfate testing

As previously discussed, the results of outdoor exposure tests have shown that physical sulfate attack may be a significant cause of distress, especially when considering exposure to sodium sulfate and for exposure conditions in which wicking action results in distress above the soil line. To further evaluate the physical form of sulfate attack, a separate study was initiated in which mortar specimens were immersed in different sulfate solutions and subjected to rapid temperature changes, the type of accelerated testing regime that Folliard and Sandberg (1994) found to be extremely damaging to concrete.

As described in Section 4.2.4, various mortar specimens were cast and immersed in different sulfate solutions (sodium sulfate or magnesium sulfate at concentrations of 10, 20, and 30%), then subjected to rapid temperature changes. Mortar mixtures with different w/cm ratios (0.4 and 0.7), different cement types (Type I and Type V), and with and without air-entraining agent were cast and tested. Mass loss was used as a simple index for quantifying distress.

Some general trends became quite evident after subjecting the various mortar specimens to over 150 cycles of temperature changes. Mortar mixtures with a w/cm of 0.4 showed very little distress, regardless of the cement type or sulfate solution in which they were exposed. Mortar mixtures with a w/cm of 0.7 exhibited significant distress, as manifested in substantial mass loss, when exposed to high concentrations of sodium sulfate solution, as shown in Figure 4-23. This figure shows the mass loss for mortar with a 0.7 w/cm containing Type V cement – similar distress was observed for Type I cement, further suggesting that this form of attack is physical in nature and not sensitive to cement chemistry. No distress was observed for any of the mortar specimens exposed to magnesium sulfate. This observation is consistent with the outdoor exposure site, where the only physical sulfate attack was observed for sodium sulfate

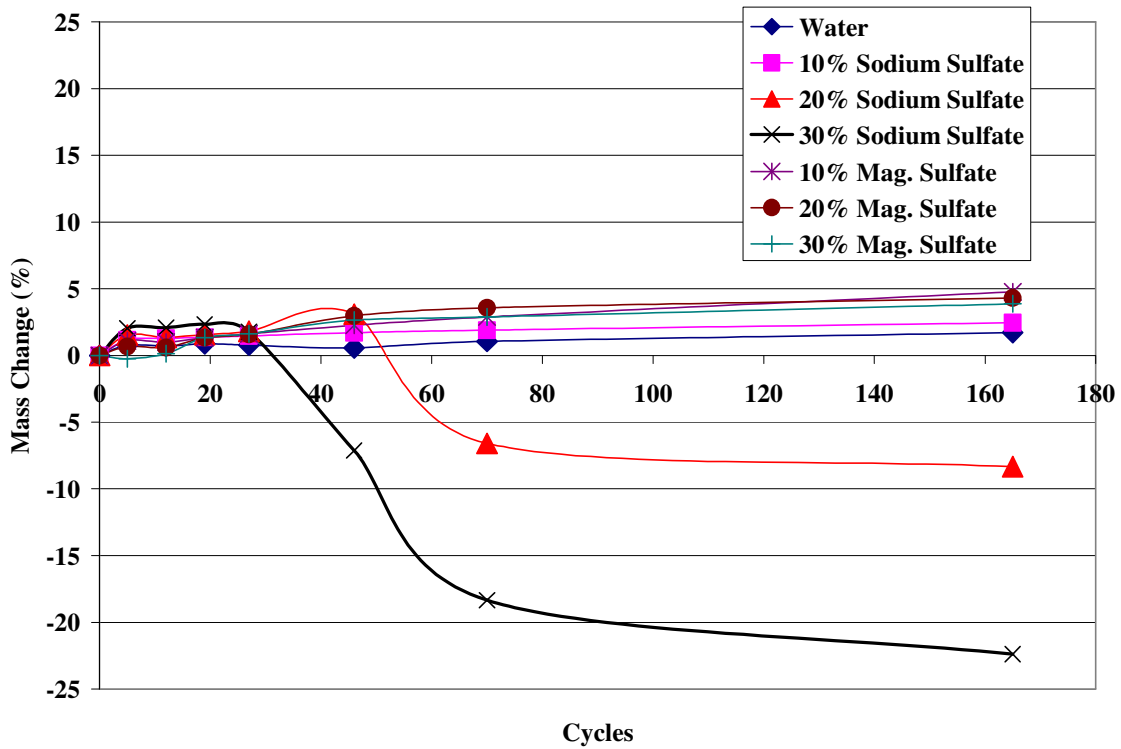


Figure 4-23: Physical sulfate testing of non-air-entrained mortars containing Type V cement (w/cm=0.7)

Figure 4-24 shows mass loss results for mortars (w/cm=0.7) containing either Type I or Type V cement and for each cement type, non-air-entrained and air-entrained mortars were evaluated. This graph shows that air entrainment slightly delays the onset of deterioration, but as was reported by Folliard and Sandberg (1994), air-entrained voids eventually become filled with sodium sulfate and their effectiveness in alleviating stresses caused by salt crystallization rapidly decreases. This graph also illustrates that the response to physical sulfate attack is quite similar between Type I and Type V cements, as previously discussed. Figure 4.25 shows the before and after images of a specimen that was damaged by physical sulfate attack in this testing regime.

In summary, the most important findings from this study on physical salt attack were that the best method of preventing distress is by using lower w/cm, that sodium sulfate is the main sulfate form causing physical sulfate attack, that cement type has little influence on distress, and that air entrainment provides short-term protection, but not long-term protection, against physical sulfate attack.

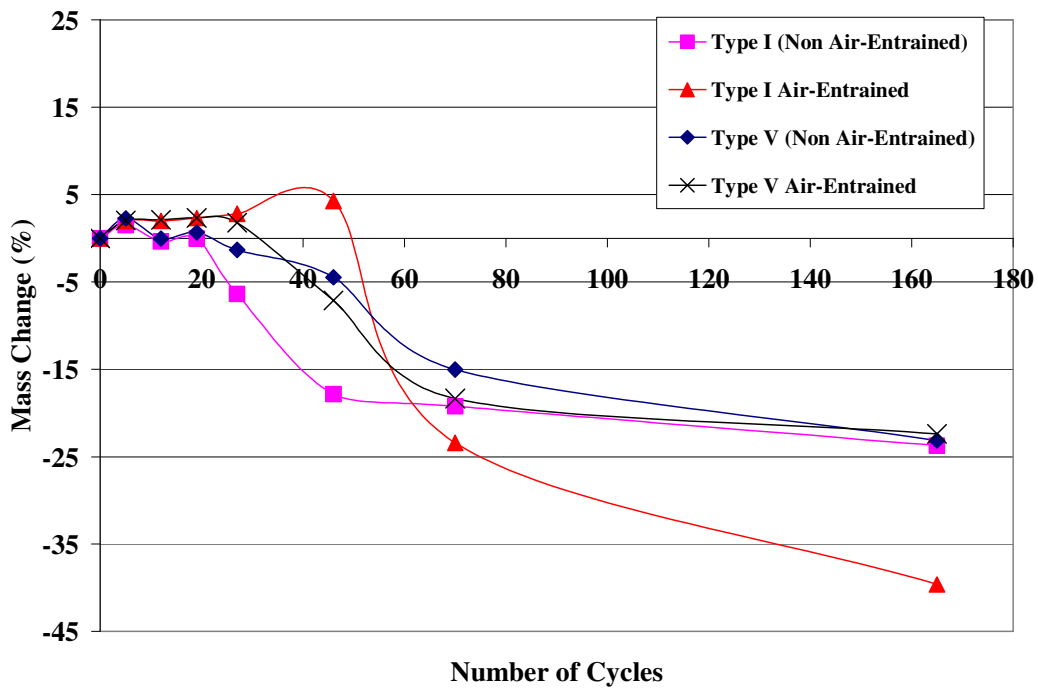


Figure 4-24: Physical sulfate testing of air-entrained and non-air-entrained mortars (w/cm=0,7) immersed in 30% sodium sulfate solution and subjected to temperature changes.



Figure 4-25: Mortar specimens before and after physical sulfate testing. The mixture contained Type V cement at 0.7w/cm. The disk on the left was prior to testing and the disk on the right went through 150 cycles.

4.5 Discussion

In the majority of the concrete testing including outdoor and indoor conditions, prisms in sodium sulfate conditions performed the worst. According to expansion criteria, expansions were first observed in prisms placed in sodium sulfate conditions followed by those in magnesium sulfate. It is usually noted that magnesium is the most severe sulfate that attacks concrete due to the many hydration products that are attacked. However, aggressiveness of sodium sulfate in both mortar and concrete testing showed damage at earlier time periods. The formation of brucite is known to create a protective layer on prisms attacked by magnesium sulfate; which may suggest the delayed attack on the prisms. Mixtures in calcium sulfate did not expand past 0.1% expansion after 18 months in any concrete mixture; however, damage is noticed on the exterior of the prisms. The

low solubility of gypsum does not get to the middle of the prisms to show appreciable expansions. The majority of the expansion is near the surface of the sample as shown by ettringite formation from XRD analysis and visibly by the deteriorated corners of the samples. Prisms submerged in the outdoor sodium sulfate conditions performed the worse of all the sodium sulfate conditions. These prisms performed worse than their counterparts indoors due to the wet/dry cycles that occur, extreme temperatures, and the physical sulfate attack.

The deterioration mechanism behind each of the conditions was clearly visible even without any analytical testing. Each of the sulfates deteriorated in different ways. Prisms placed in calcium sulfate began to deteriorate by scaling of the surface. Below the scaling, prisms were still sound, and did not show softening as noticed in the prisms placed in sodium and magnesium sulfate. Prisms placed in sodium sulfate conditions showed deterioration as evidenced by cracking along the corners of the prism before expansions began. A continual layered process of deterioration occurred with prisms in sodium sulfate. The layering attack was similar to findings by Gollop and Taylor (1994) which shows the progression of attack into the concrete from sodium sulfate. The corners eventually fell apart and more cracking occurred at the freshly exposed surface. Physical sulfate attack deterioration occurred on samples that were exposed to the atmosphere (no soil contact zone) in the sodium sulfate outdoor exposure condition. Magnesium sulfate caused a softening on the exterior of the prisms. Once expansion began, large cracks formed on the concrete, and unlike prisms in sodium sulfate, these

prisms remained intact with the large cracks. Once significant expansion occurred (>1%), the prisms did eventually fall apart along these cracks.

Mixtures containing 40% Class C fly ash generally exhibited enhanced performance over mixtures containing 20% Class C fly ash, which was generally the opposite when testing similar mortar bars in ASTM C 1012. The curing regime between the mortar and concrete mixtures was different which might suggest reasoning behind the difference. Concrete mixtures were allowed to moist cure for 28 days prior to placement into each of their corresponding solutions. ASTM C 1012 testing provides an accelerated curing regime in a water bath for 24 hours followed by limewater storage until a strength of 2850 psi (20 MPa) is achieved. The permeability may be lower for specimens after 28 days of wet curing especially with 40% Class C fly ash. Sulfate milling provided similar results in that ettringite formation was lower in specimens with 40% Class C fly ash.

Sulfate profiling by progressive milling provided an understanding of the chemical formation of hydration and reaction products forming in the different mixtures. In most mixtures, including those that did not exhibit expansion, ettringite formation was identified in the outer layer of the prism. Ettringite formation generally decreased further into the prisms; however, in some high w/cm mixtures, ettringite formation within the bulk of the specimen approached that near the surface. Gypsum formation increased in content near the outer portion when expansions occurred. The increased gypsum formation is forming and not converting to ettringite if there is not a source of aluminate.

The calcium hydroxide increased as the milling depth increased into concrete especially for prisms in sodium sulfate. The decreased depletion of calcium hydroxide did not allow further ettringite formation to occur further into prism. The profiling at regular intervals was a better technique than crushing the entire bulk mortar bar in chapter 3.

ASTM C 1012 mortar mixtures deteriorated more quickly with the addition of Class C fly ash. A large difference was noticed between mortar bar testing and concrete testing that had the same materials. Mortar bars expanded and deteriorated at a faster rate. The concrete prisms did not expand after 18 months where as their comparative mortar mixtures began to fail at 6 months. This was true for all three sulfate types tested. This difference in behavior may be attributed to differences in paste content, specimen size, curing conditions or other factors.

Overall, a disconnect does exist between laboratory testing and field concrete suffering from external sulfate attack. The worse conditions with concrete prisms placed in the outdoor sodium sulfate exposure site that had temperature effects responded better than mortar specimens stored indoors

4.6 Conclusions

This chapter presented and discussed the results of an outdoor sulfate exposure site in Austin, Texas which compared concrete mixtures in various sulfate conditions to laboratory testing of concrete and mortars. The following are the key conclusions to date from this testing:

- Concrete prisms placed in an outdoor exposure site performed differently than prisms placed in an indoor environment. The prisms deteriorated at a faster rate in the outdoor conditions, mostly due to higher average temperatures and in some cases due to temperature fluctuations and wetting drying cycles that tended to promote physical sulfate attack.
- Concrete placed in sodium sulfate performed the worst for all three sulfates tested and the submerged prisms placed in the outdoor sodium sulfate site performed the worst for all concrete placed in sodium sulfate storage conditions. The nature of physical attack associated with sodium sulfate may be the cause of the difference between the indoor and outdoor testing.
- Concrete prisms placed in calcium sulfate conditions did not expand past the 0.1% expansion criteria after 18 months of storage. However, they did show signs of deterioration on the surface of the prisms. XRD analysis showed ettringite formation occurring in this outer layer of deterioration. Prisms of the control mixtures containing Type I cement kept for 2 years began to expand.
- Concrete mixtures with 40% Class C fly ash replacements exhibited better sulfate resistance than mixtures containing 20% Class C fly ash. Expansion measurements followed by XRD analysis showed greater ettringite formation

in mixtures containing 20% Class C fly ash. This correlation was observed in both sodium and magnesium solutions.

- A large discrepancy occurs between mixtures in ASTM C 1012 mortar bar testing and concrete prisms placed in the same storage conditions. Concrete mixtures and mortars containing similar proportions showed that mortar mixtures failed more rapidly than comparative concrete specimens, perhaps due to differences in paste content, specimen size, and curing conditions.

Chapter 5. Evaluation of Concrete Structures for Potential Deterioration due to External Sulfate Attack

5.1 Introduction

External sulfate solutions containing calcium, sodium and magnesium may lead to premature concrete deterioration. However, sulfate attack caused by exposure to calcium sulfate (or gypsum), in the laboratory or in the field, has not been studied to the same extent as sulfate attack caused by sodium or magnesium sulfate. There is debate as to whether concrete can be attacked by soils or groundwater containing gypsum because of the relatively low solubility of gypsum (1440 ppm in water), as discussed in Chapter 2. Because of this limited solubility, the concentration in the pore water of adjacent soils or in nearby groundwater may remain quite low and could result in less deterioration than if the subject structure were exposed to more soluble forms of sulfate, such as magnesium or sodium sulfate. To compound this uncertainty, there have been very few laboratory

evaluations involving concrete exposed to gypsum-based solutions. As such, there is a general lack of a clear consensus as to how damaging external sources of gypsum can be to concrete.

Research performed under this project has attempted to fill in some of the missing gaps in knowledge and understanding through a comprehensive laboratory-based study, as reported in Chapter 4. The work reported in this chapter addresses this issue from another angle, through evaluations of transportation structures exposed to gypsiferous soils and groundwater throughout the state of Texas. Texas is unique in that most of the sulfate-rich regions contain gypsum as the primary form, and as such, a detailed survey of structures in these areas provides a unique opportunity to examine the true behavior of concrete exposed to external sources of gypsum.

This chapter presents the results of a comprehensive evaluation of transportation structures exposed to gypsiferous soils or gypsum-bearing groundwater. The structures investigated were all in the state of Texas. To pinpoint areas of possible sulfate attack, agricultural maps identifying sulfate-bearing soils, were utilized. According to these maps, several TxDOT-defined “districts” were selected. The El Paso, Paris, and Childress Districts showed the most promise for areas containing sulfate-bearing soils in the state of Texas. Over 200 concrete bridges, culverts, columns, and other transportation structures were visually inspected, and a subset of these were selected for further, detailed investigations. Figure 5-1 provides the locations of each site discussed in this

chapter. For the sites selected for more detailed evaluation, soil samples and groundwater samples (when available) were procured for subsequent laboratory testing, as were concrete powder samples for x-ray diffraction analysis and sulfate concentration determination. For certain structures, cores were extracted for more detailed laboratory-based evaluations, such as petrographic evaluation and scanning electron microscopy (SEM) analysis. This chapter provides a basic synopsis of the testing done to date; additional research is still in progress and will be published at a later date.

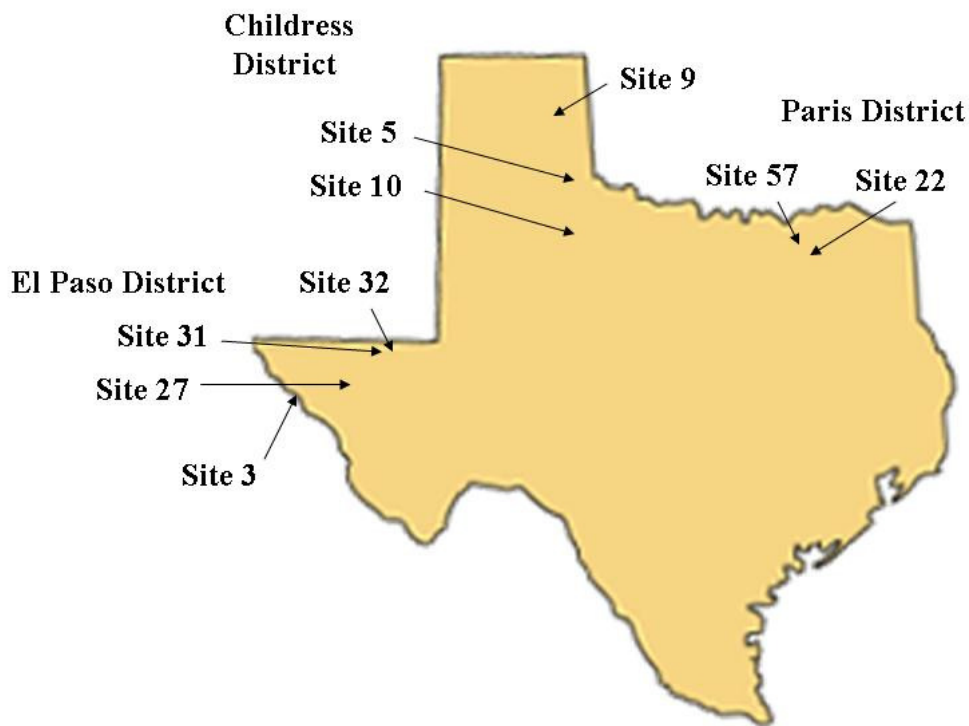


Figure 5-1: Site locations discussed within this chapter

5.2 Experimental methods

The following section provides the methodology and testing program for samples taken from areas of probable external sulfate attack in field structures. Samples taken included: water samples, soil samples, concrete powder samples, and concrete cores.

5.2.1 Water samples

When available, water samples were taken near the concrete structures where potential damage from sulfate attack was observed. Samples were retrieved by placing a 1 L Nalgene bottle into the source of water and collecting a full bottle of water. Samples were retrieved at multiple locations (e.g. upstream, downstream, etc.) at a given site. Once the samples were returned to the laboratory, a turbidimeter was used to measure the sulfate content. The turbidimeter measures the scattering of light that is being passed through a suspension of materials. The water samples were mixed with barium chloride, which reacts to form barium sulfate, which creates a suspension in the solution. The solution was then placed into the turbidimeter which measures NTU (Nephelometric Turbidity Units). A calibration curve was then created to relate the NTU to sulfate concentration. Figure 5-2 provides a calibration curve for calcium sulfate, sodium sulfate, and magnesium sulfate. The calibration curve was nearly the same for all three sulfate types.

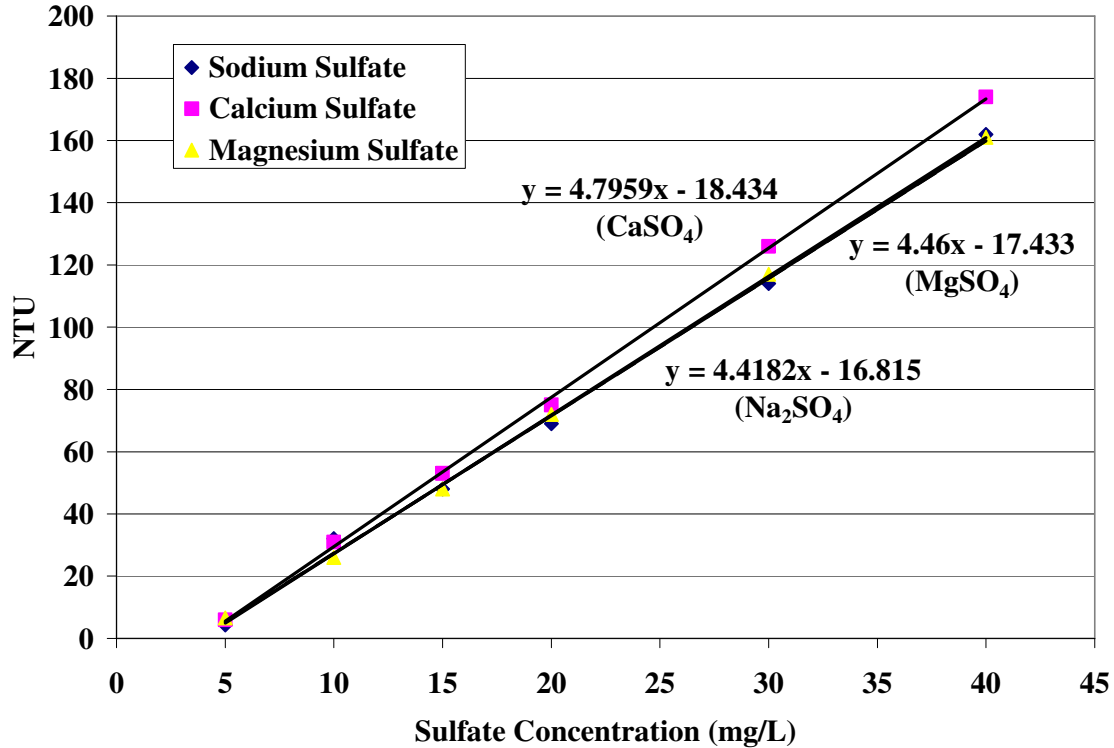


Figure 5-2: Calibration curve for sulfate using the turbidimeter

The unknown field samples were then measured against the calibration curve. Any readings above the calibration range were diluted to fit into the range of the calibration curve.

5.2.2 Soil samples

Soil samples were taken from different locations at each field site where sulfate attack was suspected. Two testing standards were used for the evaluation of sulfates in soils: TxDOT specification TEX-135-E that uses an extraction ratio of 20:1 and ASTM C 1580 that uses an 8:1 and 80:1 extraction ratio (TxDOT 1991, ASTM C 1580 2005). The two extraction ratios used in ASTM C 1580 provide a large enough range to determine if gypsum is present in the soil. The 80:1 extraction should provide enough water to

accommodate the low solubility of gypsum. Table 2-2 provides the exposure class table from ACI 201.2R. The exposure class is based on sulfate concentrations obtained from either water or soil samples collected from a given site. A higher exposure class corresponds to greater sulfate content in the soils. Each exposure class specifies w/cm and cementitious material requirements for concrete to be resistant to the amount of sulfate corresponding to the given exposure class.

5.2.3 Concrete powder samples

Concrete powder samples were taken for sulfate content and x-ray diffraction. Powder samples were taken from both deteriorated and non-deteriorated surfaces using a power drill. The determination of sulfate content was based on a method discussed by Hime (2001). Samples were passed through a No. 30 sieve and then 5 grams of the sieved material was digested in 20 ml of 1:4 HCl solution. The sample was then filtered and tested for sulfate content with a turbidimeter following the same methodology discussed in section 5.2.1. The samples were also tested in the XRD following the test procedure in section 3.2.3

5.2.4 Concrete cores

Concrete cores were taken from the most accessible locations on the affected structures. Core diameters of 2 in (50 mm) and 4 in (100 mm) were taken. Five cores were removed from most of the structures, with two to three from either a deteriorated or non-deteriorated section of the structure. After the cores were removed, they were labeled and placed into individual plastic bags. Samples of the cored concrete were used for

scanning electron microscopy. The SEM sample preparation procedure for the SEM is given in section 3.2.4.

5.3 Results and discussion

This section is divided into the three TxDOT districts investigated: Childress, Paris, and El Paso Districts. Each district contains geographical areas where deterioration from external sulfate attack is possible. In total, over 200 sites were investigated and they were numbered sequentially, whether deterioration due to external sulfate attack was suspected or not. Due to the large number of sites investigated, only the results from selected sites will be presented herein. The last section of this chapter presents preliminary results on a long-term study underway in the El Paso District. Appendix D provides agricultural maps with the site locations of the districts investigated. The site labels are not in continuous order since many sites visited did not have any deterioration.

5.3.1 Childress District

In general, the least amount of damage was observed in the Childress District. The location of the Childress District is southeast of Amarillo and west of Forth Worth. Three potential sites were investigated for possible damage from external sulfate attack. Site 5 consisted of damage to a concrete wall below a bridge on US 83. Site 9 had riprap damage below a bridge. Riprap is a sloped wall of concrete used hold back earth/soil to prevent erosion. Site 10 was a bridge on FM 2278 that had deteriorating columns.

5.3.1.1 Site 5

Site 5 has damage to the concrete base that supports an old steel bridge on US 83. Figure 5-2 shows the damage on the wall. The sulfate content of the soil was analyzed according to ASTM C 1580 and was found to be 0.04%, which constitutes a Class 0 exposure. This location is in the lowest classified exposure classification. The semi-quantitative XRD Rietveld analysis from the concrete powder only showed an increase in monosulfate in the area of deterioration. The good section had a monosulfate content of 0.56% while the deteriorated section content was 6.61%. In addition, the amount of ettringite and gypsum detected did not change between the two areas. Concrete cores taken from this location were not analyzed since the sulfate content was low in the soil and the XRD results did not show any significant deleterious reaction products.



Figure 5-3: Damage to the lower part of a wall below US 83 in Childress District

5.3.1.2 Site 9

The location of Site 9 is on FM 1547 in Shamrock, Texas which is east of Amarillo, Texas. Deterioration at this site is occurring on the riprap. Riprap is concrete that is used along the embankments below a bridge to hold back earth/soil. It is a low quality concrete. The sulfate content in the soil was 0.04% which is classified as Class 0 exposure. The concrete powder samples analyzed by XRD did not show any ettringite or gypsum formation.

5.3.1.3 Site 10

The last sampled site in the Childress District showed the most potential for external sulfate attack by visual inspection. Figure 5-3 shows one of the six columns sampled at site 10 which is a bridge on FM 2278 located south of Childress, Texas.



Figure 5-4: Damage to a bridge column on FM 2278, south of Childress, Texas

Sulfate content in the soils was 0.05%, which falls into a Class 0 exposure. Table 5-2 shows the sulfate content in the powder collected from this bridge. The sulfate content is greater near the top of the columns. An in-situ milling method to provide a sulfate profile would likely be more suitable for such an analysis but was not employed here.

Table 5-1: Sulfate content of concrete powders from locations in the Childress District

Location	%SO4
FM 2278 SO Bottom	0.51
FM 2278 SO Middle	0.40
FM 2278 SO TOP	0.47
FM 2278 SM Bottom	0.26
FM 2278 SM Middle	0.50
FM 2278 SM TOP	0.66
FM 2278 NO Bottom	0.26
FM 2278 NO Middle	0.42
FM 2278 NO TOP	0.46
FM 2278 NM Bottom	0.33
FM 2278 NM Middle	0.33
FM 2278 NM TOP	0.89

Table 5-3 provides the XRD quantitative results from the two outer columns at this location. The XRD results from this location did not indicate any signs of sulfate attack occurring in the concrete. A total of 12 powder samples were analyzed from this site and all XRD results showed similar products indicating little to no sulfate attack.

Table 5-2: Semi-quantitative XRD Rietveld analyses from columns SO and NO in the Childress District

Location	Ettringite (%)	Gypsum (%)	Portlandite (%)
SO Bottom	1.43	0.33	0.50
SO Middle	0.07	0.82	0.76
SO Top	0.13	0.62	0.89
NO Bottom	0.30	0.55	0.59
NO Middle	0.09	0.54	0.25
NO Top	0.25	0.52	0.30

5.3.1.4 Summary of Childress District findings

This district had few structures affected from external sulfate attack. Findings concluded that the locations sampled were located in Class 0 exposure which suggests that no

sulfate damage would be expected. In the case of Site 10 that had visible damage possibly from external sulfate attack, the XRD scans did not indicate any deleterious reaction products resulting from external sulfate attack for any of the columns as shown in Table 5-2. Only a small percentage of all the concrete structures in this district were visually inspected, but those that showed the most signs of distress were selected for evaluation and these were not found to be suffering from external sulfate attack. Further investigations that are beyond the scope of this research project would be needed to determine the type of attack causing the visible deterioration evidenced in a small number of structures in this district.

5.3.2 Paris District

The Paris district is located between Dallas and Texarkana, in the northeast part of the state of Texas. A total of 100 bridges, culverts, and other concrete structures were inspected. A total of five structures were selected for detailed evaluation; Sites 22 and 57 are discussed below. Site 22 is a culvert on Highway 19, north of Sulphur Springs and Site 57 is a bridge showing signs of distress in the columns that is located on State Highway 11 northwest of Sulphur Springs.

5.3.2.1 Site 22

Site 22, located on Highway 19 north of Sulphur Springs has several deteriorating culverts. The distress shown in Figure 5-4 is one of the culverts observed at site 22. It was common to see this distress throughout the majority of this district. The distress begins near the base of the culvert and continues upward to 2 ft (0.66 m). The observed

distress appears similar to acid attack; however, external sulfate attack and and/or freeze thaw attack may lead to such observed distress. While the paste remains intact, the aggregate has dissolved or lost its cohesion to the cement paste matrix. Similar distress was found on bridge columns. Based on the water samples (10 ppm SO₄) taken from this location had minimal sulfates which would place this location into Class 0 exposure. ASTM C 1580 was used for measuring the sulfate content of the soil for this location. The sulfate content for this location was 0.07%, which would place this location into Class 0 exposure. There was not a significant change between the two extraction ratios tested which might mean that gypsum may not be the main sulfate. At this location, one of the culverts was being excavated to remove the soil from the bottom. Figure 5-5 shows the partially excavated soil in the culvert. It has not yet been determined, but the area above the soil level shows signs of distress which is often associated with physical salt attack. Table 5-4 provides the semi-quantitative XRD results on a deteriorated and non-deteriorated section of the culvert. There are no formations of ettringite or gypsum in any of the XRD scans from any of the deteriorated culverts/columns in the district. Physical salt attack does not form any deleterious products as no chemical changes are occurring to the paste.

Table 5-3: Semi-quantitative Rietveld analyses taken from two sections from a culvert at Site 22

Location	Ettringite (%)	Gypsum (%)	Monosulfate (%)	Portlandite (%)
Site 22 Deteriorated	0.76	0.22	4.3	0.04
Site 22 Non-deteriorated	1.39	0.07	2.99	0.11



Figure 5-5: Deterioration commonly found in culverts in the Paris District. The distress begins near the base of the culvert and continues up the side, likely in line with the highest level of water.



Figure 5-6: Deterioration of a culvert above the soil level, with no deterioration visible below the level of the soil (after excavation).

5.3.2.2 Site 57

This bridge is situated on SH 11 northwest of Sulphur Springs, Texas. Figure 5-6 shows the observed deterioration. A large portion of the cross section of the columns has deteriorated with reinforcing bars visibly showing. Similar to Site 22, the sulfate levels in the soils (0.08%) tested with TEX-135-E classify it as a class 0 exposure. Table 5-5 provides the XRD Rietveld analyses from the damaged and undamaged sections of the columns.



Figure 5-7: Deteriorated concrete columns from a bridge in the Paris District

Table 5-4: XRD results from Site 57 in the Paris District

Location	Ettringite (%)	Gypsum (%)	Monosulfate (%)	Portlandite (%)
Site 57 Deteriorated	1.39	0.07	2.99	0.11
Site 57 Non-deteriorated	0.76	0.22	4.31	0.04

The XRD results did not show significant amounts of ettringite or gypsum in either sample. Further testing is needed to determine the cause of the damage occurring to these structures. Sample retrieval for future powder samples may consist of taking powders at specified depth intervals. The creek below was dry on the day of sample retrieval which did not allow for water samples to be collected.

5.3.2.3 Summary of Paris District findings

The damage shown in the culverts in this district is very widespread and further investigations are needed to identify the cause(s) of distress. Preliminary results may suggest physical salt attack on these structures as distress was primarily observed at evaporative fronts. The sulfate levels from the soil samples were quite low, generally below a Class 1 exposure according to Table 2-2. Site 22 had sulfate contents of 0.07% and site 57 had sulfate contents in the soil of 0.08%. Site 57 did provide a significant loss on cross section from each column, but XRD analyses concluded that sulfate attack may not be occurring. The retrieval process may not be providing an accurate measurement of the concrete powder collected. Future testing should include milling into the concrete to provide different depths to determine a sulfate concentration profile in the concrete, and cores should be extracted and examined petrographically.

5.3.3 El Paso District

Sites in the El Paso district exhibited the most significant signs of sulfate attack-like distress in Texas. The four most distinct cases will be discussed. Three of the locations include riprap damage while the fourth case involves concrete right of way (ROW)

markers in the area. Sites 3, 31 and 32 all have riprap damage and Site 27 is the location of the deteriorated ROW markers.

5.3.3.1 Site 3

Site 3 is located on Interstate 10 near mile marker 57, just outside of El Paso. Figure 5-7 shows the damage to the riprap under the bridge. Several other bridges in the area show similar distress in the riprap. The paste is lost on the surface and many of the aggregates are loosened while others are barely clinging onto the paste below. In a few areas, the top layer of the concrete has separated from the layer below. A soil sample taken at the base of the riprap shows 0.01% SO₄ using ASTM C 1580 and 0.06% SO₄ using TEX-135-E. According to ACI 201.2R, both of these would be classified as Class 0 exposure according to Table 2-2. Powder samples were taken from the base (0.06% SO₄) and top (0.14% SO₄) of the riprap embankment. The sulfate content is greater in the upper part of the embankment. Sulfates may concentrate on the surface of the concrete further up the embankment away from running water that may remove the sulfates off of the concrete on the bottom section. Riprap is usually made with a high w/cm and could lead to accelerated damage, compared to concrete with a lower w/cm.



Figure 5-8: Riprap deterioration occurring on the embankment below a bridge

5.3.3.2 Site 31

Another location with riprap damage is on FM 652, east of Guadalupe National Park, near the Texas and New Mexico Border. Figure 5-8 shows the disintegrated riprap at this location. The riprap damage is more severe than the damage seen in the Childress District and Site 3 in this district.



Figure 5-9: Riprap deterioration at Site 31 in the El Paso District

The sulfate content in the soil was 0.07% as per ASTM C 1580 and 0.18% SO₄ as per TEX-135-E, which brackets the cut-off point between Class 0 and Class 1 exposures of 0.1% SO₄. Table 5-5 shows the sulfate content in the concrete taken from the bottom, middle and top of the embankment. Sulfate levels in the riprap increase in the vertical direction, as was the case for Site 3.

Table 5-5: Sulfate content of concrete powder taken from the riprap at site 31

Location	SO ₄ (%)
Bottom	0.68
Middle	0.83
Top	1.38

Semi-quantitative XRD Rietveld analysis conducted on the same powders showed an increase in gypsum content from one sample to the next as one moves vertically up the

embankment. The gypsum content was 3% at the base of the embankment, 10% in middle, and 15% at the top. The increase in gypsum may suggest wicking of salts up the embankment leading to concentrations increasing near the top. Ettringite formation was minimal at each of the three locations on the embankment suggesting little transformation of hydration products to ettringite.

5.3.3.3 Site 32

This site is very near Site 31 and exhibits the same type of deterioration in the riprap. Figure 5-9 shows the riprap damage at this location. The sulfate content at this location fits into the Class 1 exposure classification (0.1% SO₄ as per ASTM C 1580 and 0.15% SO₄ as per TEX-135-E).



Figure 5-10: Deteriorated riprap at Site 32 located on FM 652 in the El Paso District

5.3.3.4 Site 27

The most significant signs of attack on concrete specimens occurred on right-of-way (ROW) markers along the roadways. The ROW markers are pyramid shaped with a height of 48 in (1.2 m) consisting of an 8 in (200 mm) square base and 4 in (100 mm) square top. The marker is positioned 30 in (0.75 m) into the soil. The TxDOT ROW Marker specification is in Appendix D. The ROW markers are constructed with two #3 reinforcement bars. Depending on the roadway, there are about 20 ROW markers per mile and more markers occur on curves which are used as station points for surveying. On a roadway, two ROW markers are placed directly across from each other. The initial discovery of a deteriorated ROW marker was at Site 27, located on SH 54 north of Van Horn, Texas. Figure 5-10 shows a photograph which is typical of the many deteriorated ROW markers in this region. The sulfate content of the soil on the surface was 0.91% SO₄, classifying it as very severe Class 3 exposure. Based on preliminary evaluations of these ROWs, a more detailed investigation was launched as discussed next.



Figure 5-11: ROW marker deteriorating in west Texas.

A long-term study on ROW markers located in the El Paso District is currently underway at the Concrete Durability Center (CDC) at The University of Texas at Austin to investigate the mechanisms of deterioration and to determine if external sulfate attack has occurred. According to preliminary tests, sulfate content in the soils in El Paso fell into a Class 3 exposure and gypsum was the primary type of sulfate. To allow for a detailed laboratory-based evaluation of deteriorated ROW markers, a total of eight ROW markers were removed and brought back to the CDC for subsequent testing. Six of these ROW markers were replaced with new ROW markers, cast at the CDC using selected concrete mixtures and constructed as per TxDOT specifications. Figure 5-11 shows the location of the ROW markers removed and replaced north of Van Horn, Texas. Table 5-6 shows the mixtures used in replacing the existing ROW markers. Two types of fly ashes were

tested in addition to two different w/cm. These materials and mixture proportions were selected based on previous testing at the CDC (see Chapter 4) to produce some mixtures that were expected to perform and other mixtures that were expected to perform poorly in a sulfate environment (Class C fly ash with high w/cm).

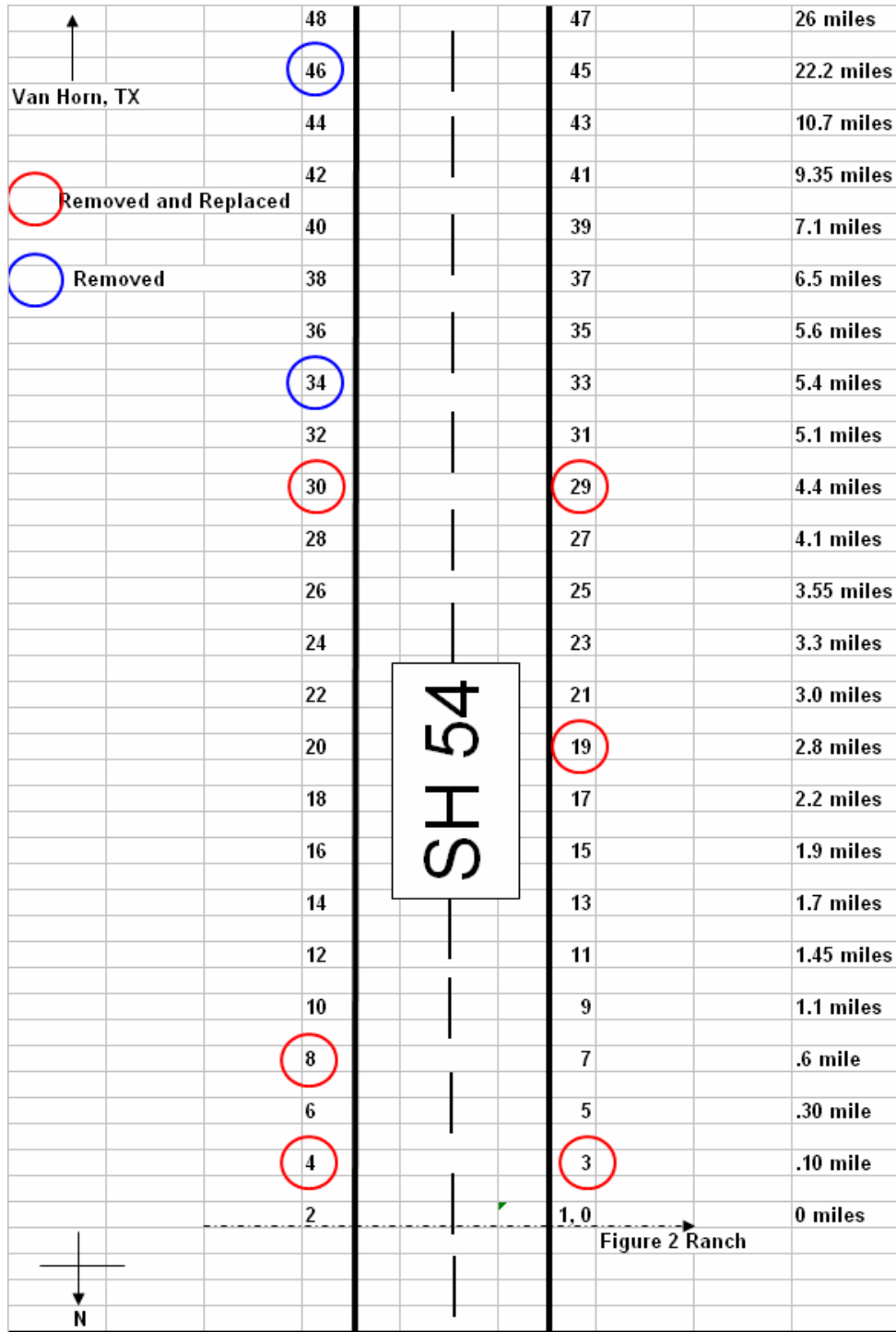


Figure 5-12: Location of the removed and replaced ROW markers along SH 54 north of Van Horn, Texas

Table 5-6: Concrete mixtures made for ROW markers in west Texas

Mix #	Cement	Fly Ash	w/cm
1	Type I	-	0.4
2	Type I	-	0.7
3	Type I	40% C	0.4
4	Type I	40% C	0.7
5	Type I	20% F	0.4
6	Type I	20% F	0.7

Figure 5-13 shows an image of the placement of a new ROW marker in the existing hole left by the removal of a deteriorated ROW marker. At each ROW marker location, soil samples were removed from the top, middle, and bottom of the hole corresponding to depths of 0, 15 in (380 mm), and 30 in (760 mm).



Figure 5-13: Placement of new ROW marker in the existing location of the deteriorated ROW marker

Figure 5-14 shows the sulfate content of the soil for each of the locations. The sulfate percentage from the 8:1 and 80:1 extraction ratio are shown to highlight the large difference between the two ratios. A difference of magnitude 10 is noticed between the two ratios which suggests gypsum is present in the soil. TEX-135-E, which uses a 20:1 extraction ratio, yielded sulfate contents near 2% for all the locations. Following the ACI 201.2R classification of severity of soils, both 20:1 and 80:1 extraction methods would fall into the most severe levels of exposure. The 8:1 extraction ratio would be considered a moderate sulfate exposure.

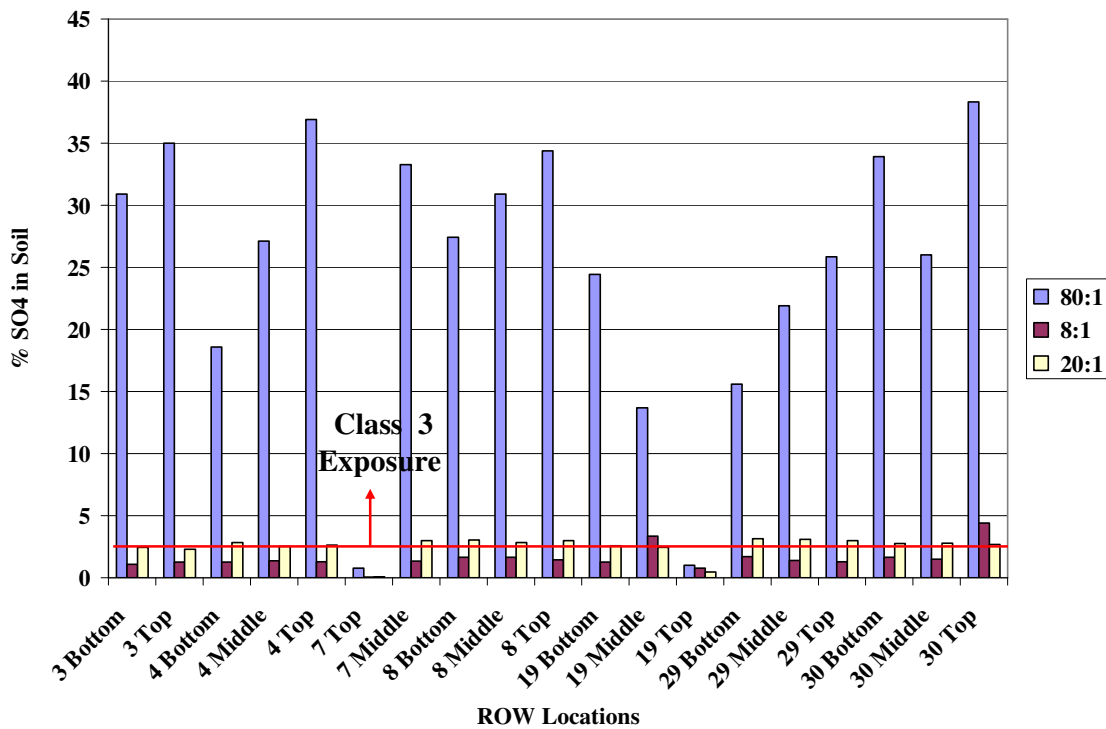


Figure 5-14: The sulfate content of soils taken from each of the ROW locations using ASTM C 1580 and TEX-135-E Test Methods

Preliminary results showed signs of sulfate-related deteriorations occurring in the ROW markers. Figure 5-15 provides the XRD Rietveld analysis from the ROW markers. Concrete powder was taken near the ground level of the marker. Chemical attack from gypsum (calcium sulfate) is known to produce ettringite formation. All but one of the markers removed showed significant ettringite and gypsum formation. The high level of sulfates in the soil and the deleterious products formed indicate damage induced by external sulfate attack from gypsiferous soils.

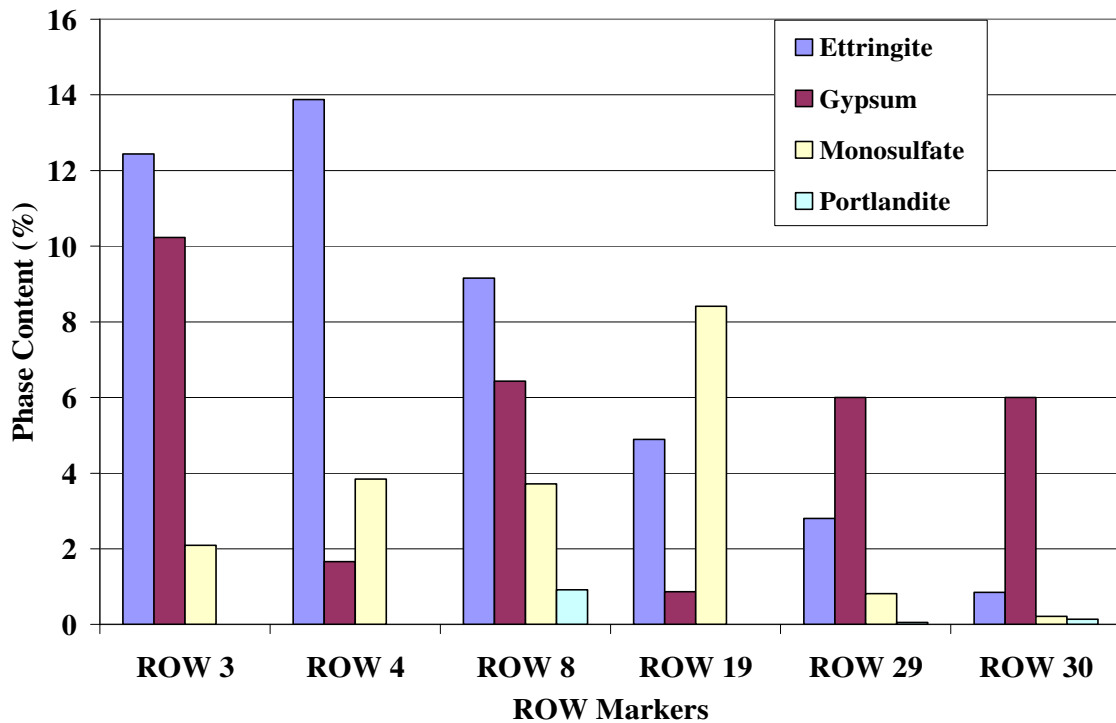


Figure 5-15: Semi-quantitative XRD Rietveld analyses from ROW markers in the El Paso District

Ongoing testing on the ROW markers includes milling for sulfate profiles on three different locations on the marker. Profiling was performed every 0.12 in (3 mm) to a depth of 0.48 in (12 mm) on the following sections of the marker: near the bottom of the

marker (bottom of the hole), middle of the marker, (soil level), and top of the marker(exposed area). In addition, samples are being prepared for analysis by scanning electron microscopy.

The long-term study of these ROW markers began in April 2007 when the newly constructed ROW markers were placed into each of the existing ROW marker locations. Figure 5-15 shows a new ROW marker with Class C fly ash at 0.4 w/cm after three months of exposure. It will likely take several years to see any deterioration for the new ROW markers cast specifically to show deterioration (i.e. specific water/cm, fly ash combinations). ROW markers with Class F Fly ash at 0.4 w/cm should perform the best; while ROW markers with Class C fly ash at 0.7 w/cm would be expected to fail the earliest. The performance of these ROW markers will be tracked and reported in future publications. In addition, selected ROW markers were cast and are being monitored at the outdoor sulfate exposure site at the CDC in Austin.



Figure 5-16: New ROW marker with Class C fly ash at 0.4 w/cm after 3 months of exposure in gypsiferous soils

5.3.3.5 Summary of El Paso findings

The visual damage to structures in this district and the subsequent forensic evaluations have shown that external sulfate attack in gypsiferous soils is occurring in the El Paso district, although this distress appears to be limited to relatively poor quality concrete used for non-structural applications (ROW markers, riprap, etc.) Additional research is in progress, but the findings are significant in that it has been confirmed that external sulfate attack has occurred in Texas, albeit on a limited number of non-critical structures.

5.4 Conclusions

The investigation into external sulfate attack in Texas resulted in examining over 250 concrete structures in three districts. The following are conclusions made from the investigation of concrete structures for external sulfate attack.

- 12 structures throughout the three districts have shown visual signs of deterioration similar to sulfate attack in the state of Texas.
- It was concluded that the Childress District did not have any structures deteriorated from external sulfate attack.
- The Paris District had many culverts and bridges potentially damaged from physical salt attack. Preliminary results indicate that chemical attack is not occurring on these structures. The deterioration is occurring in the evaporative section of the structures usually above a water line or soil level.
- The El Paso District showed the most deterioration. Riprap, constructed from high w/cm concrete, exhibited some distress in relatively low sulfate concentrations, perhaps due to the relatively poor quality of the concrete. Gypsum formation within the matrix was detected, and sulfate concentrations were found to increase vertically as one move up the embankments, suggesting that sulfates are rising by wicking action and accumulating towards the top of the elements.
- ROW markers in the El Paso district showed significant deterioration, which was confirmed to be caused by external sulfate attack. XRD analyses show ettringite formation occurring in the ROW markers. More detailed evaluation

of ROWs, removed from service are in progress and will be presented in future publications and in the final project report to be submitted to TxDOT in 2009.

- The use of varying sulfate extraction ratios, through the combined use of ASTM C 1580 and TEX-135-E, did allow for the identification of gypsum in soils. More research is needed to determine how best to analyze the results from sulfate extracts and how to apply these results to specifications aimed at preventing external sulfate attack

Chapter 6: Conclusions and Future Work

6.1 Conclusions

This dissertation described a comprehensive study on laboratory and field evaluations of mortars and concretes exposed to external sulfates. Although substantial progress has been made in the research described in this dissertation, some key issues are still being investigated, particularly issues related to underlying mechanisms and microstructural aspects of sulfate attack. However, based on the research detailed in this dissertation, the following conclusions can be made:

- In general, the use of high-calcium fly ash in the study showed poor sulfate resistance. The deterioration tended to increase as the dosage of Class C fly ash was increased. However, the incorporation of a second SCM (silica fume, slag, UFFA) helped to substantially improve the sulfate resistance of mixtures containing these Class C fly ashes
- Mechanistic studies using XRD and SEM identified the key modes of failure and also identified the chemical and physical benefits of using ternary blends in sulfate environments.
- Detailed evaluations of the mineralogy of Class C fly ashes were performed using XRD analyses for the crystalline phases and SEM (and EDS) analyses for the glassy phases, and a linkage is suggested between the mineralogy of the glassy phase and sulfate resistance.
- Concrete prisms placed in sodium sulfate expanded the quickest and showed faster deterioration than prisms placed in magnesium and calcium sulfate.

Prisms in the submerged sodium sulfate conditions deteriorated quicker than control prisms kept indoors at 73 °F (23 °C).

- Prisms in magnesium sulfate ultimately expanded the greatest of all the sulfate types and showed large cracks rather than deteriorating/expansion noticed in sodium sulfate prisms.
- Prisms in the different calcium sulfate conditions did not expand at 18 months but did show signs of deterioration on the surface of the prisms. In the outdoor calcium exposure site, prisms only show deterioration below the soil level. Due to visible damage on prisms, prisms in the indoor calcium solutions were kept for 2 years, after which they began to expand. This helps to confirm that concrete exposed to external sources of gypsum can, in fact, suffer from sulfate-related deterioration.
- XRD analysis highlighted the strong impact that w/cm has on sulfate resistance of concrete. In lower w/cm mixtures, less destructive products, such as ettringite, formed as a function of distance from the exposed surface. For higher w/cm mixtures, levels of ettringite were nearly the same for milled powder samples taken from the exposed surface and similar samples taken from within the bulk of concrete prisms. The higher w/cm concrete allowed for the movement of sulfate ions into the concrete due to greater porosity.
- Mortar bars exposed to external sulfates generally expanded and/or deteriorated more rapidly and more significantly than similar concrete mixtures exposed to the identical exposure conditions. This was confirmed

through XRD analysis, in which more ettringite and gypsum was detected in mortar bars than comparable concrete prisms. Differences in behavior between mortar and concrete can likely be attributed to differences in paste content, specimen size, and curing regimes (prior to exposure in sulfate environment).

- A comprehensive field survey was performed in the three TxDOT-defined districts in Texas (Childress, Paris, and El Paso) with the highest sulfate contents in soil and/or groundwater. A total of 12 structures throughout these three districts have shown visual signs of deterioration similar to sulfate attack. Some of the key findings from these evaluations include:
 - There were no structures in the Childress District that were identified as showing signs of external sulfate attack.
 - The Paris District had many culverts and bridges potentially damaged from physical salt attack. Preliminary results indicate that chemical attack is not occurring on these structures. The deterioration is occurring in the evaporative section of the structures usually above a water line or soil level.
 - The El Paso District showed the most deterioration. Riprap, constructed from high w/cm concrete, exhibited some distress in relatively low sulfate concentrations, perhaps due to the relatively poor quality of the concrete. Gypsum formation within the matrix was detected, and sulfate concentrations were found to

increase vertically as one moves up the embankments, suggesting that sulfates are rising by wicking action and accumulating towards the top of the elements. Right-of-way (ROW) markers in the El Paso district showed significant deterioration, which was confirmed to be caused by external sulfate attack. Rietveld analyses show ettringite formation occurring in the ROW markers. More detailed evaluations of ROWs, removed from service are in progress and will be presented in future publications and in the final project report to be submitted to TxDOT in 2009.

6.2 Suggested future work

This dissertation summarized work focusing on external sulfate attack; however, there are many aspects of sulfate attack that are still unresolved, some of which are being pursued already. Although significant progress was made in the work described in this dissertation, the following topics are deserving of further attention and investigation:

- Further work on analyzing and characterizing the glassy phase of Class C fly ash should help to shed more light on the linkage between fly ash mineralogy and sulfate resistance. Most of the ashes in this study have been fully characterized (using XRD for crystalline phase and SEM for glassy phase), but it would be ideal to expand this approach to a range of other fly ashes to generate a more definitive link between fly ash mineralogy and sulfate resistance.

- More focused research is needed on accelerated test methods for external sulfate attack. ASTM C 1012 is the most common method, but several issues have been identified with this method through this research. One issue, for example, that deserves further attention is the application of 6-month expansion limits to mortar mixtures. The high C_3A cement used in this study as a control did not expand until after 6 months of immersion in sulfate solution, yet there are current guidelines, such as those put forth in ACI 201 and potentially ACI 318, that allow for performance testing and mixture approval based on 6-month expansion criteria. A wide range of portland cements should be tested using ASTM C 1012 to determine how many of these perform similarly. If it is found that this behavior is the rule and not the exception, 6-month expansion limits should not be included in guidelines or specifications.
- A wide range of mortar mixtures were evaluated in this project using ASTM C 1012. Based on these findings, other mixtures have been identified that should be evaluated in the future to fill in gaps in the current database. In addition to testing plain cement mixtures it would be quite useful to evaluate a range of ternary blends in combination with fly ashes from this study that showed poor sulfate resistance (FA1, FA2, and FA3). In addition, higher percentages of silica fume and ultra fine fly ash should be used in the testing. With a better understanding on which ternary systems work for Class C fly ash in ASTM C 1012 testing, it would be beneficial to make concrete prisms

with similar mixture proportions and test them in either the outdoor or indoor sulfate conditions.

- Concrete mixtures were cast and evaluated, both indoors and outdoors, that covered the upper and lower bounds of typical w/cm ratios, specifically w/cm values of 0.7 and 0.4. Research is needed to fill in the gaps in this w/cm range, specifically w/cm values of 0.45 and 0.5, as these are cited values in the ACI 201.2R table for different sulfate exposures.
- All of the laboratory and field testing performed in this work has focused on the performance of mortar or concrete in soils or solution with high sulfate concentrations (5% sodium sulfate, for example). Research is needed to evaluate the performance of mortar and concrete in less aggressive environments, such as those defined by Class 1 and 2 exposure in ACI 201.2R.
- A more comprehensive evaluation of structures potentially affected by external sulfate attack is needed. This evaluation should extend beyond the state of Texas and should include areas in which sodium sulfate or magnesium sulfate are prevalent. Only through detailed field evaluations can a correlation between laboratory tests and field performance be obtained, and upon achieving this objective, test methods and specifications can be refined to provide a more accurate and rationale link between defining severity of exposure and selecting appropriate preventive measures.

Appendix A: Mortar Cube Strengths for ASTM C 1012 Testing

Table A-1: Mortar cube strengths for ASTM C 1012 Testing

Mortar Strengths for ASTM C 1012 Testing										
Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)		Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)
Control	1	11,980	2,995	3,050		25%FA1	3	11,795	2,949	3,059
		12,420	3,105		5%SF	12,680		3,170		
30FA1	1	8,950	2,238	2,348		30%FA1	1	8,120	2,030	2,036
		9,835	2,459		3%SF	8,165		2,041		
30FA1	2	12,270	3,068	3,024		30%FA1	2	13,130	3,283	3,122
		11,920	2,980		3%SF	11,845		2,961		
25%FA1	1	10,585	2,646	2,633		30%FA1	1	7,990	1,998	2,013
		10,475	2,619		5%SF	8,115		2,029		
25%FA1	2	12,835	3,209	3,279		30%FA1	2	11,045	2,761	2,930
		13,400	3,350		5%SF	12,395		3,099		
35%FA1	1	7,950	1,988	2,025		35%FA1	1	7,570	1,893	1,931
		8,250	2,063		3%SF	7,875		1,969		
35%FA1	2	12,470	3,118	3,008		35%FA1	2	10,685	2,671	2,721
		11,595	2,899		3%SF	11,080		2,770		
40%FA1	1	6,765	1,691	1,954		30%FA1	3	12,125	3,031	3,013
		8,870	2,218		5%SF	11,980		2,995		
40%FA1	2	9,595	2,399	2,715		35%FA1	1	7,650	1,913	1,913
		12,125	3,031		5%SF	0		0		
40%FA1	3	11,830	2,958	3,016		35%FA1	2	10,100	2,525	2,497
		12,295	3,074		5%SF	9,875		2,469		
20%FA1 6%M3	1	11,240	2,810	2,601		35%FA1	3	12,145	3,036	3,019
		9,565	2,391		5%SF	12,005		3,001		
20%FA1 6%M3	2	11,015	2,754	2,825		40%FA1	1	6,055	1,514	1,514
		11,585	2,896		3%SF					
20%FA1 6%M3	3	15,025	3,756	3,755		40%FA1	2	9,280	2,320	2,347
		15,015	3,754		3%SF	9,495		2,374		
20%FA1 9%M3	1	10,185	2,546	2,537		40%FA1	4	12,755	3,189	3,209
		10,110	2,528		3%SF	12,915		3,229		
20%FA1 9%M3	2	12,020	3,005	2,896		40%FA1	1	6,240	1,560	1,599
		11,145	2,786		5%SF	6,550		1,638		
20%FA1 3%SF	1	10,000	2,500	2,463		40%FA1	2	8,465	2,116	2,068
		9,700	2,425		5%SF	8,075		2,019		
20%FA1 3%SF	2	13,285	3,321	3,338		40%FA1	3	9,850	2,463	2,525
		13,420	3,355		5%SF	10,350		2,588		
20%FA1 5%SF	1	10,705	2,676	2,569		40%FA1	4	11,370	2,843	2,771
		9,850	2,463		5%SF	10,800		2,700		
20%FA1 5%SF	2	12,705	3,176	3,158		30%FA1	1	8,680	2,170	2,151
		12,560	3,140		6%M3	8,530		2,133		
25%FA1 3%SF	1	9,100	2,275	2,378		30%FA1	2	14,340	3,585	3,725
		9,920	2,480		6%M3	15,460		3,865		
25%FA1 3%SF	2	11,895	2,974	3,006		20%FA2	1	9,695	2,424	2,415
		12,155	3,039		3%SF	9,625		2,406		
25%FA1 5%SF	1	8,440	2,110	1,991		20%FA2	2	13,015	3,254	3,268
		7,490	1,873		3%SF	13,125		3,281		
25%FA1 5%SF	2	9,795	2,449	2,526		25%FA2	1	9,675	2,419	2,508
		10,410	2,603		5%SF	10,385		2,596		

Table A-1 contd.: Mortar cube strengths for ASTM C 1012 Testing

Strength of Mortar Cubes for ASTM C 1012 Testing									
Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)	Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)
25%FA2	2	11,160	2,790	2,788	25%FA2	1	11,840	2,960	2,883
		11,140	2,785				11,220	2,805	
30%FA2	1	8,985	2,246	2,279	25%FA2	1	12,815	3,204	3,186
		9,250	2,313				12,670	3,168	
30%FA2	2	10,030	2,508	2,601	20%FA2	1	9,105	2,276	2,276
		10,780	2,695				5%SF	0	
30%FA2	3	11,915	2,979	2,997	20%FA2	2	10,460	2,615	2,570
		12,060	3,015				5%SF	10,100	
35%FA2	1	7,870	1,968	1,999	20%FA2	3	11,940	2,985	3,033
		8,120	2,030				5%SF	12,320	
35%FA2	2	9,415	2,354	2,424	25%FA2	1	8,190	2,048	2,048
		9,975	2,494				3%SF	0	
35%FA2	3	11,145	2,786	2,936	25%FA2	2	9,870	2,468	2,485
		12,340	3,085				3%SF	10,010	
40%FA2	1	5,460	1,365	1,365	25%FA2	3	13,305	3,326	3,291
							3%SF	13,020	
40%FA2	2	7,315	1,829	1,896	20%FA2	1	13,360	3,340	3,318
		7,850	1,963				3%SF	13,185	
40%FA2	3	8,765	2,191	2,313	25%FA2	1	8,650	2,163	2,205
		9,735	2,434				5%SF	8,990	
40%FA2	5	11,780	2,945	2,918	25%FA2	3	12,315	3,079	3,203
		11,560	2,890				5%SF	13,305	
20%FA2 6%M3	1	10,495	2,624	2,561	30%FA2	1	7,555	1,889	1,919
		9,995	2,499				3%SF	7,800	
20%FA2 6%M3	2	15,585	3,896	3,815	30%FA2	2	11,345	2,836	2,812
		14,935	3,734				3%SF	11,150	
20%FA2 9%M3	1	10,545	2,636	2,627	30%FA2	3	12,045	3,011	3,036
		10,470	2,618				3%SF	12,245	
20%FA2 9%M3	2	12,905	3,226	3,321	35%FA2	1	7,380	1,845	1,845
		13,660	3,415				3%SF	0	
35%FA2 9%M3	1	10,685	2,671	2,617	35%FA2	3	12,005	3,001	2,983
		10,250	2,563				3%SF	11,860	
35%FA2 9%M3	2	11,175	2,794	2,769	30%FA2	1	7,525	1,881	1,881
		10,975	2,744				5%SF	0	
35%FA2 9%M3	3	11,665	2,916	2,979	30%FA2	3	10,670	2,668	2,668
		12,165	3,041				5%SF	0	
35%FA2 6%M3	1	11,150	2,788	2,686	30%FA2	4	12,170	3,043	2,911
		10,340	2,585				5%SF	11,115	
35%FA2 6%M3	2	11,485	2,871	2,887	35%FA2	1	6,525	1,631	1,631
		11,610	2,903				5%SF	0	
30%FA2 9%M3	1	12,305	3,076	3,084	35%FA2	3	8,990	2,248	2,375
		12,365	3,091				5%SF	10,010	
30%FA2 6%M3	1	9,425	2,356	2,334	35%FA2	4	11,415	2,854	2,823
		9,250	2,313				5%SF	11,170	
30%FA2 6%M3	2	11,765	2,941	2,867			0		0
		11,170	2,793				0		

Table A-1 contd.: Mortar cube strengths for ASTM C 1012 Testing

Strength of Mortar Cubes for ASTM C 1012 Testing										
Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)		Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)
40%FA2 3%SF	1	6,155	1,539	1,539		20%FA1 25%SL	3	11,590	2,898	2,925
			0					11,810	2,953	
	3	10,170	2,543	2,540		35%FA1 6%M3	1	7,290	1,823	1,823
		10,150	2,538					0		
	4	11,505	2,876	2,741			2	10,250	2,563	2,563
		10,425	2,606					0		
	5	11,905	2,976	2,990			3	11,450	2,863	2,914
		12,015	3,004					11,865	2,966	
40%FA2 5%SF	1	6,040	1,510	1,510		40%FA1 6%M3	1	6,475	1,619	1,619
			0					0		
	3	9,615	2,404	2,431			2	11,080	2,770	2,759
		9,830	2,458					10,995	2,749	
	4	10,380	2,595	2,584			3	13,080	3,270	3,315
		10,290	2,573					13,440	3,360	
	5	11,780	2,945	2,986		40%FA1 9%M3	1	5,660	1,415	1,415
		12,110	3,028					0		
25%FA1 9%M3	1	7,475	1,869	1,869			3	10,465	2,616	2,589
			0					10,250	2,563	
	2	11,145	2,786	2,924			4	11,180	2,795	2,764
		12,250	3,063					10,930	2,733	
25%FA1 6%M3	1	8,650	2,163	2,163			5	12,940	3,235	3,213
			0					12,760	3,190	
	2	13,025	3,256	3,165		25%FA1 20%Sl _a	1	6,230	1,558	1,558
		12,295	3,074					0		
35%FA1 9%M3	1	6,160	1,540	1,540			3	7,960	1,990	1,990
			0					0		
	2	8,615	2,154	2,154			5	12,045	3,011	3,084
			0					12,625	3,156	
	3	10,685	2,671	2,656		25%FA1 25%Sl _a	1	5,685	1,421	1,421
		10,560	2,640					0		
	4	11,785	2,946	2,891			2	7,770	1,943	1,943
		11,340	2,835					0		
30%FA1 9%M3	1	8,810	2,203	2,203			4	10,860	2,715	2,635
			0					10,220	2,555	
	2	10,985	2,746	2,749			5	12,920	3,230	3,171
		11,010	2,753					12,450	3,113	
	3	13,250	3,313	3,362		20%FA2 20%Sl _a	1	8,635	2,159	1,079
		13,645	3,411					0		
20%FA1 20%Sl _a	1	8,390	2,098	2,098			2	12,140	3,035	2,969
			0					11,615	2,904	
	2	11,065	2,766	2,766		20%FA2 25%Sl _a	1	6,435	1,609	1,609
			0					0		
	3	13,250	3,313	3,362			2	10,280	2,570	2,572
		13,645	3,411					10,295	2,574	
20%FA1 25%	1	8,110	2,028	2,221			3	12,015	3,004	3,040
		9,655	2,414					12,305	3,076	

Table A-1 contd.: Mortar cube strengths for ASTM C 1012 Testing

Strength of Mortar Cubes for ASTM C 1012 Testing										
Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)		Cube ID	Days	Raw Data, (lbf)	Strength, (psi)	Average, (psi)
25%FA2 20%Sl _a	1	7,065	1,766	1,766		25%FA3 9%M3	2	12,160	3,040	2,974
			0		11,635			2,909		
	2	9,465	2,366	2,366		35%FA3	1	8,000	2,000	2,000
			0					0		
	3	11,915	2,979	2,951			2	11,610	2,903	2,971
		11,690	2,923		12,155			3,039		
25%FA2 25%Sl _a	1	5,390	1,348	1,348		40%FA3	1	8,750	2,188	2,188
			0					0		
	2	7,785	1,946	1,946			2	10,100	2,525	2,539
			0		10,210			2,553		
	3	9,500	2,375	2,422			3	12,055	3,014	3,027
		9,875	2,469		12,160			3,040		
	4	11,750	2,938	2,900		35%FA3 3%SF	1	8,150	2,038	2,038
		11,450	2,863					0		
20%FA3	1	12,345	3,086	3,066			2	10,150	2,538	2,585
		12,180	3,045					0		
25%FA3	1	11,360	2,840	2,671			3	11,965	2,991	3,016
		10,005	2,501		12,165			3,041		
	2	13,170	3,293	3,359		35%FA3 5%SF	1	7,410	1,853	1,853
		13,705	3,426					0		
30%FA3	1	9,845	2,461	2,461			2	10,900	2,725	2,719
			0		10,850			2,713		
	2	11,345	2,836	3,103			3	11,165	2,791	2,956
		13,480	3,370		12,485			3,121		
30%FA3 3%SF	1	8,720	2,180	2,180		40%FA3 3%SF	1	6,255	1,564	1,564
			0					0		
	2	11,775	2,944	2,824			2	9,910	2,478	2,478
		10,820	2,705					0		
30%FA3 5%SF	1	8,420	2,105	2,105			3	10,930	2,733	2,720
			0		10,830			2,708		
	2	11,980	2,995	2,947			4	12,685	3,171	3,092
		11,595	2,899		12,050			3,013		
20%FA3 6%M3	1	10,845	2,711	2,679		40%FA3 5%SF	1	5,975	1,494	1,494
		10,585	2,646					0		
	2	13,890	3,473	3,321			2	8,895	2,224	2,224
		12,680	3,170					0		
20%FA3 9%M3	1	9,845	2,461	2,492			3	10,770	2,693	2,712
		10,090	2,523		10,925			2,731		
	2	13,995	3,499	3,444			4	11,770	2,943	2,949
		13,560	3,390		11,825			2,956		
25%FA3 6%M3	1	10,030	2,508	2,631		30%FA3 6%M3	1	10,035	2,509	2,509
		11,020	2,755					0		
	2	13,340	3,335	3,202			2	14,115	3,529	3,513
		12,275	3,069		13,990			3,498		
25%FA3 9%M3	1	9,270	2,318	2,326		30%FA3 9%M3	1	9,355	2,339	2,339
		9,335	2,334					0		

Appendix B: ASTM C 1012 Results

Table B-1: ASTM C 1012 results for FA3

FA3	Ternary	6 Month	9 Month	12 Month	18 Month
20%		0.062	305 (1)	X	X
20%	3% SF	0.041	0.065	0.164	0.573 (2)
20%	5% SF	0.061	0.102	0.181 (1)	0.373 (2)
20%	6% UFFA	0.039	0.051	0.052	0.066
20%	9% UFFA	0.039	0.044	0.05	0.06
20%	20% Slag	0.06	0.080	.117 (3)	X
20%	25% Slag	0.054	0.076	0.087 (1)	0.194 (2)
25%		0.061	0.052 (5)	.131 (5)	X
25%	3% SF	0.058	0.229	0.471 (4)	X
25%	5% SF	0.056	0.089	0.217	0.251 (4)
25%	6% UFFA	0.05	0.078	0.07	0.104
25%	9% UFFA	0.045	0.055	0.057	0.071
25%	20% Slag	0.096 (1)	0.258 (5)	X	X
25%	25% Slag	0.063	0.17 (2)	X	X
30%		0.06	.095 (2)	X	X
30%	3% SF	0.041	0.215	0.267 (3)	0.25 (5)
30%	5% SF	0.06	0.080	0.117	0.119 (3)
30%	6% UFFA	0.053	0.079	0.17	0.107 (1)
30%	9% UFFA	0.049	0.062	0.086	0.093
35%		0.074	0.337 (3)	X	X
35%	3% SF	0.092	0.287 (2)	X	X
35%	5% SF	0.056	0.075	0.087	0.128
35%	6% UFFA	0.051	0.071	0.093	0.101
35%	9% UFFA	0.047	0.061	0.095	0.124
40%		0.072	-	-	-
40%	3% SF	0.101	0.126 (2)	0.324 (3)	.599 (4)
40%	5% SF	0.037	0.053	0.083	0.096
40%	6% UFFA	0.057	0.064	0.081	0.089
40%	9% UFFA	0.071	0.080	0.097	0.108

Table B-2: ASTM C 1012 results for FA4

FA4	Ternary	4 Month	6 Month	9 Months	12 Months
20%		0.073	X	X	X
20%	3% SF	0.06 (2)	.21 (3)	X	X
20%	6% UFFA	0.03	0.060	0.09	X
25%		0.059	0.1472 (1)	0.112 (5)	X
25%	3% SF	0.2585	X	X	X
25%	6% UFFA	0.0378	0.173 (3)	X	X
30%		0.225 (4)	X	X	X
35%		0.113 (4)	X	X	X
40%		0.113 (2)	X	X	X

Table B-3: ASTM C 1012 results for FA5

FA5	Ternary	4 Month	6 Month	9 Months	12 Months
20%		0.068	0.174	X	X
25%		0.1632	X	X	X
30%		0.2195 (4)	X	X	X
35%		.1326 (1)	X	X	X
40%		0.0592 (1)	X	X	X

Table B-4: ASTM C 1012 results for FA6

FA6	Ternary	4 Month	6 Month	9 Months	12 Months
20%		0.074	0.632	X	X
20%	3% SF	0.047	0.068	0.14	X
25%		0.2218	X	X	X
25%	3% SF	0.0825	0.060	.10475 (2)	X
30%		0.1015	X	X	X
35%		0.118	X	X	X
40%		0.1366	X	X	X

Table B-5: ASTM C 1012 results for FA7

FA7	Ternary	4 Month	6 Month	9 Months	12 Months
20%		0.104	X	X	X
20%	3% SF	0.0475	X	X	X
20%	6% UFFA	0.0268	0.057	0.13	0.3805 (3)
25%		-	X	X	X
25%	3% SF	0.1	X	X	X
25%	6% UFFA	0.034	0.060	0.072	0.20275
30%		56 day all broken		X	X
35%		0.139	X	X	X
40%		0.088 (4)	X	X	X

Table B-6: ASTM C 1012 results for FA8

FA8	Ternary	4 Month	6 Month	9 Months	12 Months
20%		0.355	0.405	-	-
20%	3% SF	0.04	0.09	-	-
20%	6% M3	0.052	0.088	0.145	0.196
25%		3403 (3 Month)		X	X
25%	3% SF	0.08	X	X	X
25%	6% UFFA	0.157	X	X	X
30%		0.723	X	X	X
35%		.121 (56 Days)		X	X
40%		.093 (28 Days)		X	X

Appendix C: Concrete Mixture Expansions and Mass Change Results

Table C-1: Expansion and mass change data for Type I/II ternary blend mixtures in calcium sulfate solutions

Mix ID	Age (Months)	Calcium Sulfate 1012		Calcium Submerged		Calcium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C2FC20-4	3	0.01	0.17	0.00	0.20	0.00	0.01
C2FC20-4	6	0.01	0.17	0.01	0.22	0.00	-0.03
C2FC20-4	9	0.01	0.35	0.01	0.30	-0.01	-0.04
C2FC20-4	12	0.00	0.27	0.02	0.30	0.01	0.03
C2FC20-4	18	0.01	0.27	0.01	0.26	0.00	0.07
C2FC20-7	3	0.03	0.42	0.00	-0.40	0.00	-0.07
C2FC20-7	6	0.03	0.37	0.01	-0.64	0.01	-0.20
C2FC20-7	9	0.02	0.50	0.02	-1.00	0.01	-0.34
C2FC20-7	12	0.04	0.13	0.03	-2.00	0.02	-0.26
C2FC20-7	18	0.02	-0.51	0.04	-3.10	-0.01	-0.33
C2FC40-4	3	0.04	0.20	0.00	-0.04	-0.01	0.07
C2FC40-4	6	0.04	0.31	0.00	0.03	-0.01	0.10
C2FC40-4	9	0.03	0.34	0.00	0.09	-0.02	-11.13
C2FC40-4	12	0.06	0.44	0.00	0.02	-0.02	0.05
C2FC40-4	18	0.07	0.48	-0.03	0.04	-0.04	0.06
C2FC40-7	3	0.01	0.29	0.01	0.05	0.01	0.00
C2FC40-7	6	0.01	0.33	0.00	0.19	0.00	0.06
C2FC40-7	9	0.01	0.44	0.01	0.22	0.01	-0.13
C2FC40-7	12	0.03	0.73	0.00	0.15	0.00	0.01
C2FC40-7	18	0.03	0.76	0.00	0.12	0.00	0.02
C2FF20-4	3	0.00	0.15	0.00	0.15	-0.01	0.01
C2FF20-4	6	0.02	0.20	0.00	0.20	-0.01	0.02
C2FF20-4	9	0.01	0.20	0.01	0.25	0.00	-0.04
C2FF20-4	12	0.02	0.28	0.01	0.26	0.00	0.05
C2FF20-4	18	0.02	0.29	0.01	0.27	0.00	0.08
C2FF20-7	3	0.00	0.00	-0.01	-0.08	-0.01	-0.01
C2FF20-7	6	0.02	0.11	-0.01	-0.03	0.00	0.03
C2FF20-7	9	0.01	0.17	0.01	-0.11	-0.01	-0.21
C2FF20-7	12	0.01	0.29	0.01	-0.08	-0.02	-0.05
C2FF20-7	18	0.01	0.31	0.00	-0.08	-0.02	0.10
C2FC30S3-4	3	0.00	0.07	0.01	0.00	0.00	0.00
C2FC30S3-4	6	0.00	0.11	0.02	0.06	0.01	-0.04
C2FC30S3-4	9	0.00	0.15	0.02	0.18	0.01	-0.02
C2FC30S3-4	12	0.01	0.26	0.02	0.21	0.02	-0.02
C2FC30S3-4	18	0.01	0.28	0.02	0.20	0.02	0.05
C2FC30S3-7	3	0.00	0.04	-0.01	0.00	-0.01	0.00
C2FC30S3-7	6	0.00	0.10	0.00	0.15	0.00	0.00
C2FC30S3-7	9	0.00	0.14	0.00	0.25	0.00	0.01
C2FC30S3-7	12	0.00	0.30	0.01	0.22	0.00	-0.02
C2FC30S3-7	18	0.00	0.33	0.01	0.26	0.00	0.08

Table C-2: Expansion and mass change data for Type V ternary blend mixtures in calcium sulfate solutions

Mix ID	Age (Months)	Calcium Sulfate 1012		Calcium Submerged		Calcium Vertical	
		Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)	Expansion (%)	Mass Change (%)
C5FC20-4	3	0.04	0.37	0.00	0.39	-0.01	0.14
C5FC20-4	6	0.03	0.53	0.01	0.46	0.00	0.12
C5FC20-4	9	0.06	0.55	0.02	0.53	0.01	0.27
C5FC20-4	12	0.07	0.51	0.01	0.53	0.00	0.14
C5FC20-4	18	0.05	0.52	0.00	0.58	-0.01	0.30
C5FC20-7	3	0.01	0.11	0.01	0.24	0.24	0.00
C5FC20-7	6	0.02	0.24	0.00	0.06	0.06	0.05
C5FC20-7	9	0.03	0.45	0.02	0.03	0.03	0.04
C5FC20-7	12	0.03	0.34	0.03	-0.01	-0.01	-0.03
C5FC20-7	18	0.05	0.43				
C5FC40-4	3	0.03	0.28	0.00	0.21	-0.01	-0.02
C5FC40-4	6	0.02	0.30	0.00	0.31	0.00	0.03
C5FC40-4	9	0.07	0.31	0.01	0.32	0.00	0.05
C5FC40-4	12	0.06	0.40	0.01	0.32	0.00	0.04
C5FC40-4	18	0.06	0.41	-0.01	0.28	-0.01	0.09
C5FC40-7	3	0.00	0.26	-0.01	0.34	-0.02	0.01
C5FC40-7	6	0.00	0.24	0.00	0.30	-0.01	0.11
C5FC40-7	9	-0.01	0.41	0.00	0.27	0.00	0.08
C5FC40-7	12	0.02	0.46	0.00	0.21	-0.01	0.08
C5FC40-7	18	0.01	0.49	0.02	0.25	-0.02	0.12
C5FF20-4	3	0.01	0.08	0.00	-0.28	0.00	-0.05
C5FF20-4	6	0.00	0.10	-0.01	0.11	-0.01	-0.05
C5FF20-4	9	0.01	0.12	0.00	0.18	0.00	-0.08
C5FF20-4	12	0.02	0.09	0.00	0.20	0.01	0.00
C5FF20-4	18	0.02	0.10	-0.01	0.24	0.02	0.03
C5FF20-7	3	0.00	0.10	0.00	0.00	0.01	0.02
C5FF20-7	6	0.01	0.12	0.00	0.06	0.01	0.01
C5FF20-7	9	0.01	0.13	0.01	0.12	0.01	-0.03
C5FF20-7	12	0.01	0.20	0.01	0.39	0.01	0.07
C5FF20-7	18	0.02	0.23	0.01	0.49	0.01	0.11
C5FC30S3-4	3	0.00	0.17	-0.01	-0.04	-0.02	-0.04
C5FC30S3-4	6	0.00	0.17	-0.01	0.20	-0.01	-0.05
C5FC30S3-4	9	0.01	0.39	-0.01	0.09	-0.02	-0.01
C5FC30S3-4	12	0.01	0.44	-0.01	0.04	-0.02	-0.02
C5FC30S3-4	18	0.01	0.48	-0.01	0.06	-0.02	-0.02
C5FC30S3-7	3	0.00	0.20	-0.03	0.11	-0.03	0.12
C5FC30S3-7	6	0.01	0.18	-0.08	0.05	-0.06	0.13
C5FC30S3-7	9	0.02	0.24	-0.08	0.10	-0.07	0.18
C5FC30S3-7	12	0.02	0.27	-0.08	0.06	-0.07	0.16
C5FC30S3-7	18	0.01	0.27	-0.08	0.09	-0.04	0.17

Appendix D: District and County Maps

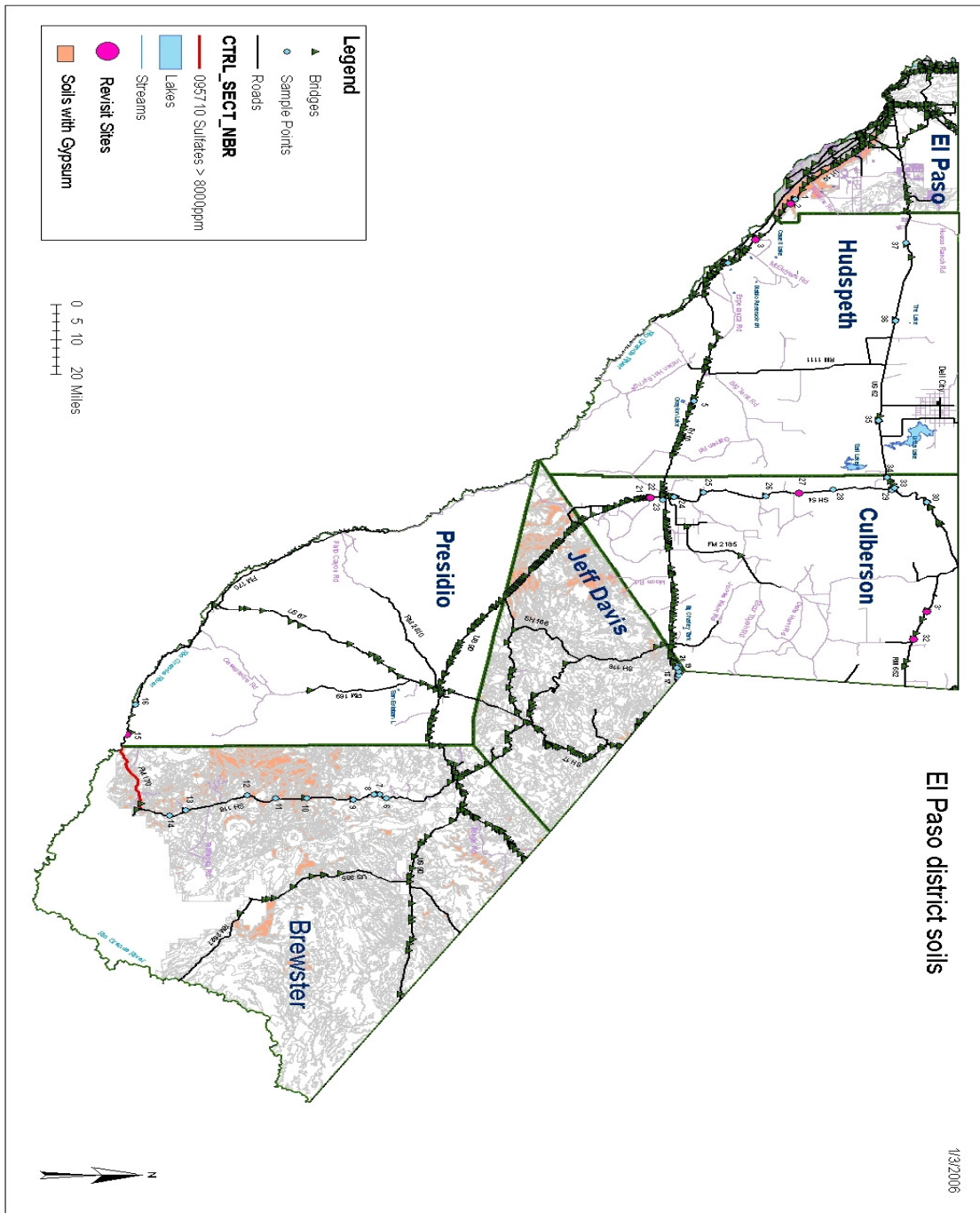


Figure D-1: Map of soils in the El Paso District

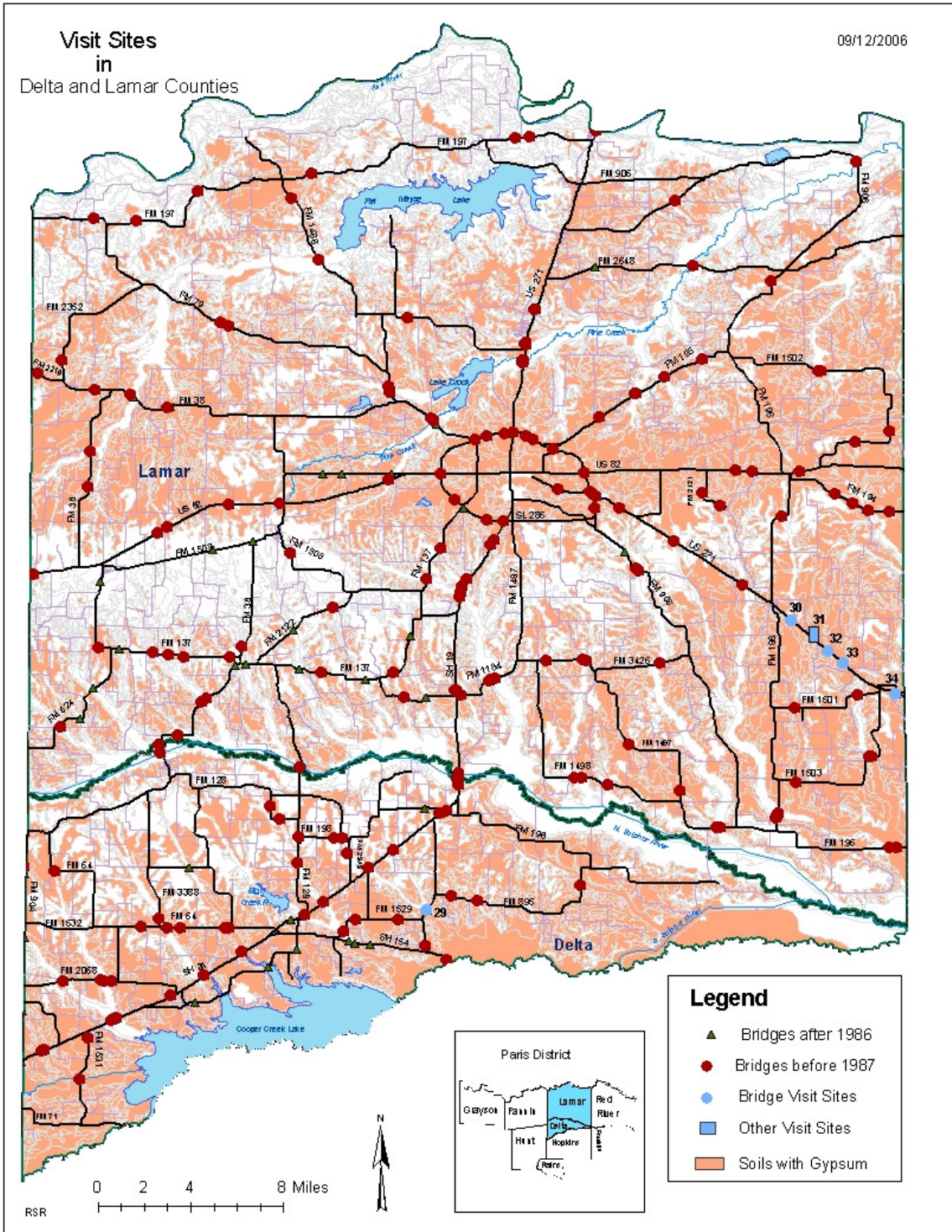


Figure D-2: Map of soils in the Paris District

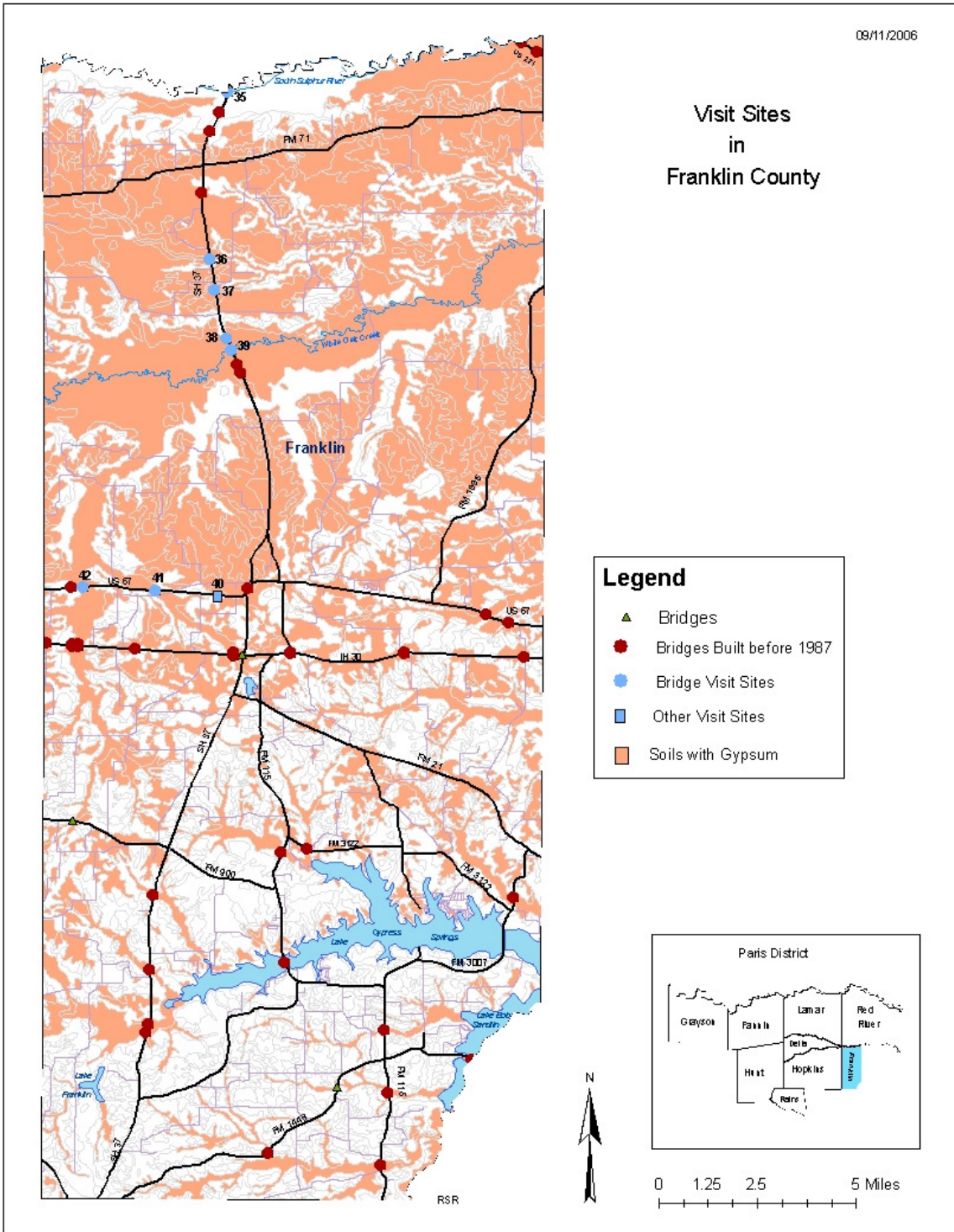


Figure D-3: Map of soils of Franklin county in the Paris District

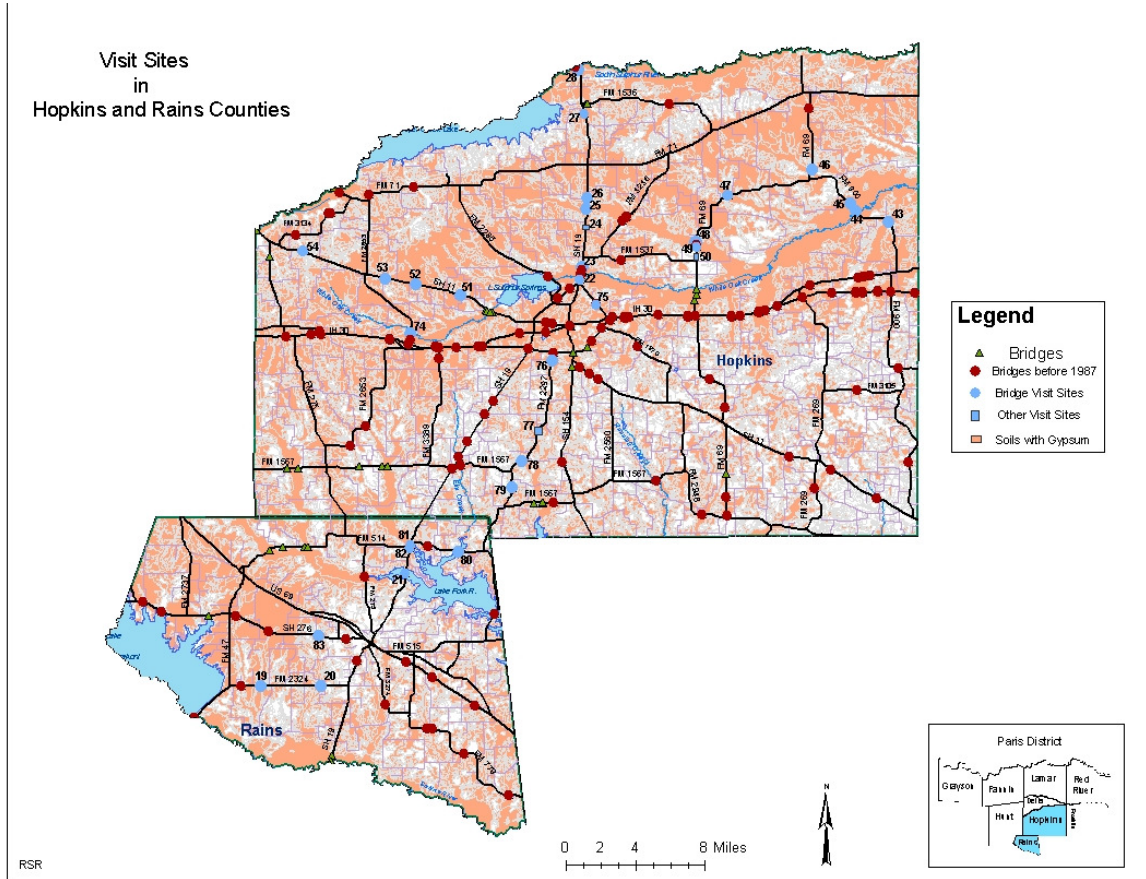


Figure D-4: Map of soils of Hopkins and Rains counties in the Paris District

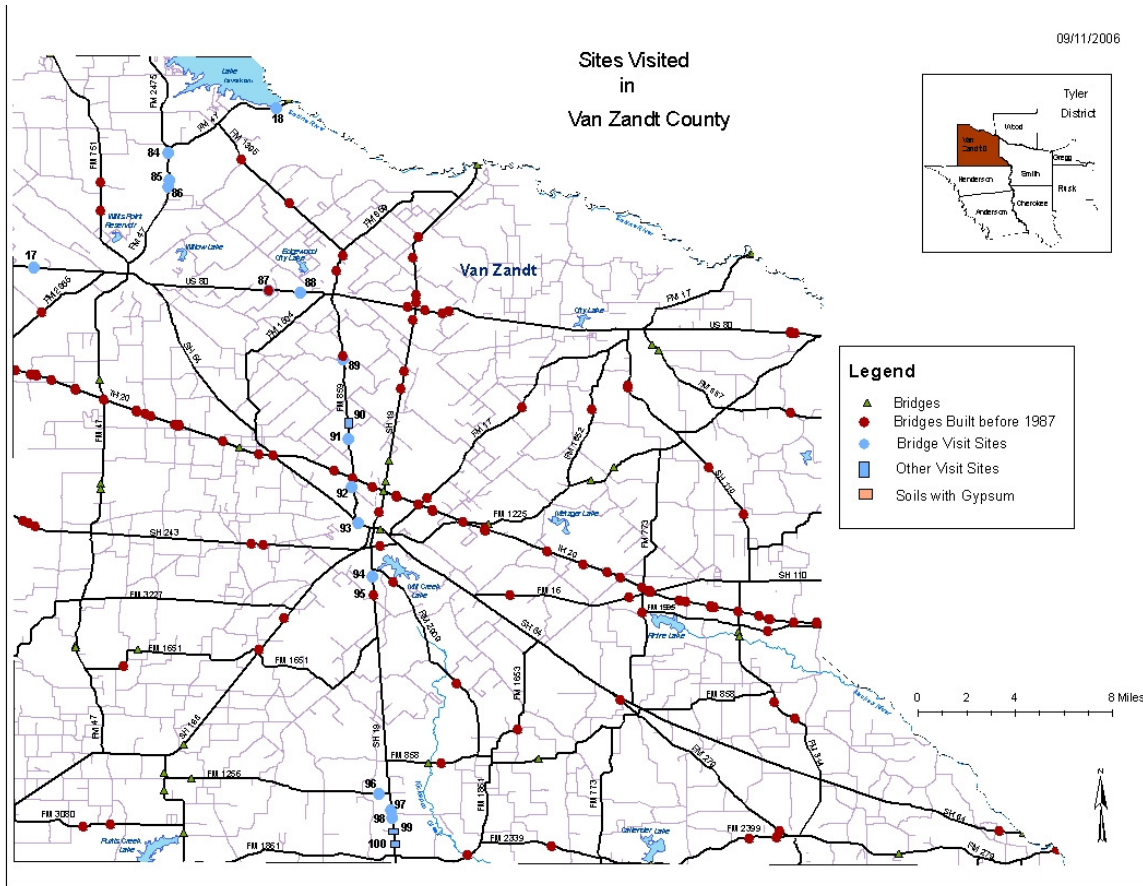
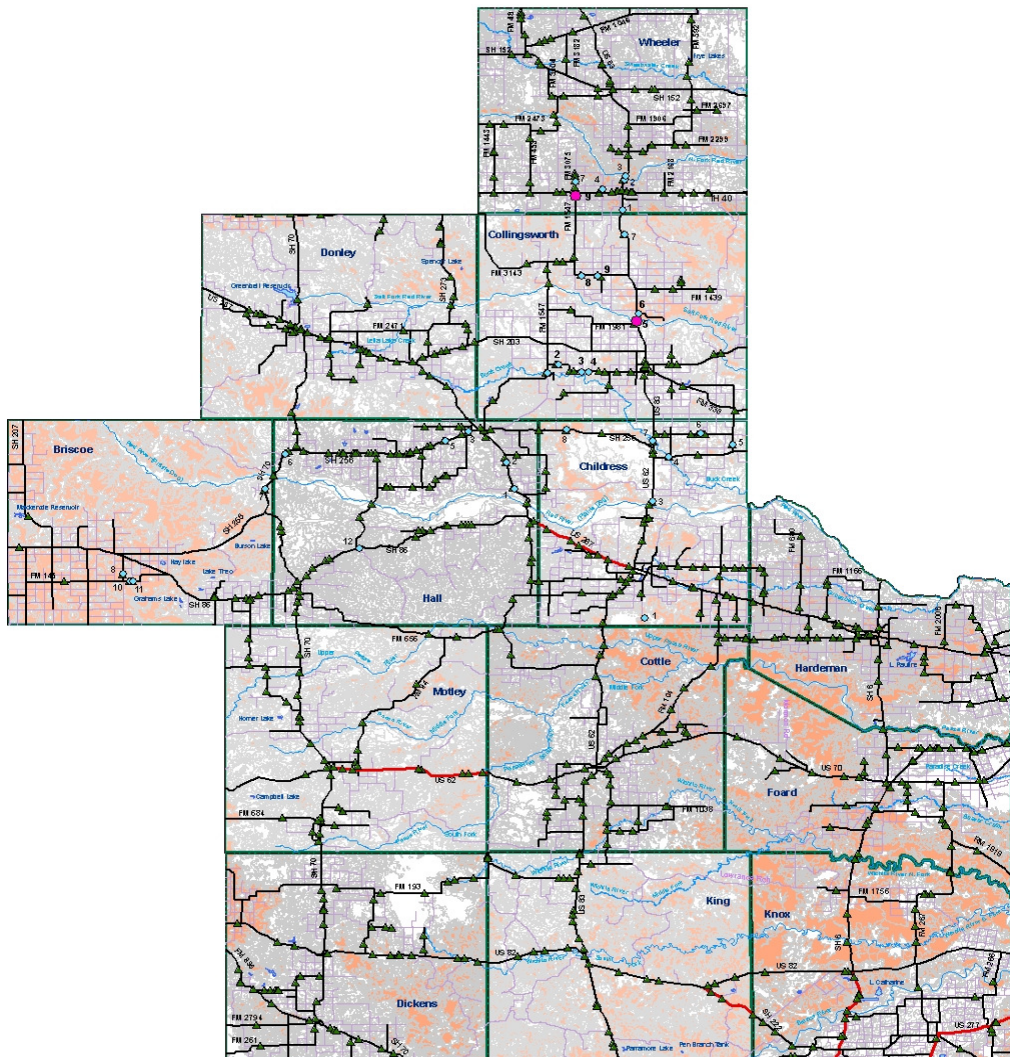


Figure D-6: Map of soils of Van Zandt county in the Paris District

Childress District Soils

1/4/06



Legend

- Sample Points
- ▲ Bridges
- Revisit Sites
- Soils with Gypsum

Roads

- Roads
- County Roads

CTRL_SECT_NBR

- 004212 Sulfates > 8000ppm
- 009805
- 014601
- 015702
- 049603

— Lakes

— Streams

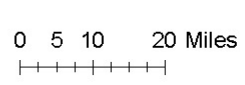


Figure D-7: Map of soils in the Childress District

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Vita

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