March 2021

The Effect of Cement and Blast Furnace Slag Characteristics on Expansion of Heat-Cured Mortar Specimens

Jair G. Burgos

University of South Florida

Follow this and additional works at: https://digitalcommons.usf.edu/etd

Part of the Civil Engineering Commons, and the Materials Science and Engineering Commons

Scholar Commons Citation

This Thesis is brought to you for free and open access by the USF Graduate Theses and Dissertations at Digital Commons @ University of South Florida. It has been accepted for inclusion in USF Tampa Graduate Theses and Dissertations by an authorized administrator of Digital Commons @ University of South Florida. For more information, please contact scholarcommons@usf.edu.
The Effect of Cement and Blast Furnace Slag Characteristics on Expansion of Heat-Cured Mortar Specimens

by

Jair G. Burgos

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering
Department of Civil and Environmental Engineering
College of Engineering
University of South Florida

Major Professor: Abla Zayed, Ph.D.
Gray Mullins, Ph.D.
Natallia Shanahan, Ph.D.
Dhanushika Mapa, Ph.D.

Date of Approval:
March 3, 2021

Keywords: Internal Sulfate Attack, Delayed Ettringite Formation, High Alumina Slag

Copyright © 2021, Jair G. Burgos
Dedication

This work is dedicated to my parents and family; their love and support has continuously inspired me to keep excelling in my educational career. I must also dedicate this work to my fiancé without whose enduring support and love, I would not have grown to be the person I am today.
Acknowledgments

I would like to thank everyone who has supported me in my research but especially my major professor, Dr. Abla Zayed, whose unwavering dedication and guidance were invaluable throughout my research experience. I would also like to extend thanks to my committee members – Dr. Mullins, Dr. Shanahan, and Dr. Mapa – for their consideration, knowledge, and counsel in my defense and final thesis.

I must also extend gratitude to my research cohort: Hai Zhu, Nicholas Fowler, Dhanushika Mapa, Farzaneh Nosouhian, Mustafa Fincan, and Dr. Yuriy Stetsko. My graduate educational career would have been meaningless without their tireless support and advice throughout my Master’s. Thank you to Hai, Mustafa, and Dr. Stetsko for spending late nights and early mornings on weekdays and weekends with me ensuring my scans were done properly and promptly. Thanks to Dhanushika, Farzaneh, and Hai for always willing to give advice when asked for or to clarify and to fill in gaps in my knowledge. Thanks to Nicholas for being a friend who lifted my spirits during work days and always had a song of the day to look forward to. I wish you all great success in your lives’ endeavors.

Additionally, extended thanks to the Florida Department of Transportation and the Civil and Environmental Engineering Department for both their financial support.
# Table of Contents

List of Tables ...........................................................................................................iii

List of Figures ..........................................................................................................v

Abstract ....................................................................................................................ix

Chapter 1 Introduction ..............................................................................................1

Chapter 2 Literature Review ......................................................................................6
  2.1 Introduction .......................................................................................................6
  2.2 Ettringite Formation .......................................................................................7
  2.3 Conditions for DEF .........................................................................................8
  2.4 Physical Characteristics Affecting DEF .........................................................10
    2.4.1 Temperature and Humidity ........................................................................10
    2.4.2 Cement Fineness .......................................................................................12
    2.4.3 Microcracks ..............................................................................................12
  2.5 Chemical Characteristics Affecting DEF .......................................................13
    2.5.1 Alkali Content .........................................................................................13
    2.5.2 C₃S and C₃A Content ...............................................................................14
    2.5.3 Sulfate Content .......................................................................................14
    2.5.4 Sulfate-to-Aluminate Ratio .....................................................................14
    2.5.5 Pozzolans and SCM Addition in Blended Cements ..................................15
  2.6 Role of Hydrogarnet in DEF ..........................................................................18
  2.7 Mix Design Parameters Affecting DEF .........................................................18
  2.8 Effect of Slag Addition on DEF ......................................................................19
  2.9 Effect of Limestone Addition on DEF ............................................................20
  2.10 Major Findings and Gaps in the Literature ...................................................21

Chapter 3 Materials and Methodology ...................................................................23
  3.1 Cement and Slag Composition ......................................................................23
  3.2 Mortar Bar Composition and Preparation .....................................................24
  3.3 Heat Curing Regime .......................................................................................26
  3.4 X-Ray Diffraction Analysis ..........................................................................28

Chapter 4 Results and Discussion .........................................................................29
  4.1 DEF Index ......................................................................................................29
  4.2 Expansion after Heat Treatment .....................................................................30
    4.2.1 Control Mixes .........................................................................................30
4.2.2 As-Received Mixes with 60% Slag Replacement ........................................33
4.2.3 As-Received Mixes with 35% Slag Replacement ........................................37
4.2.4 Sulfate-Optimized Slag Blended Mixtures ................................................38
4.3 XRD Results ................................................................................................41
    4.3.1 Control Mixes .........................................................................................41
    4.3.2 As-Received Mixes with 60% Slag Replacement ........................................46
    4.3.3 Sulfate-Optimized Mixes .........................................................................53
    4.3.4 As-Received Mixes with 35% Slag Replacement ........................................59

Chapter 5 Conclusions and Recommendations ....................................................66

References ........................................................................................................68

Appendix A: Copyright Permissions ......................................................................75
Appendix B: Expansion Charts .............................................................................78
Appendix C: XRD Charts ....................................................................................81
List of Tables

Table 2.1 Cement Composition used in Swedish Railroad Ties [4] ..............................6
Table 3.1 Cement Chemical and Physical Characteristics ........................................24
Table 3.2 Ground Blast Furnace Slag Chemical and Physical Characteristics ..........24
Table 3.3 Mineralogical Cement Composition Determined by XRD .........................25
Table 3.4 Mineralogical Slag Composition Determined by XRD ..............................25
Table 3.5 Optimized Sulfate Content for Blended Mixtures Studied .........................26
Table 4.1 Calculated DEF Index [31] Values for Cements Studied ...........................30
Table 4.2 Calcium Sulfoaluminate and Calcium Aluminate Phase Composition
Development and Transformation of Cement BB and 60% Slag 14B and its 1 and 2 Day Sulfate Optimized Mixes ..........................................................58
Table 4.3 Calcium Sulfoaluminate and Calcium Aluminate Phase Composition
Development and Transformation of Cement C and 60% Slag 10F and its 1 and 2 Day Sulfate Optimized Mixes ..........................................................58
Table 4.4 Calcium Sulfoaluminate and Calcium Aluminate Phase Composition
Development and Transformation of Cement Z and 60% Slag 14B and its 1 and 2 Day Sulfate Optimized Mixes ..........................................................59
Table 4.5 Calcium Sulfoaluminate and Calcium Aluminate Phase Composition
Development and Transformation of Cement TIL and 60% Slag 14B and its 1 and 2 Day Sulfate Optimized Mixes ..........................................................59
Table 4.6 Calcium Sulfoaluminate and Calcium Aluminate Phase Composition
Development and Transformation of 65% Cement C with 35% Slag 17 ..........64
Table 4.7 Calcium Sulfoaluminate and Calcium Aluminate Phase Composition
Development and Transformation of 65% Cement C with 35% Slag 14B ..........64
Table 4.8 Chemical Characteristics of Cement C with 35% Slag Replacement Mixes ......64
Table 4.9 Ettringite Content and Expansion at 180 Days of Storage of Cement C with 35% Slag Replacement Mixes .................................................................65
List of Figures

Figure 1.1 Cracking caused by expansion in a concrete bridge column after 15 years in service adapted from Thomas et al. [11] .........................................................2

Figure 2.1 Curves of ettringite decomposition at various water vapor pressures for decomposition and reformation reactions, replotted with permission from [33] ........10

Figure 3.1 Modified Fu heat curing regime for internal sulfate attack of mortar specimens ........27

Figure 4.1 Expansion of control bars subjected to heat curing ........................................31

Figure 4.2 Expansion of as-received cement BB mixes with 60% slag replacement ...........34

Figure 4.3 Expansion of as-received cement C mixes with 60% slag replacement ............34

Figure 4.4 Expansion of as-received cement TIL mixes with 60% slag replacement ........35

Figure 4.5 Expansion of as-received cement THIL mixes with 60% slag replacement ........35

Figure 4.6 Expansion of as-received cement TTC mixes with 60% slag replacement ........36

Figure 4.7 Expansion of as-received cement Z mixes with 60% slag replacement.............36

Figure 4.8 Expansion of as-received cement C mixes with 35% slag replacement............37

Figure 4.9 Expansion of sulfate optimized cement BB mixes with 60% slag 14B ..............39

Figure 4.10 Expansion of sulfate optimized cement C mixes with 60% slag 10F ............39

Figure 4.11 Expansion of sulfate optimized cement TIL mixes with 60% slag 10F ...........40

Figure 4.12 Expansion of sulfate optimized cement Z mixes with 60% slag 10F ............40

Figure 4.13 Correlation of ettringite content and expansion of all control cement mixes at 4 months of age (HCR6) .................................................................43

Figure 4.14 Phase assemblage of 100% cement BB .......................................................43

Figure 4.15 Phase assemblage of 100% cement C ..........................................................44
Figure 4.16 Phase assemblage for 100% cement TIL ..................................................44
Figure 4.17 Phase assemblage for 100% cement THIL .............................................45
Figure 4.18 Phase assemblage for 100% cement TTC .............................................45
Figure 4.19 Phase assemblage for 100% cement Z .................................................46
Figure 4.20 Phase assemblage of 60% cement BB and 40% slag 8 as-received ..........47
Figure 4.21 Phase assemblage of 60% cement BB and 40% slag 10C as-received ....48
Figure 4.22 Phase assemblage of 60% cement BB and 40% slag 10F as-received ....48
Figure 4.23 Phase assemblage of 60% cement BB and 40% slag 14B as-received ....49
Figure 4.24 Phase assemblage of 60% cement BB and 40% slag 17 as-received ..........49
Figure 4.25 Phase assemblage of 60% cement C and 40% slag 17 as-received ..........50
Figure 4.26 Phase assemblage of 60% cement TIL and 40% slag 17 as-received .........51
Figure 4.27 Phase assemblage of 60% cement THIL and 40% slag 17 as-received .........51
Figure 4.28 Phase assemblage of 60% cement TTC and 40% slag 17 as-received ..........52
Figure 4.29 Phase assemblage of 60% cement Z and 40% slag 17 as-received ..........52
Figure 4.30 Phase assemblage for cement BB with 60% slag 14B as-received ..........53
Figure 4.31 Phase assemblage for cement BB with 60% slag 14B
1-day sulfate optimized mix .................................................................54
Figure 4.32 Phase assemblage for cement BB with 60% slag 14B
2-day sulfate optimized mix .................................................................54
Figure 4.33 Phase assemblage for cement TIL with 60% slag 14B as-received ..........55
Figure 4.34 Phase assemblage for cement TIL with 60% slag
14B 1-day sulfate optimized mix ............................................................55
Figure 4.35 Phase assemblage for cement TIL with 60% slag
14B 2-day sulfate optimized mix ............................................................56
Figure 4.36 Ettringite content for cement BB with 60% slag 14B sulfate-optimized mixes ....57
Figure 4.37 Ettringite content for cement TIL with 60% slag 14B sulfate-optimized mixes ……57
Figure 4.38 Ettringite content for cement C with 35% slag replacement at different ages ……61
Figure 4.39 Monosulfate content for cement C with 35% slag replacement at different ages ……62
Figure 4.40 Phase assemblage for cement C with 35% slag 17 ……………………………………..62
Figure 4.41 Phase assemblage for cement C with 35% slag 14B …………………………………….63
Figure B.1 Expansion of sulfate optimized cement BB mixes with slag 8 ………………………………78
Figure B.2 Expansion of sulfate optimized cement BB mixes with slag 10C ……………………………79
Figure B.3 Expansion of sulfate optimized cement BB mixes with slag 10F ……………………………79
Figure B.4 Expansion of sulfate optimized cement TIL mixes with slag 14B ……………………………80
Figure B.5 Expansion of sulfate optimized cement Z mixes with slag 14B ………………………………80
Figure C.1 Phase assemblage of 40% cement BB mixes with (a) 60% S8 as-received, (b) 60% S8 1-day sulfate optimized, and (c) 60% S8 2-day sulfate optimized ………………………………………..81
Figure C.2 Phase assemblage of 40% cement BB mixes with (a) 60% S10C as-received, (b) 60% S10C 1-day sulfate optimized, and (c) 60% S10C 2-day sulfate optimized ………………………………..82
Figure C.3 Phase assemblage of 40% cement BB mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized ………………………………………83
Figure C.4 Phase assemblage of 40% cement C mixes as-received with (a) 60% S8, (b) 60% S10C, (c) 60% S14A, and (d) 60% S14B ……………………………………….84
Figure C.5 Phase assemblage of 40% cement C mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized …………………………………………..85
Figure C.6 Phase assemblage of 40% cement TIL as-received with 60% S14A …………………….86
Figure C.7 Phase assemblage of 40% cement TIL mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized ………………………………..87
Figure C.8 Phase assemblage of 40% cement THIL mixes as-received with
(a) 60% S8, (b) 60% S10C, and (c) 60% S10F .................................88

Figure C.9 Phase assemblage of 40% cement Z mixes as-received with
(a) 60% S8, (b) 60% S10C, and (c) 60% S14A .................................89

Figure C.10 Phase assemblage of 40% cement Z mixes with (a) 60% S10F
as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F
2-day sulfate optimized .................................................................90

Figure C.11 Phase assemblage of 40% cement Z mixes with (a) 60% S14B
as-received, (b) 60% S14B 1-day sulfate optimized, and (c) 60% S14B
2-day sulfate optimized .................................................................91
Abstract

Delayed ettringite formation (DEF) is a durability issue that typically occurs in concrete exposed to high temperatures at an early age such as precast elements and massive concrete structural elements. There are many advantages to precast concrete such as its quality control, better safety control, and reusable forms, which make them cheaper than casting on site [1]. Heat curing of precast concrete is conducted to obtain high early-strength. However, in doing so, durability issues can arise in the form of internal sulfate attack also known as DEF, if the internal temperature of concrete exceeds 70°C. Past this threshold, ettringite decomposes and after subsequent years in service and in the presence of sufficient moisture, the ettringite will reform within the concrete resulting in expansion and eventually failure. Ground granulated blast furnace slag (GGBFS, slag) is often used in blended concrete mixtures for both economic and environmental purposes but it also possesses durability benefits. ACI 201.2R-16 (Guide to Durable Concrete) [2] recommends a minimum of slag replacement level of 35%, for concrete elements which can potentially exceed 70°C, is sufficient to reduce the potential of DEF occurrence. However, this replacement threshold does not account for variable cement and slag chemistries, mineralogy, and physical characteristics. Depending on the chemistry of the cement or slag and the level of replacement, slag can mitigate the effects of DEF or prevent expansion entirely from occurring. Therefore, this study aims to identify the characteristics of cementitious systems that are of significance to DEF phenomenon.

Six different cements were used in this study; namely, Type I, Type I high alkali, Type II, Type II moderate heat cement (MH) of low alkali content, and Type II (MH) of moderate alkali
content. These were blended with 6 different slags of variable chemical and physical characteristics at two replacement levels of 60% and 35% by weight. The heat treatment cycle used had a maximum temperature of 95 °C and a residence time of 36 hours. The specimens were subsequently stored in saturated lime water and measured for expansion regularly over the course of the experiment. X-Ray diffraction scans were also performed to confirm the presence and evolution of ettringite among other phases in each mix.

The results show that 35% high alumina slag replacement does not necessarily prevent expansion when blended with Type I high alkali cement. The degree of expansion was found to be related to the slag alumina content with high alumina slags showing earlier and higher expansion. Increasing slag replacement levels from 35% to 60% suppressed DEF for all blended systems studied. The results of this study indicate the need to further examine ACI recommendations for the minimum replacement level for heat-cured blended cementitious materials that should be used to suppress DEF especially in the light of the variability of modern cements and slag chemistries.

The work reported in this thesis was partially funded by the Florida Department of Transportation (FDOT) under contract number BDV25 977-63 (Correlation of Slag Cement Composition with Durability of Portland Cement-Slag Concrete). Most of the collected data (charts and tables) are shared between the Final Report of the named project and this thesis.
Chapter 1  Introduction

Cement is one of the most widely used and versatile construction materials in the world. Typically, limestone (a source of calcium oxide) and clay (a source of aluminosilicates) are calcined in a kiln at high temperatures exceeding 1400°C to form reactive calcium silicates and calcium aluminate compounds [3]. The product of the clinkering process is known as clinker. The clinker is then grounded into a fine powder with a source of calcium sulfate such as gypsum, hemihydrate and/or anhydrite to produce portland cement. This is how most cements are globally produced; consequently, the exact chemistry of the cement varies depending on the composition of the raw materials, e.g., limestone and clay. Once cement is mixed with water, it reacts to form various calcium, alumina, and silica hydrates, which bind aggregates together to create concrete. It is used to make everything from skyscrapers to highways to bridges. Structural concrete can be precast or cast in-place depending on the element size and application, where it would be subjected to different environmental conditions.

Precast concrete is where the concrete is poured into a mould and is cured in a controlled environment, typically a factory or plant. The finished cured concrete element would then be transported to its final destination and installed on-site. Precast elements can include smaller products such as exterior walls and railway ties to larger architectural pieces in a skyscraper and roadway/bridge sections. To make precast concrete economically feasible, manufacturers would often use high-early strength cements and/or heat curing in the precast products. High-early strength cements, as the name suggests, have high strength development in early ages and are typically higher in tricalcium silicates and aluminates and fineness such as Type III cements [4].
Heat curing of precast elements enhances its strength development. This can be achieved either with steam curing under ambient pressure or radiant sources of heat such as hot air, water, oil, or heating blankets [5]. High pressure steam curing can be done in an autoclave, but this is reserved for smaller concrete elements. Reports have found durability issues in concrete that has been subjected to high temperature heat curing where there can be deleterious expansion after many years in service [6]–[10]. Figure 1.1 shows an example of such expansion adapted from Thomas et al. [11], where the concrete column is suspected to have had an internal temperature rise exceeding 70°C. This expansion is attributed to the reformation of ettringite in the concrete, which is an expansive hydration product of cement. The ettringite which forms during initial stages of hydration decomposes during the high temperature curing; while in service over the course of many years, the ettringite reforms in concrete resulting in expansion of the concrete element [7], [12]. This phenomenon is called delayed ettringite formation (DEF) and it is one of the most deleterious problems facing the precast concrete industry. DEF is also a durability issue for non-heat cured concrete such as mass concrete elements. It has been previously reported that internal concrete temperatures can rise up to and in excess of 80 °C even without applying heat [5] in mass concrete elements. This is another instance of where the phenomenon of DEF can occur.

![Figure 1.1](image1.jpg)

**Figure 1.1** Cracking caused by expansion in a concrete bridge column after 15 years in service adapted from Thomas et al. [11]
Apart from being a highly versatile construction material, concrete is the most widely consumed material in the world by mankind, second only to water [13]. The manufacturing of concrete is also notorious for being one of the major contributors to global warming. The cement industry contributes approximately 8% of global CO$_2$ emissions [14]. One method of combating this is by reducing the amount of cement used in concrete by using one or more of the available supplementary cementitious materials (SCMs).

One popular supplementary cementitious material is ground granulated blast furnace slag (GGBFS, slag). Previous research indicates that calcium aluminate SCMs such as slag, are able to mitigate the effect of DEF in heat cured concretes [15]–[22]. Other SCMs have shown to be capable of mitigating or completely eliminating the effects of DEF such as metakaolin (MK) or fly ash (FA), specifically class F fly ash at certain replacement levels [15]–[17], [21]. However, unlike MK or Class F FA, the chemical and physical composition of slags is more variable and changes depending on its source and manufacturing method.

Several researchers obtained different threshold values for slag replacement to prevent expansion related to DEF. These threshold values can range from 30% [20] up to 40% [21] replacement by weight and anywhere in between. The biggest faux-pas in these studies that incorporate slag to study its efficacy to prevent DEF is that they tend to only use one type of slag in their entire study. For example, Fu [20] only used one supply of slag in his study which had no alkali, was low SO$_3$ content (1.5%), and had moderate amount of aluminate (10.5%). Although Ramlochan [15] used two supplies of Grade 100 slag in his study, he noted they had similar chemical compositions conforming to ASTM C989 with moderate aluminate content (9.4%). Similar to having multiple cements to account for their chemical variability, multiple slags must also be used to account for their variability in chemical composition when studying their effect on
DEF especially in the different combinations within blended cements. This combined with a lack of a standard heat-curing regime for studying DEF leading to variability in curing temperatures and soaking times leads to gaps in the literature, especially with higher alumina slags and higher alkali cements. Thus, the focus of this research is to assess the effectiveness of slags of variable characteristics on suppressing DEF phenomenon in slag blended cementitious systems.

Several types of portland cements with variable chemical, mineralogical and physical characteristics were used in this study in addition to limestone cement. A total of 6 cements were used in this study; namely, Type I, Type I of high alkali content (Type I (HA)), two Type II cements, and two Type II (HA) cements. Additionally, six slags were included and the selection of slags was based on their alumina and alumina-to-magnesia ratio. Since the current slags of higher alumina content require sulfate optimization for better sulfate durability, the concept of sulfate optimization and its effect on DEF phenomenon was also examined here using 1- and 2-day sulfate optimized blended mixtures. Using sulfated slags in blended cements can actually increase the compressive strength of a concrete mixture [23]. Optimization was conducted according to ASTM C563 [24].

Another important factor that was considered in this study is the slag replacement level and its effectiveness on suppressing DEF in the slag blended cementitious mixtures. Two levels of replacements were considered: 35% (precast) where lower replacement levels are desirable to minimize the effect of slag content on the early strength gain, and a 60% replacement (mass concrete) to maximize the effectiveness of slag in lowering concrete temperature rise. The slag blended mixtures were heat cured at high temperature and then placed in a saturated lime solution to monitor expansion according to ASTM C490 [25].
The findings of this study can then be used to guide and identify appropriate replacement levels of slags of variable chemical, physical and mineralogical characteristics that can suppress DEF phenomenon in slag blended concrete.
Chapter 2  Literature Review

2.1 Introduction

Delayed ettringite formation (DEF) is typically defined in the literature as the reformation of secondary ettringite after concrete has substantially hardened due to internal sulfate attack (ISA), in which none of the sulfates have originated from the external environment [12]. It is associated with expansion in concrete that has been heat-treated during its curing or if mass concrete elements experience temperatures above 70°C during its casting [2], [5]. It has been identified as a problem since the 1980s originally in steam-cured railroad ties [6], [26], [27]. Ettringite formation in DEF should not be confused with primary ettringite formation, which itself is part of the initial cement hydration process. This type of ettringite is typically innocuous in non-heat treated concrete while concrete is still in its plastic state [27]. The ettringite formed in the early stages of cement hydration is sometimes referred to as early ettringite formation (EEF) [7].

Table 2.1 adapted from Sahu and Thaulow [6], shows a summary of the cement composition used in the concrete for railroad ties that experienced DEF in Sweden. There was no supplementary cementitious material and only a superplasticizer was used. This cement which proved susceptible to DEF appears to be high in alkali content, sulfate content, as well as fineness and the cement is low in aluminate and C₃A.

<table>
<thead>
<tr>
<th>Component</th>
<th>C₃S</th>
<th>C₃A</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂Oₑq</th>
<th>SO₃/Al₂O₃</th>
<th>Fineness</th>
<th>C₃S</th>
<th>C₃A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt%/wt.</td>
<td>m²/kg</td>
<td>wt %</td>
<td>wt %</td>
</tr>
<tr>
<td>Value</td>
<td>59</td>
<td>8</td>
<td>4.4</td>
<td>3.5</td>
<td>3.7</td>
<td>1.16</td>
<td>0.84</td>
<td>550</td>
<td>59</td>
<td>8</td>
</tr>
</tbody>
</table>
2.2 Ettringite Formation

Not all ettringite formation is detrimental to the concrete element; that is, not all ettringite formation is related to internal sulfate attack. EEF or primary ettringite is when ettringite forms homogenously and immediately after mixing; it is innocuous. EEF can be advantageous for the development of shrinkage-compensating concrete using expansive cements [7]. Ettringite forms when gypsum (C₅₀H₂) and tricalcium aluminate (C₃A) react in a through-solution reaction. The initial formation of ettringite follows the chemical reaction in Equation 2.1 [3]. For this reaction to proceed the sulfate must dissolve and react with calcium, aluminum, and water [28]. The calcium alumino-sulfate hydrate product formed is what is called ettringite.

\[ \text{C}_3\text{A} + 3\text{C}_5\text{H}_2 + 26\text{H} \rightarrow \text{C}_6\text{A}\text{S}_3\text{H}_{32} \text{ (ettringite)} \]  
Equation 2.1

It should be noted that a very similar reaction also occurs with tetracalcium aluminate ferrite (C₄AF) to form a phase very similar to ettringite but with some of the aluminate substituted with ferrite, i.e., C₆(A,F)S₃H₃₂. But if all the sulfate source (C₅₀H₂) is consumed before all the C₃A has reacted then the ettringite transforms into another calcium sulfoaluminate hydrate product with only a third of the sulfate, typically referred to as “monosulfate” [3] as shown in Equation 2.2.

\[ 2\text{C}_3\text{A} + \text{C}_6\text{A}\text{S}_3\text{H}_{32} + 4\text{H} \rightarrow 3\text{C}_4\text{A}\text{S}_4\text{H}_{12} \text{ (monosulfate)} \]  
Equation 2.2

Monosulfate can form before ettringite if the C₃A consumes the sulfate ions faster than they can dissolve from the gypsum during the initial hydration process [3]. This implies that a certain minimum concentration of sulfate must be available for the formation of ettringite in
concrete. Thus, monosulfate forms when there is insufficient sulfate to form ettringite from the available alumina in cement. But ettringite can reform from monosulfate if a new sulfate source is reintroduced to the cementitious system following the reaction in Equation 2.3 [3].

\[
\begin{align*}
\text{C}_4\text{A}\tilde{\text{S}}\text{H}_{12} + 2\text{C}\tilde{\text{S}}\text{H}_2 + 16\text{H} &\rightarrow \text{C}_6\text{A}\tilde{\text{S}}_3\text{H}_{32} \\
\text{Equation 2.3}
\end{align*}
\]

When the formation of ettringite happens in hardened concrete, heterogenous expansion can result in cracking and spalling. This forms the basis for external sulfate attack. Internal sulfate attack requires a few more parameters as will be discussed in the proceeding sections. When there is an insufficient sulfate source, the C\text{3A} might react too quickly with water and form calcium aluminate hydrates. These rapidly-formed hydrates are unstable and subsequently react to form hydrogarnet (C\text{3AH}_6), a sulfate-free calcium aluminate hydrate. The hydrogarnet forms according to the reaction in Equation 2.4 [3].

\[
\begin{align*}
\text{C}_3\text{A} + 21\text{H} &\rightarrow \text{C}_4\text{AH}_{13} + \text{C}_2\text{AH}_8 + 2\text{C}_3\text{AH}_6 \text{ (hydrogarnet)} + 9\text{H} \\
\text{Equation 2.4}
\end{align*}
\]

2.3 Conditions for DEF

It has been established that DEF is one of the main durability issues facing field concrete which includes precast concretes cured at a high temperature [6] or mass concrete where the internal temperature rise occurs due to heat generation released from the hydration of cementitious material [2], [29]. Laboratory studies have shown that expansion occurs when portland cement (PC) mortars and concretes are exposed to elevated temperatures and subsequently stored in moist conditions at room temperature [30]. Durability issues of steam-cured and massive concrete
elements in the field that have been exposed to moist service environments for several years, have
been attributed to DEF [31]. Several studies have established three necessary conditions for DEF
to occur [7], [10], [12], [15], [16], [18], [32].

I. An excessive rise in temperature (greater than ~70 °C) during curing either from steam
curing or high heat of hydration

II. The presence of sulfates in the cementitious system, i.e., not from the external environment

III. A sufficiently moist service environment

Through experimental work on high-sulfate content concretes cured at room and high
temperatures, Collepardi [7] established that the thermal decomposition and subsequent
reformation of ettringite can only occur when concrete elements are subjected to high temperatures
(steam-cured at 80-90°C). In this study, the sulfur contents ranged from 1-2% and 2-4% as SO3 in
the clinker phase and in the PC respectively. Expansion from ettringite reformation was favored
in the concrete elements with pre-existing cracks and high sulfur content in the clinker phase and
PC [7]. It is generally accepted that the ettringite decomposes during high temperature curing and
reforms slowly after over several months or years [12], [15], [18], [31], [33]–[35]. Many factors
can affect the potential for DEF to occur. These factors include physical composition, chemical
composition, and mix design. Since the focus of the current study includes incorporation of slag
limestone cements, their effects on DEF will be expounded.
2.4 Physical Characteristics Affecting DEF

2.4.1 Temperature and Humidity

Zhou and Glasser [36] studied phase-pure ettringite produced from reagent grade tricalcium aluminate and gypsum. They found that the critical temperature where pure ettringite starts to decompose was around 70 °C and it completely decomposes at 120 °C into gypsum, hemihydrate, and amorphous material. They discovered that when reducing the temperature while increasing the humidity, ettringite reforms as shown in Figure 2.1 replotted with permission from their study.

![Figure 2.1 Curves of ettringite decomposition at various water vapor pressures for decomposition and reformation reactions, replotted with permission from [36]](image)

The formation and decomposition curves divide the phase diagram into three distinct regions. On the left of the hysteresis, ettringite is both stable and persistent. On the right of the hysteresis, ettringite is unstable and cannot form spontaneously. Within the hysteresis, ettringite will not decompose significantly but once decomposed, it will not reform spontaneously [36]. This pseudo-phase diagram of ettringite demonstrates how at approximately 70°C ettringite within
concrete systems can begin to decompose appreciably, which is in agreement with the first condition necessary for DEF to occur mentioned earlier. Since Zhou and Glasser worked with pure ettringite, only the dissociated sulfate in the forms of gypsum and hemihydrate were available for the reformation of ettringite. This is in agreement with the second condition necessary for DEF. As they found, only with increased humidity will the once decomposed ettringite reform with decreasing temperature. Thus, this corroborates the third condition necessary for DEF. Their research did not study the rate of ettringite decomposition or reformation.

Zhou and Glasser’s work [36] are crucial for understanding ettringite stability but to understand how it behaves in a complex environment such as a cementitious systems, other parameters besides temperature and humidity which affect the deformation and reformation of ettringite need to be evaluated. Taylor et al. [12] reviewed multiple studies reported on DEF in actual cementitious systems. Since sulfate is released from ettringite as it decomposes at ~70°C or higher [36], the calcium silicate hydrate (C-S-H) phase and the pore solution in the cementitious system start to compete with the ettringite for those sulfate sources and this competition increases with pH of the pore solution [12], [37]. Several characterization techniques including Nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) have shown that after the heat treatment only poorly crystalline monosulfate and some hydrogarnet are left in the cementitious systems; rarely can traces of ettringite be detected [12], [37]. After heat treatment, most of the aluminate and sulfate become bound in the outer C-S-H phase [12], [15], [18], [30], [38]–[40]. Studies have shown that the aluminum (Al) is firmly bound in the C-S-H phase [41] while the sulfate (SO₄²⁻) is more loosely bound, i.e. adsorbed in the C-S-H phase [42].

Divet and Randriambololona [42] studied the influence of temperature on the adsorption capacity of sulfate in the C-S-H phase. Their results showed that the adsorption capacity of the
calcium silicate hydrate phase increases with temperature. They believe that this is a result of the increase in temperature causing partial desorption of hydroxide ions (OH\(^{-}\)) and interlayer water which creates positive sites attracting more of the negative sulfate ions.

2.4.2 Cement Fineness

An increase in cement fineness leads to higher risk of expansion [15], [18], [20], [43], [44]. The finer the cement, the higher the heat evolution from hydration and thus increasing the temperature rise of concrete [45]. This can increase the risk for expansion if the internal temperature exceeds 70°C. As Tosun [43] reported, cement fineness plays an important role to both the pore structure porosity and rate of expansion related to DEF in heat cured mortars. During early ages of hydration, coarser cement grains allow further ingress of water to react with unhydrated cement resulting in a porous microstructure leading to an initial increase in expansion. At later ages of hydration, ettringite formation slows down in paste made with coarser grains because of the difficulty of water penetration into deeper regions of unhydrated cement. Finer cement grains can reduce the moisture uptake because they produce a dense, low-porosity microstructure [43]. In later ages, this slow moisture penetration causes expansion when other conditions are met, namely available sulfate and aluminate ions for ettringite formation [43].

2.4.3 Microcracks

Microcracking favors DEF since it provides a nucleation site for ettringite to form and begins to exert expansive pressure on the surrounding walls of the microcracks [5], [15], [19], [20], [46]. The presence of microcracks also increases the permeability of the cured concrete which can lead to alkali leaching. Famy [39] found that alkali leaching decreases the pore solution pH which
promotes sulfate desorption from the C-S-H phase leading to the formation of ettringite, resulting in expansion. This is explained further in the next section. Microcracks also facilitate faster diffusion of reactive ions crucial to the formation of ettringite. These ions include Ca\(^{2+}\) and Al\(^{3+}\) resulting in greater desorption of sulfate from the C-S-H phase at earlier ages [15], [16], [18].

2.5 Chemical Characteristics Affecting DEF

2.5.1 Alkali Content

The alkali content of the pore fluid influences the solubility of ettringite. As the pore fluid alkali content increases in tandem with increasing temperature, the ettringite solubility also increases [47]. Divet and Randriambololona [42] studied the effect of pH and temperature of the sulfate adsorption capacity of the pure C-S-H phase in concrete; they found that a mean of 0.68 mmol of sulfate ions are adsorbed per gram of C-S-H. They discovered that as the pH and temperature of the system increases, both the amount of sulfates adsorbed and the rate of adsorption onto the C-S-H phase increase. They hypothesized that in basic media such as the pore solution of concrete, the adsorption of sulfate ions is largely controlled by the thickness of the diffusive layer between the C-S-H phase and the sulfate ions [42]. This ionic strength of the sulfate depends heavily on the basicity of the pore solution of concrete which is influenced by alkali content of cement [42]. Famy [39] found similar results in her study where the amount of sulfates adsorbed into the C-S-H phase increased with the alkali content of the cement during heat curing. She also found that during subsequent storage at ambient temperatures, the alkalis control the amount of sulfate that is desorbed from the C-S-H phase which is used to form ettringite.
2.5.2 C₃S and C₃A Content

C₃S contributes to the heat of hydration and to both early and overall strength development in concrete [3]. C₃A is the primary source of aluminate for ettringite and also contributes to the heat of hydration but not as much as C₃S does. Their release of heat has the potential for exacerbating the temperature rise during hydration of large mass concrete elements thus worsening its potential for DEF [3], [18]. For this reason, Type III PC is most susceptible to DEF since it has a higher C₃A and sulfate content than in Type I or Type II cements [4], [48]. Higher temperatures enable Type III cements to hydrate quickly and form more C-S-H gel during the critical heat-curing period which leads to DEF [48].

2.5.3 Sulfate Content

In general, added sulfates such as gypsum dissolves rapidly and contribute to EEF whereas clinker sulfates are relatively insoluble and are unavailable for EEF, but may contribute to DEF [7], [15], [18], [43]. At the elevated temperatures, the dissolved sulfates from the ettringite become adsorbed in the C-S-H phase and when the temperature returns to ambient conditions this excess sulfate in the C-S-H phase is slowly released in the hardened concrete where it can form ettringite or other sulfoaluminate phases [18]. Thus, a higher cement sulfate content results in more ettringite formation, which can lead to more expansion. However, ettringite formation also depends on the amount of available aluminate, which is discussed in the next section.

2.5.4 Sulfate-to-Aluminate Ratio

Multiple studies have found a correlation between the expansion and the sulfate-to-aluminate molar ratio (SO₃/Al₂O₃) in the cement as well as the squared sulfate-to-aluminate molar ratio [(SO₃)²/Al₂O₃] in cements [16], [18], [31], [34], [44]. These parameters were suggested to be
critical to expansion as it relates to the amount of sulfoaluminate phase that can be formed and thus influencing the amount of ettringite that can form during the initial stages of hydration. But no one has yet found a clear relationship between the molar ratio and the amount of expansion related to DEF. Ramlochan [16] found the most expansion related to DEF occurred when the molar ratio is close to one (1.0). Zhang et al. [34] worked with low sulfate and mostly high alkali clinkers blended with gypsum to make cement; they found the most expansion related to DEF at a molar ratio of 1.1 with a minimum value of 0.8. Different minimum ranges as low as 0.7 have been reported for susceptibility to DEF [18], [49]. Day [46] suggested that to avoid serious expansion, a low SO$_3$/Al$_2$O$_3$ mass ratio and a low alkali content are needed.

2.5.5 Pozzolans and SCM Addition in Blended Cements

Ordinary Portland Cement (OPC) and limestone PC have shown to expand more than blended cements with partially replaced SCMs such as fly ash or metakaolin. Normally, OPC produces large quantities of C-S-H which leads to a higher susceptibility to DEF since the C-S-H phase is required to adsorb the sulfate initially for subsequent slow release [32]. The addition of slag and pozzolans can reduce expansion potential in heat-cured concrete but limited research has been done to understand the exact mechanism by which slag and pozzolans suppress expansion [16]. Pozzolans are any reactive aluminosilicate material that can either be found naturally or produced industrially as a byproduct. The amorphous silica found in pozzolans reacts with calcium hydroxide that has formed as a result of cement hydration and forms more calcium silicate hydrate (C-S-H) [3]. This is called a pozzolanic reaction and in its simplest form can be presented as in the equation 2.5 [3].
While it is the reactive silica in pozzolans that primarily reacts with hydrated cement, some pozzolans contain significant amounts of reactive alumina that create a different reaction which produces calcium aluminate hydrates (C-A-H) in the following reaction [3]. This reaction is very similar to the pozzolanic reaction above whereas instead of silica, alumina reacts (Equation 2.6).

\[
\text{CH} + \text{A} + \text{H} \rightarrow \text{C-A-H} \quad \text{Equation 2.6}
\]

Some researchers find that the ability of a pozzolan to prevent expansion in heat cured cements is dependent on the amount of reactive alumina [16], [18], [34], [44]. One explanation is that the pozzolans such as metakaolin or fly ash produce a denser pore structure which is less permeable to alkali leaching. This reduces the potential for ettringite to form thus reducing the potential for expansion from DEF [16], [18], [21], [32].

Incorporating supplementary cementitious materials such as pozzolans and slag influence the phases formed in cementitious systems when heat cured at high temperatures exceeding 70°C. It is suggested that higher amounts of reactive alumina, which in turn lowers the \(\text{SO}_3/\text{Al}_2\text{O}_3\) ratio, can lead to more monosulfoaluminate (AFm) formation during heat curing or that it can favor the transformation of ettringite into monosulfoaluminate [15]. The literature suggests that during heat curing at temperatures exceeding 70°C, monosulfoaluminate is the favored more-stable phase over ettringite, thus it is detected after heat curing [15]. Once the specimen has been stored at normal ambient temperature, ettringite is more stable than monosulfoaluminate and becomes the favored calcium sulfoaluminate phase [15], [28], [50]. However, if there is sufficient alumina available in
the system after heat curing while the sulfate is desorbed from the C-S-H phase during storage in ambient temperature, the monosulfate is not believed to convert to ettringite but ettringite is still forms likely from stochiometric amounts of alumina and sulfate. Subsequently, Ramlochan [15] suggests that expansion due to DEF is only expected in cementitious systems where sufficient monosulfoaluminate forms during the heat curing process from the decomposition of ettringite.

Some of the most common pozzolans used in the cement industry include fly ash, silica fume, and metakaolin. Fly ash (class F) and metakaolin have been well documented to reduce the potential for DEF even at 20% replacement [15], [16], [31], [32], [51]. According to Silva et al. [21], silica fume is able to prevent expansion with replacement levels of 10% or more. However, Ramlochan et al. [16] concluded that it is not very effective at preventing expansion; they observed expansion in Type III cements with 15% silica fume replacement after more than two-and-a-half years. Ramlochan et al. [16] concluded that silica fume does not prevent expansion but overly prolongs the onset of expansion if the replacement level is less than 20%. These SCMs are able to reduce the potential for expansion since they produce a denser less permeable microstructure via pozzolanic reactions producing more C-S-H and consuming excess sulfate [15]. The incorporation of pozzolans with reactive alumina decreases the SO$_3$/Al$_2$O$_3$ ratio which tends to not favor expansion. A lower SO$_3$/Al$_2$O$_3$ molar ratio due to an increase in available reactive alumina reduces the potential for ettringite to reform since there is insufficient sulfate in stochiometric amounts to react for ettringite formation [16]. Taylor et al. [19] suggests that if there is too much Al$_2$O$_3$ then monosulfate instead of ettringite forms.
2.6 Role of Hydrogarnet in DEF

Yang and Sharp [52] found that when the curing temperature exceeds 85°C, hydrogarnet becomes the only stable alumina-bearing phase in heat cured portland cements. They concluded that when ettringite and monosulfate decompose at high temperature, a significant portion of aluminate derived from the decomposition becomes a part of the formation of hydrogarnet. Subsequently, an increase in inert hydrogarnet also increases the potential for ettringite formation after heat curing since it raises the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio in favor of ettringite formation. Their observations suggest that hydrogarnet does not react with sulfate during hydration at ambient or elevated temperatures.

2.7 Mix Design Parameters Affecting DEF

Water-to-cement (w/c) ratio can influence the potential of DEF in a given cement mix. As stated in the literature [15], [30], higher w/c ratios accelerates the onset of expansion due to DEF. This may be due to the fact that higher w/c ratios lead to less dense microstructures thus increasing the permeability of the mix, allowing easier ion exchange and moisture penetration for the formation of DEF.

The aggregate type and grading also can influence the potential for DEF in a given concrete mix design. Fu [31], [48] found two correlations between fine aggregate, i.e. sand, and DEF: (1) finer sands lead to more expansion and (2) coarser sands develop expansion slower. Finer sands increase expansion possibly by influencing the formation of microcracks where ettringite can form during the pre-heat curing stage [48]. Through his experimental work, Fu [31], [48] found that coarse 20/30 standard quartz sand also leads to more expansion than standard graded sand but can develop expansion slower than fine sands [48]. Reactive aggregates can lead to phenomena such
as alkali silica reaction (ASR) which can trigger expansion caused by DEF [15], [18], [39]. Aggregates contaminated with reactive silica or contaminated with gypsum (an extra source of sulfate) can create an expansive reaction leading to ASR. This leads to more microcracks in the microstructure which can promote DEF to occur. Limestone coarse aggregate were found to reduce and/or delay the onset of expansion compared to quartz coarse aggregates possibly to the higher susceptibility to ASR [19], [31], [49], [53]. In Taylor et al.’s [19] work, they noted that ASR and DEF tend to occur together but ASR usually begins before the onset of DEF. They also noted during the heat curing treatment, ASR can create damage which eventually becomes aggravated by the effects of DEF. When studying DEF, it is crucial to eliminate the possibility of ASR by using non-contaminated aggregate.

2.8 Effect of Slag Addition on DEF

Slag has more controversy around its varied chemistry and replacement levels. Ramlochan had found that 50% replacement of slag is enough to prevent expansion [38] while 25% replacement may only reduce the ultimate expansion and/or delay the onset of expansion but not prevent it [15]. Several researchers have been searching for the critical value of slag replacement that would prevent DEF in heat cured concrete elements. Silva et al. [21] found 40 wt% slag replacement to be sufficient to prevent expansion from DEF; while, Ramlochan [15] found as low as 35 wt% slag replacement is sufficient. The American Concrete Institute (ACI) under 201.2R-16 section 6.2.2 recommends that at a minimum 35% replacement of slag compliant with ASTM C989 is sufficient to prevent expansion when concrete temperature is between 70°C and 85°C [2]. Their recommendation comes from the work of Ramlochan [15] who concluded that slag conforming to ASTM C989 should be used at replacement levels of 35% or higher for cements.
with high sulfate and/or alkali contents. He concluded that the expansion caused by DEF is not
directly a result from the reformation of ettringite in gaps or voids but from the transformation of
monosulfoaluminate (AFm) that is finely intermixed with the outer C-S-H phase into ettringite.
During the reformation of ettringite after heat treatment, slag is preferential to monosulfate as a
source of aluminate and slag can accomplish this without expansion occurring.

The reactive alumina present in slags can help to prevent expansion by moving the
SO$_3$/Al$_2$O$_3$ ratio away from the critical pessimum; however, some of the alumina from slags may
be present in unreactive phases such as hydrogarnets and stratlingite and may not form ettringite
[16]. Slag incorporation can also reduce expansion by consuming portlandite during hydration
resulting in denser less-permeable pore structure, which inhibits the reformation of ettringite in
later ages. It can also reduce the pH of the pore solution and lower its sulfate concentrations
resulting in less sulfate uptake by the C-S-H phase during heat curing [12], [16], [42]. The less
sulfate that becomes intermixed with the C-S-H phase, the less monosulfate will be able to
transform into ettringite in the outer C-S-H phase resulting in expansion.

2.9 Effect of Limestone Addition on DEF

Limestone addition has been reported to delay and reduce the potential for expansion
cau## caused by DEF [22]; it can even prevent expansion in ternary cements at sufficient replacement
levels. Deboucha et al. [22] found that a ternary blend of cement closest to Type III containing
40% slag and 5% limestone filler was sufficient to prevent expansion over more than 750 days.
With the same limestone filler content (5%) and less slag replacement (10% and 20% slag)
expansion was either reduced or delayed [22]. They found a clear relationship between limestone
and slag replacement in ternary blended cements. Deboucha et al. concluded that calcite from
limestone filler and aluminate phases from slag produce hemicarboaluminate and monocarboaluminate phases. These reduce the potential of expansion by (1) stabilizing ettringite during high-temperature heat curing, (2) by decreasing porosity of the binder, and (3) by decreasing the total heat released due to dilution effects and the different hydration kinetics of the slag [22].

Asamato et al. [51] studied the effects of carbonate ions from limestone in DEF. They found that 15 wt% replacement of limestone powder in Japanese high early strength cement (3.2 wt% SO3) can actually result in expansion due to DEF when subjected to high temperature heat curing. Their cementitious system has a total sulfate content of 6.2 wt% by adding 3 wt% more sulfates in the form of potassium sulfate to accelerate DEF in their study. Another study reported that increasing the weight replacement of limestone powder in heat cured cementitious systems results increased expansion due to DEF [21]. Without slag as a source of alumina, the carbonate ions may react with monosulfate to form hemicarboaluminate or monocarboaluminate, releasing sulfate ions into the pore solution; these excess sulfate ions can then react with monosulfate in the outer C-S-H product resulting in expansion due to DEF [51].

2.10 Major Findings and Gaps in the Literature

From the literature, one of the most important factors that creates the existence of DEF as a durability concern is the curing temperature during heat treatment of concrete. When the temperature exceeds 70°C, ettringite begins to decompose into monosulfate and the released sulfate ions become adsorbed into the outer C-S-H matrix [7], [15], [19], [33], [36], [42], [50]. If this can be avoided, expansion from DEF should not occur. The C₃A, sulfate, and alkali content of cement seems to predominantly affect the potential for ettringite formation leading to expansion
from DEF [7], [15], [18]–[20], [39], [43], [44]. It should be noted that ettringite formation after heat curing does not necessarily mean expansion occurs [15], [52].

SCMs are capable of mitigating or eliminating expansion related to DEF in the appropriate replacement levels. Thus far, slag has been shown to prevent expansion from occurring with a minimum of 35-40% replacement by weight [15], [21]. Many studies have focused mainly on high early strength cements similar to ASTM Type III cements in their research since this cement chemistry is most susceptible to DEF [15], [16], [21], [22], [30], [48]. Some researchers have focused on studying the variability of cement chemistry by incorporating a variety of cements or clinker types similar to Type I, Type II and Type III in their work [30], [39], [48]. The few studies that have studied the incorporation of slag to mitigate DEF have used relatively low alumina slags (<10%) [15], [16], [21], [22]. These studies focused mainly on replacement level thresholds and not on the variability of slag chemistry. Thus, this research aims to fill in the gap on the effect of variable slag chemistry especially alumina content on expansion due to DEF. It also aims to shed light on the minimum replacement threshold to prevent expansion from DEF set by the American Concrete Institute.
Chapter 3  Methodology

This chapter of the thesis presents the materials and their composition used in this study as well as the methods and tests performed.

3.1 Cement and Slag Composition

Six cements and six slags were used in this study. These cements include, ASTM C150 [4] Type I (cement BB), Type I with high alkali content (HA) (cement C), Type II (MH) (cement TTC), Type II (MH(HA)) (cement Z) and ASTM C595 [54] Type IL with approximately 10% (cement TIL) and 14% (cement THIL) limestone content. The six slags used were named according to their alumina contents from 8% to 17% (S8, S10F, S10C, S14A, S14B, and S17). S10C and S10F have approximately similar alumina contents, but S10F was a finer grind. Slags 14A and 14B, were received from different slag suppliers and have approximately similar chemical composition, but a higher gypsum and limestone contents in slag S14B. Table 3.1 through Table 3.4 show the oxide chemical composition, specific gravity (SG) and the Blaine fineness (BF) of the cements and slags used. The oxide chemical composition was obtained using X-ray fluorescence spectroscopy (XRF) analysis according to ASTM C114 [55]. Blaine fineness (BF) and specific gravity (SG) were determined according to ASTM C204 [56] and ASTM C188 [57], respectively.
Table 3.1 Cement Chemical and Physical Characteristics

<table>
<thead>
<tr>
<th>Analyte</th>
<th>BB</th>
<th>C</th>
<th>TIL</th>
<th>THIL</th>
<th>TTC</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>19.53</td>
<td>19.00</td>
<td>19.16</td>
<td>19.14</td>
<td>20.21</td>
<td>19.41</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>5.51</td>
<td>5.90</td>
<td>4.61</td>
<td>4.52</td>
<td>5.00</td>
<td>4.64</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>1.79</td>
<td>2.80</td>
<td>3.74</td>
<td>3.54</td>
<td>3.78</td>
<td>3.06</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>64.27</td>
<td>60.80</td>
<td>62.40</td>
<td>62.11</td>
<td>63.60</td>
<td>62.77</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>1.05</td>
<td>2.50</td>
<td>1.12</td>
<td>1.08</td>
<td>0.32</td>
<td>3.01</td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>3.93</td>
<td>4.00</td>
<td>2.47</td>
<td>2.44</td>
<td>2.55</td>
<td>3.25</td>
</tr>
<tr>
<td>Na₂O (%)</td>
<td>0.11</td>
<td>0.32</td>
<td>0.17</td>
<td>0.17</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Na₂O&lt;sub&gt;eq&lt;/sub&gt; (%)</td>
<td>0.38</td>
<td>1.05</td>
<td>0.38</td>
<td>0.36</td>
<td>0.22</td>
<td>0.65</td>
</tr>
<tr>
<td>K₂O (%)</td>
<td>0.41</td>
<td>1.10</td>
<td>0.32</td>
<td>0.29</td>
<td>0.32</td>
<td>0.95</td>
</tr>
<tr>
<td>Total</td>
<td>99.83</td>
<td>99.82</td>
<td>99.98</td>
<td>99.91</td>
<td>99.40</td>
<td>100.21</td>
</tr>
<tr>
<td>SG</td>
<td>3.04</td>
<td>3.15</td>
<td>3.11</td>
<td>3.13</td>
<td>3.12</td>
<td>3.08</td>
</tr>
<tr>
<td>Blaine Fineness (m&lt;sup&gt;2&lt;/sup&gt;/kg)</td>
<td>356</td>
<td>436</td>
<td>483</td>
<td>488</td>
<td>428</td>
<td>412</td>
</tr>
<tr>
<td>Mean Particle Size (μm)</td>
<td>14.03</td>
<td>16.5</td>
<td>10.8</td>
<td>12.75</td>
<td>12.29</td>
<td>13.46</td>
</tr>
</tbody>
</table>

Table 3.2 Ground Granulated Blast Furnace Slag Chemical and Physical Characteristics

<table>
<thead>
<tr>
<th>Analyte</th>
<th>S8</th>
<th>S10C</th>
<th>S10F</th>
<th>S14A</th>
<th>S14B</th>
<th>S17</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>38.44</td>
<td>36.34</td>
<td>36.67</td>
<td>34.39</td>
<td>33.39</td>
<td>30.47</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>7.82</td>
<td>10.69</td>
<td>10.09</td>
<td>13.95</td>
<td>13.80</td>
<td>17.07</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>0.47</td>
<td>0.79</td>
<td>1.06</td>
<td>0.54</td>
<td>0.84</td>
<td>0.46</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>39.18</td>
<td>39.23</td>
<td>38.33</td>
<td>42.15</td>
<td>42.00</td>
<td>35.49</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>10.71</td>
<td>10.70</td>
<td>10.81</td>
<td>5.14</td>
<td>5.60</td>
<td>10.96</td>
</tr>
<tr>
<td>Total SO₃ (%)</td>
<td>2.18</td>
<td>2.03</td>
<td>2.17</td>
<td>2.96</td>
<td>3.10</td>
<td>2.87</td>
</tr>
<tr>
<td>Sulfide, Sulfur (%)</td>
<td>0.59</td>
<td>0.86</td>
<td>0.79</td>
<td>0.54</td>
<td>0.60</td>
<td>0.59</td>
</tr>
<tr>
<td>SO₃ as sulfate (%)</td>
<td>0.18</td>
<td>0.05</td>
<td>0.11</td>
<td>1.03</td>
<td>1.22</td>
<td>1.39</td>
</tr>
<tr>
<td>Na₂O (%)</td>
<td>0.28</td>
<td>0.26</td>
<td>0.30</td>
<td>0.24</td>
<td>0.23</td>
<td>0.48</td>
</tr>
<tr>
<td>Na₂O&lt;sub&gt;eq&lt;/sub&gt; (%)</td>
<td>0.56</td>
<td>0.40</td>
<td>0.52</td>
<td>0.42</td>
<td>0.41</td>
<td>0.68</td>
</tr>
<tr>
<td>K₂O (%)</td>
<td>0.42</td>
<td>0.22</td>
<td>0.33</td>
<td>0.29</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>Total</td>
<td>99.73</td>
<td>99.84</td>
<td>100.21</td>
<td>99.89</td>
<td>100.17</td>
<td>100.39</td>
</tr>
<tr>
<td>SG</td>
<td>2.90</td>
<td>2.91</td>
<td>2.90</td>
<td>2.90</td>
<td>2.89</td>
<td>2.92</td>
</tr>
<tr>
<td>Blaine Fineness (m&lt;sup&gt;2&lt;/sup&gt;/kg)</td>
<td>617</td>
<td>485</td>
<td>600</td>
<td>551</td>
<td>553</td>
<td>510</td>
</tr>
<tr>
<td>Mean Particle Size (μm)</td>
<td>8.28</td>
<td>10.29</td>
<td>9.03</td>
<td>10.97</td>
<td>12.55</td>
<td>9.79</td>
</tr>
</tbody>
</table>

3.2 Mortar Bar Composition and Preparation

The cements and slags were blended to prepare mortar specimens of 500 g of anhydrous cementitious material. A water-to-cement ratio (w/cm) of 0.485 and a sand-to-cementitious ratio...
of 2.75 by weight were used as recommended in ASTM C109 [58]. 20/30 graded sand was used as the fine aggregate since it was found to be most susceptible to internal sulfate attack [31]. Since this study focuses on the effect of slag replacement on cementitious systems, the w/c and sand-to-cementitious ratio were kept constant for all mixes. Mixing procedures for mixing mortar specimens outlined in section 8 of ASTM C305 [59] were followed. These mortar specimens were casted into four 1×1×11¼ in (25×25×285 mm) prisms following the procedures outlined in section 6 of ASTM C490 [25].

Table 3.3 Mineralogical Cement Composition Determined by QXRD

<table>
<thead>
<tr>
<th>Analyte</th>
<th>BB</th>
<th>C</th>
<th>TIL</th>
<th>THIL</th>
<th>Z</th>
<th>TTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>49.1</td>
<td>49.5</td>
<td>44.5</td>
<td>40.3</td>
<td>54.0</td>
<td>49.6</td>
</tr>
<tr>
<td>Belite</td>
<td>15.6</td>
<td>13.7</td>
<td>16.1</td>
<td>16.9</td>
<td>7.2</td>
<td>19.1</td>
</tr>
<tr>
<td>Aluminate</td>
<td>8.6</td>
<td>8.3</td>
<td>2.3</td>
<td>2.9</td>
<td>5.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Ferrite</td>
<td>4.2</td>
<td>7.5</td>
<td>11.8</td>
<td>10.8</td>
<td>7.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Gypsum</td>
<td>5.7</td>
<td>3.8</td>
<td>1.5</td>
<td>1.5</td>
<td>0.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>0.2</td>
<td>1.7</td>
<td>1.4</td>
<td>2</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.2</td>
<td>1.8</td>
<td>8.8</td>
<td>11.4</td>
<td>3.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Amorphous/Unidentified</td>
<td>14.2</td>
<td>9.4</td>
<td>12.5</td>
<td>12.8</td>
<td>15.7</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table 3.4 Mineralogical Slag Composition Determined by QXRD

<table>
<thead>
<tr>
<th>Analyte</th>
<th>S8</th>
<th>S10</th>
<th>S10F</th>
<th>S14A</th>
<th>S14B</th>
<th>S17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>1.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Melilite</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Merwinite</td>
<td>-</td>
<td>1.1</td>
<td>1.1</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Quartz</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amorphous/Unidentified</td>
<td>98.7</td>
<td>98.3</td>
<td>98.4</td>
<td>98.5</td>
<td>96.1</td>
<td>95.7</td>
</tr>
</tbody>
</table>

In general, mortar bars were prepared with a cement replacement of 60% by weight of slag. A separate set of bars were made with only 35% replacement by weight to assess the adequacy of
recommendation from ACI 201.2R-16, which indicates that 35% or more slag replacement can be used to minimize the risk of DEF with any ASTM C150/C150M [4] Portland cement exposed to temperatures between 75°C to 85°C [2]. Additionally, another group of bars were prepared to investigate the effect of sulfate-optimized blended mixtures on expansion caused by DEF. A reagent grade calcium sulfate hemihydrate was selected as the additional sulfate source. Sulfate optimization was performed using heat of hydration measurements according to ASTM C563 [24], with the exception of hemihydrate addition as a partial replacement of cement fraction. Instead, hemihydrate was added as a partial replacement of the slag portion because nowadays cements are already sulfated by the producers and slag producers often add gypsum to high-alumina slags during the grinding process. Table 3.5 shows the optimum sulfate contents of the blended mixtures studied.

Table 3.5 Optimized Sulfate Content for Blended Mixtures Studied

<table>
<thead>
<tr>
<th>Cement</th>
<th>Slag</th>
<th>Optimum SO$_3$% in Total System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As Received</td>
</tr>
<tr>
<td>BB</td>
<td>S8</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>S10C</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>S10F</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td>S14B</td>
<td>2.30</td>
</tr>
<tr>
<td>C</td>
<td>S10F</td>
<td>1.67</td>
</tr>
<tr>
<td>TIL</td>
<td>S10F</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>S14B</td>
<td>1.72</td>
</tr>
<tr>
<td>Z</td>
<td>S10F</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>S14B</td>
<td>2.13</td>
</tr>
</tbody>
</table>

3.3 Heat Curing Regime

Fu [31] established a heat curing regime to accelerate DEF phenomenon, which included a high temperature moist cycle at 95°C, 100% relative humidity, and a drying cycle. This curing regime was adopted here but modified to simulate the heat evolution experienced from field mass
concrete slabs in Florida [60]. Immediately after casting, the mortar bars were placed in curing containers and were subjected to the heat curing regime shown in Figure 3.1, in an environmental chamber. The specimens were precured at 23°C for 4 hours (HCR1). Then the temperature was raised to 95°C at a rate of 20°C/hr (HCR2) and it was maintained at 95 °C for 36 hours (HCR3). Lastly, the specimens were cooled at a rate of 20°C/hr until reaching 23°C (HCR4). Throughout the cycle, the environmental chamber was maintained at 100% relative humidity.

![Figure 3.1 Modified Fu heat curing regime for internal sulfate attack of mortar specimens](image)

At the point HCR4 (end of the heating curing regime), the mortar prisms were removed from the oven and initial length readings were taken with a Humboldt© length comparator compliant to ASTM C490 [25]. After the initial readings, the mortar prisms were stored in saturated lime water at 23°C in compliance with ASTM C511 [61]. The mortar bars were measured for expansion at ages of 1, 7, 21, and 28 days of storage in saturated lime water and then measured
every month thereafter. For calculating expansion, the 1-day measurement was taken as the initial reading.

### 3.4 X-Ray Diffraction Analysis

In conjunction with the mortar specimens, 100g paste samples of the same composition and w/cm ratio as the mortars were made and subjected to the same heat curing regime. In total, 69 different mixtures were prepared. The paste samples were mixed with a DeWalt™ DC759 cordless power drill for 1 minute before casting. These paste samples were used in quantitative x-ray diffraction (QXRD) analysis to identify and quantify the phases present in the cementitious system at each point in the heat curing regime (HCR1-HCR4). The scans were performed in a Phillips X’Pert PW3040 Pro diffractometer with a X’Celerator Scientific detector and CuK$_{\alpha}$ X-ray source. Tension and current were set to 45 kV and 40 mA, respectively. Scans were conducted in the angular range of 7–70° 2θ with a step size of 0.0167° 2θ. The paste samples at corresponding curing ages (HCR1-HCR4) were crushed and ground with a mortar and pestle and then were loaded into the diffractometer. Further, QXRD analysis was also conducted at later ages (at HCR5-HCR7) after storage in saturated lime water to examine phase assemblage evolution. These samples were also crushed with a mortar and pestle then were sieved through a 45 μm sieve to obtain the passing fraction for the analysis. Once the samples were loaded into the diffractometer sample holder, using a back-loading technique to minimize preferred orientation, they were placed on a spinner stage spinning at 30 rpm to improve the counting statistics [62]. Phase quantification was obtained with the Rietveld refinement functionality of the Panalytical HighScore Plus 4.5 software.
Chapter 4  
Results and Discussion

4.1 DEF Index

Several researchers have tried to characterize the properties of cements and clinkers that lead to expansion [34], [44]. They have attempted to correlate the degree of expansion using a numerically simple formula related to cement characteristics. Zhang et al [34] developed his DEF index that can give useful insight for predicting expansion of cements. Their index (Equation 4.1) takes into account three important parameters that influence expansion the most: sulfate content, aluminate (C₃A) content, and the alkali content.

$$\text{DEF Index [34]} = \left( \frac{\text{SO}_3}{\text{Al}_2\text{O}_3} \right)_M \times \frac{\text{(SO}_3^+ \text{C}_3\text{A})_W}{10} \times \sqrt{\text{Na}_2\text{O}_{eq}}$$  
Equation 4.1

The M subscript signifies the molar ratio (weight ratio_A/B × molar mass_B/molar mass_A) of the sulfate to aluminate content in the cement. The W subscript signifies the weight percentage of sulfate (determined by QXRD) and tricalcium aluminate (determined by Bogue calculations). In their study, they found the critical DEF index threshold value to be 1.1 where cements with values below the 1.1 threshold did not show expansion [34]. Table 4.1 summarizes the DEF index of each cement studied here. The shortcomings of using this index to predict expansion is that it does not account for the exact curing conditions experienced by concrete such as temperature and soaking time. It also cannot account for SCMs in blended concrete mixtures. Additionally, the use of tricalcium aluminate, based on Bogue potential compound composition formula, might not be
accurate in predicting the actual tricalcium aluminate content in portland cement. It might therefore be an inaccurate measure of predicting expansion.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>BB</th>
<th>C</th>
<th>TIL</th>
<th>THIL</th>
<th>Z</th>
<th>TTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>5.51</td>
<td>5.90</td>
<td>4.61</td>
<td>4.52</td>
<td>4.64</td>
<td>5.00</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.93</td>
<td>4.00</td>
<td>2.47</td>
<td>2.44</td>
<td>3.25</td>
<td>2.55</td>
</tr>
<tr>
<td>SO₃/Al₂O₃</td>
<td>0.71</td>
<td>0.68</td>
<td>0.54</td>
<td>0.54</td>
<td>0.70</td>
<td>0.65</td>
</tr>
<tr>
<td>Na₂Oeq</td>
<td>0.38</td>
<td>1.05</td>
<td>0.38</td>
<td>0.36</td>
<td>0.65</td>
<td>0.22</td>
</tr>
<tr>
<td>C₃A (Bogue)</td>
<td>11.58</td>
<td>10.90</td>
<td>5.89</td>
<td>5.99</td>
<td>7.12</td>
<td>6.86</td>
</tr>
<tr>
<td>BF [m²/kg]</td>
<td>356</td>
<td>436</td>
<td>483</td>
<td>488</td>
<td>412</td>
<td>428</td>
</tr>
<tr>
<td>DEF Index (Zhang [34])</td>
<td>0.87</td>
<td>1.32</td>
<td>0.35</td>
<td>0.35</td>
<td>0.75</td>
<td>1.09</td>
</tr>
</tbody>
</table>

4.2 Expansion after Heat Treatment

Expansion data for control mixtures, slag blended cementitious mixtures, and sulfate-optimized slag blended mixtures will be presented in the following sections. A total of 68 mixtures were studied in this research.

4.2.1 Control Mixes

Figure 4.1 shows the expansion of the control mixes with plain cements, for more than a year of storage in saturated lime water at 23°C, following heat curing. All the cement types studied here expanded significantly. Implementing Zhang’s DEF index, only cements C and TTC should experience expansion but clearly all of the cements expanded after heat curing with Type I cements, BB and C, experiencing the highest level of expansion, well over 1.0%, in the first 120 days of storage. They also showed the highest rate of expansion among plain mixtures studied here. Both cements contained the highest SO₃ content (~4.0%) and C₃A content (11.58% and 10.90% respectively) and had the highest SO₃/Al₂O₃ ratio of approximately 0.7 (weight basis).
The high C₃A and SO₃ contents for cements BB and C would enhance the potential for ettringite formation during early stages of hydration [2], [15], [44]. Heat treatment is expected to decompose primary ettringite with subsequent reformation at ambient conditions. Confirmation of such a trend would be revealed through phase assemblage studies discussed later. This would explain why they had such a high rate of expansion and ultimate expansion in comparison to the other 4 cements.

Cement C and BB have similar alite content (49.1% and 49.5% respectively) and aluminate content (8.6% and 8.3%, respectively) based on QXRD analysis; however, cement C expanded initially at a higher rate suggesting that ettringite reformation is highly favorable in this cement likely triggered by its high alkali content (1.05% Na₂Oₑq). A high alkali environment favors sulfate adsorption into the C-S-H phase at higher temperatures; thus, favoring ettringite reformation after heat treatment [42]. Their expansion appears to have stabilized at 1.5% and 1.3% for cement BB and cement C, respectively.

![Figure 4.1 Expansion of control bars subjected to heat curing](image-url)
The second group of cements, cements Z, TIL and THIL, showed an initial lower rate of expansion, with limestone cements showing stabilization in expansion at an age of 1 year. Cement Z continues to expand at a higher rate than any other cement in storage, increasing in expansion even after a year. Cement Z has an ultimate expansion appreciably higher than cements TIL and THIL, which contained approximately 10% and 14% limestone contents, respectively. TIL and THIL have similar levels of sulfate (~2.4%) while Z has more sulfate (3.3%). Cement Z has higher aluminate content than cements TIL and THIL in addition to its higher alkali content. Additionally, cement Z had the highest alite content (54.0%) amongst all cements studied here. According to Zhang et al [34], high sulfates, aluminates, and alkali content enhances the potential for DEF occurrence. Kelham [44] indicated that alite content in cement influences the stability of ettringite during high temperature curing by the amount of C-S-H that rapidly forms during hydration. The C-S-H phase adsorbs the sulfate and some of the aluminate is substituted in this phase which acts to destabilize the ettringite at high temperatures [44].

Although cements TIL and THIL have more C₄AF (11.38% and 10.77%, respectively) than cements Z, BB, or C, C₄AF is able to contribute to ettringite formation but its relatively low reactivity does not seem to play a significant role in expansion from DEF. Another reason why TIL and THIL may not have expanded as much as cement Z, would be due to the presence of limestone in the TIL and THIL cements. The higher limestone contents would help to form a denser paste structure in the hydrated cement thus hindering the transportation of ions for the reformation of ettringite after heat treatment [21]. Their limestone content also contributes to clinker dilution during hydration, thus leading to less expansion. The presence of calcite in these cements reduced the total expansion but not the onset of expansion. Cement THIL contains more limestone than cement TIL thus cement THIL displayed less expansion (0.63%) than cement TIL.
(0.73%). These results suggest that Type I cements are more vulnerable to DEF than Type II (MH) and Type IL cements. The presence of calcite is also known to affect phase assemblage in the hydrated cementitious system. QXRD results discussed later will further explain the observed expansion trends in the control mixtures.

4.2.2 As-Received Mixes with 60% Replacement

Figure 4.2 through Figure 4.7 show the expansion of all as-received mixes studied here with 60% slag replacement and organized by the cement used. The expansion data shows that 60% cement replacement with any of the slags was enough to prevent expansion even after one year. None of the mixes that incorporated 60% slag exceeded expansion of more than 0.01% at an age of 1 year.

The first observation from the expansion data is that the use of 60% slag for any cement-slag combination was enough to prevent expansion even with the high temperature heat curing at 95°C and a soaking time of 36 hours. Even the highly sulfated cementitious mixtures, optimized for sulfate content, did not exhibit any signs of deleterious expansion for the testing age reported here. This confirms previous observations made by Ramlochan et al. and Silva et al. [16], [21], where 50% and 40% replacement were sufficient replacement levels to prevent expansion in heat cured mortar. Silva et al. [21] suggested that the slag’s ability to consume calcium hydroxide during hydration via pozzolanic reactions is how it inhibits expansion. Ramlochan et al. [16] suggested that it is the slag’s reactive alumina content which helps inhibit expansion by lowering the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio below the pessimum.

The results presented here provide proof that for structures incorporating Type I, Type I (HA), Type IL, and Type II (MH) cements can be protected from DEF phenomenon by using slag
at 60% replacement of the cement weight. For other concrete elements, where slag replacement level is lower, testing is required to ensure that lower replacement levels would still prevent DEF, especially if the temperature of the concrete element is expected to be between 70°C and 85°C during curing or service life [2].

![Figure 4.2 Expansion of as-received cement BB mixes with 60% slag replacement](image)

**Figure 4.2 Expansion of as-received cement BB mixes with 60% slag replacement**

![Figure 4.3 Expansion of as-received cement C mixes with 60% slag replacement](image)

**Figure 4.3 Expansion of as-received cement C mixes with 60% slag replacement**
Figure 4.4 Expansion of as-received cement TIL mixes with 60% slag replacement

Figure 4.5 Expansion of as-received cement THIL mixes with 60% slag replacement
Figure 4.6 Expansion of as-received cement TTC mixes with 60% slag replacement

Figure 4.7 Expansion of as-received cement Z mixes with 60% slag replacement
4.2.3 As-Received Mixes with 35% Replacement

Since cement C was one of the cements most susceptible to expansion, attributed to its high alkali and C₃A content, it was chosen to test the adequacy of ACI’s 201.2R-16 [2] recommendation of at least 35% slag replacement to prevent DEF in concrete experiencing high temperatures at any time during its life. Figure 4.8 shows the current expansion of as-received mixes made with cement C and 35% slag replacement. With such a low slag replacement, cement C showed appreciable expansion with slags S17 and S14B after about 2 months in storage. These slags were able to delay the onset of expansion and significantly reduce the ultimate expansion; nonetheless, they could not prevent expansion in cement C blends after heat curing at high temperatures.

![Figure 4.8 Expansion of as-received cement C mixes with 35% slag replacement](image)

Slag 17 and slag 14B started expansion in less than 1 month in storage, similar to the control bars of cement C. Out of all the slags used in this study, S17 and S14B have the highest sulfate
contents at 1.39% and 1.22% respectively. S17 also has the highest alumina content among all slags (17.07%) followed by S14B (13.08%). These results indicate that for slags of higher alumina and sulfate content, using 35% slag replacement level for cements of high sulfate, C₃A, and alkali contents, is insufficient to protect against DEF expansion.

4.2.4 Sulfate-Optimized Slag Blended Mixtures

Figure 4.9 to Figure 4.12 shows the expansion of sulfate optimized mixes compared to their as-received counterparts. Mix IDs that have “L1” and “L2” signify that those mixes have an optimized sulfate content based on one- and two-day calorimetry studies, respectively. These mix IDs also contain two numbers displayed in parentheses. The first number is the total sulfate content in only the slag (including the hemihydrate addition). The second number is the total sulfate content in the whole system; this number is sum of the total sulfate content from the cement, slag, and hemihydrate. These are the same sulfate contents shown in Table 3.5. The remainder of the expansion charts of the other sulfate optimized mixes can be found in appendix B.

For the limited testing age reported here, none of the sulfate optimized mixes experienced deleterious expansion when slag was used at 60% replacement. However, increasing the sulfate content was accompanied by a slight increase in expansion, with a maximum expansion of 0.02%. This suggests that at 60% slag replacement level, sulfate optimization of slag, conducted to enhance external sulfate durability of the cementitious systems, did not enhance the potential for delayed ettringite formation. However, it is unclear if lower slag replacement levels would produce similar expansion behavior.
Figure 4.9 Expansion of sulfate optimized cement BB mixes with 60% slag 14B

Figure 4.10 Expansion of sulfate optimized cement C mixes with 60% slag 10F
Figure 4.11 Expansion of sulfate optimized cement TIL mixes with 60% slag 10F

Figure 4.12 Expansion of sulfate optimized cement Z mixes with 60% slag 10F
4.3 QXRD Results

The findings from the phase assemblage studies are presented in Figure 4.14 to Figure 4.42. QXRD was conducted during the heat curing cycle as well as at specified ages of extended curing in saturated lime water. The cumulative weight percentages of the phases add up to 100% when the amorphous material is included. However, the amorphous content was omitted from the bar charts for clarity. This section only includes the QXRD results of the mixes which indicated expansion and a few key mixes such as control mixtures and cement-slag blended mixtures at 35% replacement level. Phase quantification for all the mixtures can be found in the appendix C.

4.3.1 Control Mixes

Figure 4.14 to Figure 4.19 show the phase development of all 6 control mixes. Most of the control mixtures followed a similar pattern where before the initiation of soaking at high temperature (HCR1 and HCR2), ettringite forms and it is the dominant sulfoaluminate phase along with trace amounts monosulfate at HCR2 in some mixes. These trace amounts might be a result of some ettringite beginning to decompose past the 70°C threshold. It can be inferred that most of the sulfate from the decomposed ettringite would have been adsorbed in the C-S-H phase as suggested by Ramlochan [15]. After soaking at high temperature (HCR3 and HCR4), the ettringite is completely absent and the only sulfoaluminate phase that persists is monosulfate in addition to the alumina-bearing phase hydrogarnet. After storage for three to four months at ambient temperature, (HCR5 and HCR6), ettringite reformed in all the mixes but along with other alumina-bearing phases such as hydrogarnet, hydrotalcite, hemicarboaluminate, and stratlingite.

It is also worth noting the continuous hydration of the alite and belite phases over time and formation of the amorphous C-S-H phase in the cement matrix, explaining the increase in
amorphous phase content at HCR2 to HCR3 and HCR4. The aluminate phase behaved in a similar fashion as the alite and belite, where it continues hydrating over time to form ettringite, monosulfate, hydrogarnet among other alumina-bearing phases. Another observed trend is that over time more ettringite or alumina-bearing hydrates form as the sulfate ions are desorbed from the C-S-H phase.

The more C₃A there is, the more ettringite forms with the increasing curing temperature (HCR1 and HCR2) as can be seen with cement BB and C. Both cements formed the highest ettringite content prior to the high temperature soaking period. This confirms that the rapid expansion observed for cements BB and C is due to the reformation of substantial amounts of ettringite with time. Figure 4.15 shows that hydrogarnet formed more readily than ettringite as the dominant alumina-bearing phase during storage for cement C. Cements THIL and Z also show a similar pattern where substantially more hydrogarnet forms than ettringite. Cement TTC had monosulfate and hydrogarnet as the main alumina-bearing phases after heat curing. QXRD results confirm the conclusions from Yang and Sharp [52] that with increasing temperature, hydrogarnet is the only stable alumina-bearing phase. It is the only alumina-bearing phase that remains after heat curing (HCR3 and HCR4) with some trace amounts of monosulfate remaining. The findings also indicate excellent correlation between the degree of expansion and the amount of ettringite reforming during storage as Figure 4.13 shows; the more ettringite which forms during storage after heat curing, the more expansion can be expected from the cement used.
Figure 4.13 Correlation of ettringite content and expansion of all control cement mixes at 4 months of age (HCR6)

Control BB

Figure 4.14 Phase assemblage of 100% cement BB
Figure 4.15 Phase assemblage of 100% cement C

Figure 4.16 Phase assemblage for 100% cement TIL
Figure 4.17 Phase assemblage for 100% cement THIL

Figure 4.18 Phase assemblage for 100% cement TTC
4.3.2 As-Received Mixes with 60% Slag Replacement

As noted previously, none of the as-received mixes expanded significantly (>0.1%) at 60% slag replacement. Cement BB was used in combination with every slag except 14A. Slag 14A and 14B have very similar characteristics except that 14B has higher calcite content. Slag 14B also has slightly more sulfate than 14A; they have 1.22% and 1.03% sulfate, respectively. Thus, the effects of slag 14B can be inferred for 14A. Cement BB will be used to discuss the effects of the slag chemical and mineralogical composition on the phase assemblage of the cementitious system at 60% slag replacement.

The results indicate as the slag alumina content increases, ettringite content increases prior to heat curing with the exception of slag 10F (finer grind). The as-received mixes do not form as much ettringite as the sulfate-optimized mixes which will be discussed in the next section.
Additionally, as the slag alumina content increases, more alumina-bearing phases form besides ettringite in the stages after heat curing. The most notable one is hydrogarnet; slag 14B and slag 17 which contain the highest alumina content, formed the most hydrogarnet. A similar pattern is observed with the other cements. Only slag 8 produced insignificant amounts of hydrogarnet, likely because it contains the least amount of alumina in its composition.

The amount of hydrogarnet that forms at the end of heat treatment tends to remain largely unchanged, only slightly increasing in some instances after 4 months in storage. Hydrogarnet and hydrotalcite never form prior to heat curing but only after heat curing when the ettringite had already decomposed. This is likely since hydrogarnet only seems to form at elevated temperatures above 85°C and the alumina from decomposing ettringite is necessary for its formation [52].

**Figure 4.20 Phase assemblage of 60% cement BB and 40% slag 8 as-received**
Figure 4.21 Phase assemblage of 60% cement BB and 40% slag 10C as-received

Figure 4.22 Phase assemblage of 60% cement BB and 40% slag 10F as-received
Figure 4.23 Phase assemblage of 60% cement BB and 40% slag 14B as-received

Figure 4.24 Phase assemblage of 60% cement BB and 40% slag 17 as-received
Slag 17 was chosen to study the effect of cement composition on the slag blended systems. It also has the highest potential of forming ettringite since it has the highest alumina and sulfate content among the slags studied. In general, all the cements produce very similar results with the same slag but vary in the presence and content of certain alumina-bearing phases. Cements TIL and THIL form substantial hemicarboaluminate thus corroborating the findings of Deboucha et al. [22]. The presence of hemicarboaluminate suggests that the alumina from the slag reacted with the calcite from the limestone cements instead of reacting with the sulfate in order to form ettringite. Cements C and Z produced significant amounts of hydrotalcite which can be attributed to their higher magnesium oxide (MgO) contents. Although substantial ettringite formed prior to the soaking period at HCR2, after 4 months in storage (HCR6) only negligible amounts (<1%) of ettringite reformed in all the 60% S17-as-received blended mixtures. Similar trends were observed in the other 60% slag as-received mixes. This low ettringite reformation after 4 months can explain why these mixes did not experience expansion.

![Figure 4.25 Phase assemblage of 60% cement C and 40% slag 17 as-received](image)

<table>
<thead>
<tr>
<th>Cumulative wt%</th>
<th>HCR1</th>
<th>HCR2</th>
<th>HCR4</th>
<th>HCR6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Gypsum
- Hydrotalcite
- Monosulfate
- Ettringite
- Melilite
- Periclase
- Calcite
- Aluminate
- Ferrite
- Alite
- Dolomite
- Portlandite
- Belite

**Figure 4.25 Phase assemblage of 60% cement C and 40% slag 17 as-received**
Figure 4.26 Phase assemblage of 60% cement TIL and 40% slag 17 as-received

Figure 4.27 Phase assemblage of 60% cement THIL and 40% slag 17 as-received
Figure 4.28 Phase assemblage of 60% cement TTC and 40% slag 17 as-received

Figure 4.29 Phase assemblage of 60% cement Z and 40% slag 17 as-received
4.3.3 Sulfate-Optimized Mixes

The results indicate that increasing the sulfate content in the cementitious system increases ettringite content at HCR 2. This can be seen clearly in Figure 4.30 to Figure 4.32 with the BB-60S14B blend. Slag 14B has the second highest alumina content and it formed the most ettringite at its two-day sulfate optimum with cement BB prior to soaking at 95°C. After the high temperature heat curing (HCR3 and HCR4), all the ettringite is completely decomposed into predominantly monosulfate among other aluminate-bearing phases including hydrogarnet, hydrotalcite, hemicarboaluminate, and stratlingite. After months of storage in lime solution, ettringite started to be noticeable again. Similar patterns for ettringite decomposition/reformation were observed for all other sulfate-optimized mixes made with the other cements. A similar trend can be seen with the TIL-60S14B blends from Figure 4.33 to Figure 4.35; however, after 4 months of storage, more ettringite was present in the 2-day optimized blend with about a third of the original amount of ettringite prior to heat curing at HCR2.

![Figure 4.30 Phase assemblage for cement BB with 60% slag 14B as-received](image)

**BB-60S14B-L0**
Figure 4.31 Phase assemblage for cement BB with 60% slag 14B 1-day sulfate optimized mix

Figure 4.32 Phase assemblage for cement BB with 60% slag 14B 2-day sulfate optimized mix
Figure 4.33 Phase assemblage for cement TIL with 60% slag 14B as-received

Figure 4.34 Phase assemblage for cement TIL with 60% slag 14B 1-day sulfate optimized mix
Figure 4.35 Phase assemblage for cement TIL with 60% slag 14B 2-day sulfate optimized mix

Figure 4.36 and Figure 4.37 show only the ettringite which formed in these mixes. They show that as the sulfate content within the mix increases, the amount of ettringite that forms just before soaking at 95°C (HCR1 and HCR2) increases significantly. Subsequently, on heat curing (HCR3 and HCR4), more monosulfate can be observed, including other calcium aluminate hydrates such as hydrogarnet or hydrotalcite. This suggests that during the decomposition of ettringite, the released sulfate becomes adsorbed in the C-S-H matrix while the remaining alumina transforms into monosulfate in this high temperature environment of 95°C. Only at high temperatures can the released alumina form other aluminate hydrates such as hydrogarnet [52]. Figure 4.37 shows ettringite present at HCR4 (end of heat curing) for TIL-60S14B-L2; this is the only mixture out of the 69 mixtures studied here which had ettringite present at HCR4. This is can only be explained due to experimental errors such as inaccurate temperatures during heat curing and/or time of scanning.
The increase in ettringite formation with increased sulfate content is shown for mixes of slag 14B with cements BB, Z, and TIL and the mix of Cement C with slag 10F in Table 4.2 through Table 4.5. These mixes were chosen since they had the largest formation of ettringite with each cement used. All other sulfate optimized slag blended mixtures showed similar trends but with less ettringite formation/reformation. After months in storage (HCR5-HCR7), the amount of monosulfate decreases as ettringite reforms. The release of the sulfate from the C-S-H phase might not react fast enough to actually form purely ettringite from the AFm phase. These tables show...
that as more sulfate is introduced into the system, more ettringite/monosulfate can form whereas less hydrogarnet can form. This might result from an oversaturation of sulfate within the pore solution after heat treatment thus increasing the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio in favor of ettringite formation instead of hydrogarnet or hydrotalcite.

Not all ettringite reformation is associated with expansion. None of the sulfate optimized mixes from Table 4.2 to Table 4.5 showed any signs of expansion after a year. In all these cases, where no expansion was observed, the ettringite that reforms is only a fraction of what initially formed prior to heat curing. This may suggest that the ettringite might be reforming in the pore solution spaces or voids within the paste and not as a result of the transformation of monosulfate into ettringite which is speculated to be the reason for expansion [15].

Table 4.2 Calcium Aluminate Phase Composition Development and Transformation of Cement BB and 60% Slag 14B and its 1 and 2 Day Sulfate Optimized Mixes

<table>
<thead>
<tr>
<th>Heat Curing Point</th>
<th>HCR1</th>
<th>HCR2</th>
<th>HCR4</th>
<th>HCR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate Optimized Level</td>
<td>L0</td>
<td>L1</td>
<td>L2</td>
<td>L0</td>
</tr>
<tr>
<td>Ettringite</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>Monosulfate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Stratlingite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.3 Calcium Aluminate Phase Composition Development and Transformation of Cement C and 60% Slag 10F and its 1 and 2 Day Sulfate Optimized Mixes

<table>
<thead>
<tr>
<th>Heat Curing Point</th>
<th>HCR1</th>
<th>HCR2</th>
<th>HCR4</th>
<th>HCR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate Optimized Level</td>
<td>L0</td>
<td>L1</td>
<td>L2</td>
<td>L0</td>
</tr>
<tr>
<td>Ettringite</td>
<td>1.4</td>
<td>1.7</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Monosulfate-14</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hemicarboaluminate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Stratlingite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4.4 Calcium Aluminate Phase Composition Development and Transformation of Cement Z and 60% Slag 14B and its 1 and 2 Day Sulfate Optimized Mixes

<table>
<thead>
<tr>
<th>Cement Z-Slag 14B</th>
<th>Heat Curing Point</th>
<th>HCR1</th>
<th>HCR2</th>
<th>HCR4</th>
<th>HCR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate Optimized Level</td>
<td>L0</td>
<td>L1</td>
<td>L2</td>
<td>L0</td>
<td>L1</td>
</tr>
<tr>
<td>Ettringite</td>
<td>0.8</td>
<td>1.4</td>
<td>0.6</td>
<td>2.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Monosulfate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5.1</td>
<td>3</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Hemicarboaluminate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Stratlingite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.5 Calcium Aluminate Phase Composition Development and Transformation of Cement TIL and 60% Slag 14B and its 1 and 2 Day Sulfate Optimized Mixes

<table>
<thead>
<tr>
<th>Cement TIL-Slag 14B</th>
<th>Heat Curing Point</th>
<th>HCR1</th>
<th>HCR2</th>
<th>HCR4</th>
<th>HCR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate Optimized Level</td>
<td>L0</td>
<td>L1</td>
<td>L2</td>
<td>L0</td>
<td>L1</td>
</tr>
<tr>
<td>Ettringite</td>
<td>1.3</td>
<td>1.1</td>
<td>0.3</td>
<td>1.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Monosulfate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Hemicarboaluminate</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Stratlingite</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

4.3.4 As-Received Mixes with 35% Slag Replacement

Expansion data for cement C with 35% replacement of slag 17 and slag 14B showed mortar bars of the blended mixtures expanding after about 1-2 months of storage in lime solution. QXRD analyses indicate that after 4 months (HCR6), ettringite reformed in the microstructure, shown in Figure 4.38 to Figure 4.42. Slag 17 and slag 14B have the highest amount of aluminate and sulfate out of all the slags studied.

The higher alkali content of cement C (>1% Na₂Oₗeq) results in a higher pH in the pore solution of the cementitious system. The more basic pH increases the amount of sulfate which can be adsorbed by the C-S-H phase and favors ettringite decomposition [47]. Higher temperature (>70°C) also increases the solubility of ettringite as observed by Zhou and Glasser [36]. These two
effects in tandem release a lot of the sulfate which was once bound in the ettringite. It becomes released into the pore solution and the space once occupied by ettringite. As Divet and Randriambololona [42] found, this extra sulfate is adsorbed by the C-S-H phase especially at higher temperatures, where they become loosely bound in the outer C-S-H phase [15]. These factors would favor ettringite reformation in the months after heat curing.

Slag 17, should in theory, reduce expansion the most since it has the highest amount of aluminate out of all the slags which would move the SO$_3$/Al$_2$O$_3$ ratio away from the pessimum. But in combination with cement C, which is a high alkali cement and has a large magnesium content (2.5% MgO), it becomes susceptible to DEF expansion at insufficient replacement levels. It is possible that the higher levels of MgO in cement C bind substantial amounts of the reactive aluminate into other phases such as hydrotalcite instead of ettringite [16], therefore increasing the SO$_3$/Al$_2$O$_3$ ratio and its susceptibility to expansion by DEF. This can explain why cement C formed more hydrotalcite and hydrogarnet based on the QXRD results. This effect can also be seen with the significant amounts of hydrotalcite forming in C-35S17 and C-35S14B mixes, as shown in Figure 4.40 and Figure 4.41. Slag 17 has almost twice as much magnesia (10.96% MgO) than slag 14B (5.14% MgO). This also suggests that the SO$_3$/Al$_2$O$_3$ ratio by itself is not the only parameter to control expansion. It corroborates Day’s suggestion [46] that a low SO$_3$/Al$_2$O$_3$ ratio in conjunction with a low alkali content is necessary to prevent expansion. This leads to the most prominent observation that 35% slag replacement did not effectively suppress DEF with the high alkali Type I cement (Cement C).

In the case of cement C with 35% replacement of slag 17, a lot more ettringite formed prior to the start of the soaking stage in the heat curing cycle (HCR2); subsequently, significant amounts of monosulfate were present at the end of heat curing (HCR4). The same can be said about 35%
replacement of cement C with slag 14B. This monosulfate formation is shown in Figure 4.39. There must be a slower conversion of monosulfate into ettringite during the moist storage period since it took longer for the mortar bars to start expanding compared to the control cement C specimen.

The ettringite formation in the 35% slag as-received blended mixes are compared in Figure 4.38. In the case of 35% slag 17, it appears that the ettringite reformation has begun to stagnate as its expansion is levelling off, while the monosulfate has continued to decrease. This suggests that the monosulfate is not being converted into ettringite after some time; this is shown in Table 4.6. As Ramlochan speculated it may not be the ettringite itself reforming which causes expansion but the amount of monosulfate which reforms into ettringite might be the cause for expansion [15]. The extent of this monosulfate formation necessary for expansion is still unclear and requires further investigation.

**Ettringite Formation**

![Ettringite Formation](image)

*Figure 4.38 Ettringite content for cement C with 35% slag replacement at different ages*
Figure 4.39 Monosulfate content for cement C with 35% slag replacement at different ages

Figure 4.40 Phase assemblage for cement C with 35% slag 17
Cement C is more susceptible to DEF for its higher SO₃ and aluminate content but most importantly its high alkali content. Some of the key findings regarding cement C with 35% slag replacement are summarized in Table 4.8 and Table 4.9 below. The SO₃/Al₂O₃ ratio for the system decreases with the increasing alumina content of slags which would indicate that the amount of ettringite that can potentially form and thus cause expansion should be less than that of the control cement C mix; however, this is not the case. C-35S17 has the lowest SO₃/Al₂O₃ ratio but expanded the most out of the 35% slag mixtures. These results question whether the SO₃/Al₂O₃ ratio is a reliable parameter for predicting DEF in heat cured blended cementitious mixtures.

C-35S17 formed the most ettringite prior to the soaking period (5.4%) and reformed the most ettringite (3.2%) after 6 months of storage in lime solution (HCR7) compared to the other 35% mixture. It has the highest alkali content (0.92%) and highest sulfate content of the 35% slag
blended mixtures. All of these parameters are the likeliest reasons for explaining the expansion seen in cement C with 35% slag 17 which contradicts the ACI’s recommendation of 35% slag replacement for heat cured concrete.

Table 4.6 Calcium Aluminate Phase Composition Development and Transformation of 65% Cement C with 35% Slag 17

<table>
<thead>
<tr>
<th>Mix</th>
<th>C + 35%S17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
<td>HCR2</td>
</tr>
<tr>
<td>Ettringite</td>
<td>5.4</td>
</tr>
<tr>
<td>Monosulfate-14</td>
<td>0</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>0</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>0</td>
</tr>
<tr>
<td>Hemicarboaluminate</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.7 Calcium Aluminate Phase Composition Development and Transformation of 65% Cement C with 35% Slag 14B

<table>
<thead>
<tr>
<th>Mix</th>
<th>C + 35%S14B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
<td>HCR2</td>
</tr>
<tr>
<td>Ettringite</td>
<td>3.5</td>
</tr>
<tr>
<td>Monosulfate-14</td>
<td>0</td>
</tr>
<tr>
<td>Hydrogarnet</td>
<td>0</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>0</td>
</tr>
<tr>
<td>Hemicarboaluminate</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.8 Chemical Characteristics of Cement C with 35% Slag Replacement Mixes

<table>
<thead>
<tr>
<th>Mix</th>
<th>C</th>
<th>C-35S14B</th>
<th>C-35S17</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃ Content (%)</td>
<td>4.00</td>
<td>3.03</td>
<td>3.09</td>
</tr>
<tr>
<td>Al₂O₃ Content (%)</td>
<td>5.90</td>
<td>8.67</td>
<td>9.81</td>
</tr>
<tr>
<td>SO₃/Al₂O₃ (mass ratio)</td>
<td>0.68</td>
<td>0.35</td>
<td>0.31</td>
</tr>
<tr>
<td>Na₂Oeq Content (%)</td>
<td>1.05</td>
<td>0.83</td>
<td>0.92</td>
</tr>
</tbody>
</table>
Table 4.9 Ettringite Content and Expansion at 180 Days of Storage of Cement C with 35% Slag Replacement Mixes

<table>
<thead>
<tr>
<th>Mix</th>
<th>C</th>
<th>C-35S14B</th>
<th>C-35S17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ettringite Content at HCR2 (%)</td>
<td>3.1</td>
<td>3.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Ettringite Content at HCR6 (%)</td>
<td>3.2</td>
<td>2.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Ettringite Content at HCR7 (%)</td>
<td>-</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Expansion at 180 Days</td>
<td>1.27%</td>
<td>0.07%</td>
<td>0.16%</td>
</tr>
</tbody>
</table>
Chapter 5  Conclusions and Recommendations

In this research, several cement-slag combinations with variable chemical and physical characteristics were investigated to identify their effects on DEF. To this end, length change measurements of heat cured mortar bars were examined along with the phase assemblage studies conducted by QXRD. Based on the investigation, the following conclusions can be made:

I. Plain cement systems expanded substantially, but the amount of expansion depended on the cement composition. Cements with high C$_3$A content (>10%) and high sulfate content (~4%) (Type I) expanded the most (>1.2%). Cements with low C$_3$A content (<6%) and had limestone filler expanded the least (<0.8%) (Type IL). Cement with moderate C$_3$A content (~7%) (Type II) expanded in between these two extremes.

II. For the control mixtures, the degree of expansion was directly correlated to the amount of ettringite formed during storage in lime solution following heat curing cycle.

III. It was found that 60% replacement of cement with slag, regardless of the chemical and physical composition of the latter, was sufficient to prevent expansion caused by DEF.

IV. Even when a blended cement had additional sulfate added to the mix in the form of calcium sulfate hemihydrate in conjunction with 60% slag replacement, expansion did not occur during the limited test period.

V. An increase in sulfate content, within a given cementitious system results in higher ettringite formation before heat treatment. Subsequently, more monosulfate forms after heat treatment. If adequate replacement with slag is done, in this case 60%, this increase in ettringite formation is innocuous.
VI. Slags higher in alkali (>0.5%) and higher in magnesium oxide content (~10%) will form more hydrogarnet and hydrotalcite after heat curing.

VII. The SO$_3$/Al$_2$O$_3$ ratio is insufficient, by itself, to determine if expansion due to DEF will occur.

VIII. 35% slag replacement was not adequate to prevent expansion due to DEF in slag blended cementitious mixtures prepared with Type I (HA) cement and high alumina slags (Al$_2$O$_3$≥14%).

The findings from this research should warrant a revision of the 35% slag replacement recommendation from ACI 201.2R-16 [2]. More consideration should be given to the specific chemistries and variabilities in cements and slags. ACI’s recommendation comes from the work of Ramlochan [15] in which he did not work with high alkali cements or high alumina slags.

More research is needed to determine the critical slag replacement level to eliminate expansion due to DEF when using Type I HA cements and other high alkali cements, such as Type II (HA) cement. Further work should be taken to determine the effect of soaking time and temperature on expansion. At 35% replacement, is it possible for expansion to occur if the soaking time at 95°C is reduced from 36 hours? At 60% replacement, is it possible for expansion to occur if the soaking time is increased above 36 hours? Both effects must be studied for slag blended cementitious mixtures made with modern ASTM C150 cements and currently available slags of higher alumina and sulfate contents. This will ultimately lead to more durable concrete performance.
References


[39] Charlotte Famy, “EXPANSION OF HEAT-CURED MORTARS,” Imperial College of
Science, Technology, and Medicine, 1999.


Appendix A: Copyright Permissions

The license below grants permission for Figure 1.1 in the introduction.

<table>
<thead>
<tr>
<th>License Number</th>
<th>5021050675912</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Mar 02, 2021</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Licensed Content Publication</td>
<td>Cement and Concrete Research</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Diagnosing delayed ettringite formation in concrete structures</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Michael Thomas, Kevin Folliard, Thano Drimalas, Terry Ramlochan</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Jun 1, 2008</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>38</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>6</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>7</td>
</tr>
<tr>
<td>Start Page</td>
<td>841</td>
</tr>
<tr>
<td>End Page</td>
<td>847</td>
</tr>
<tr>
<td>Type of Use</td>
<td>reuse in a thesis/dissertation</td>
</tr>
<tr>
<td>Portion</td>
<td>figures/tables/illustrations</td>
</tr>
<tr>
<td>Number of figure/tables/illustrations</td>
<td>1</td>
</tr>
<tr>
<td>Format</td>
<td>electronic</td>
</tr>
<tr>
<td>Are you the author of this Elsevier article?</td>
<td>No</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Title</td>
<td>The Effect of Cement and Blast Furnace Slag Characteristics on Expansion of Heat-Cured Mortar Specimens</td>
</tr>
<tr>
<td>Institution name</td>
<td>University of South Florida</td>
</tr>
<tr>
<td>Expected presentation date</td>
<td>Mar 2021</td>
</tr>
<tr>
<td>Portions</td>
<td>Figure 1</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Mr. Jair Burgos</td>
</tr>
<tr>
<td></td>
<td>12029 USF Richard Beard Dr</td>
</tr>
</tbody>
</table>
The permission below is for Figure 2.1 in the literature review.

Subject: Re: Copyright Use of Figure
Date: Wednesday, January 13, 2021 at 5:03:12 PM Eastern Standard Time
From: Glasser, Professor Fredrik P.
To: Burgos, Jair
Category: Blue

You have my permission. I wish you and your students success in their studies and research and am pleased to have helped.
My co-author, at that time a student, is now a successful researcher in a full time and permanent post at Universit of London
Fred Glasser

From: Burgos, Jair <jburgos@usf.edu>
Sent: 13 January 2021 20:08
To: Glasser, Professor Fredrik P. <f.p.glasser@abdn.ac.uk>
Subject: Copyright Use of Figure

CAUTION: External email. Ensure this message is from a trusted source before clicking links/attachments. If you are concerned forward this email to spam@abdn.ac.uk

Good afternoon Dr. Glasser,

I am a graduate student in my final year of my Masters in civil engineering at the University of South Florida. I am working on my thesis "The Effect of Cement and Blast Furnace Slag Characteristics in Expansion of Heat-Cured Mortar Specimens" for publication and I wanted to ask you as the coauthor for permission to use a figure from one of your previous publications in my thesis. The figure I wanted to use is Fig. 6. Curves of ettringite decomposition in your 2001 paper Thermal stability and decomposition mechanisms of ettringite at <120°C by Q. Zhou and yourself published in the cement and concrete research journal. It is shown in the attached image. Is there is someone else whom I should ask for the copyright permission, please let me know. Looking forward to your response.

Respectfully,

Jair Burgos
U93195085
Graduate Research Assistant
Department of Civil and Environmental Engineering
University of South Florida College of Engineering
4202 E. Fowler Ave, ENG 213
Tampa, Fl. 33620

The University of Aberdeen is a charity registered in Scotland, No SC013683.
The Dìthigh Òbair Dheathain na chiarannann clàraichte ann an Alba, Àir: SC013683.

[EXTERNAL EMAIL] DO NOT CLICK links or attachments unless you recognize the sender and know the content is safe.
The license below grants permission for Table 2.1 in the literature review.

<table>
<thead>
<tr>
<th>License Number</th>
<th>920288988745</th>
</tr>
</thead>
<tbody>
<tr>
<td>License date</td>
<td>Mar 01, 2021</td>
</tr>
<tr>
<td>Licensed Content Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Licensed Content Title</td>
<td>Cement and Concrete Research</td>
</tr>
<tr>
<td>Licensed Content Author</td>
<td>Sadananda Sahu, Niels Thaulow</td>
</tr>
<tr>
<td>Licensed Content Date</td>
<td>Sep 1, 2004</td>
</tr>
<tr>
<td>Licensed Content Volume</td>
<td>34</td>
</tr>
<tr>
<td>Licensed Content Issue</td>
<td>9</td>
</tr>
<tr>
<td>Licensed Content Pages</td>
<td>7</td>
</tr>
<tr>
<td>Start Page</td>
<td>1575</td>
</tr>
<tr>
<td>End Page</td>
<td>1681</td>
</tr>
<tr>
<td>Type of Use</td>
<td>reuse in a thesis/dissertation</td>
</tr>
<tr>
<td>Portion</td>
<td>figures/tables/illustrations</td>
</tr>
<tr>
<td>Number of figures/tables/illustrations</td>
<td>1</td>
</tr>
<tr>
<td>Format</td>
<td>electronic</td>
</tr>
<tr>
<td>Are you the author of this Elsevier article?</td>
<td>No</td>
</tr>
<tr>
<td>Will you be translating?</td>
<td>No</td>
</tr>
<tr>
<td>Title</td>
<td>The Effect of Cement and Blast Furnace Slag Characteristics on Expansion of Heat-Cured Mortar Specimens</td>
</tr>
<tr>
<td>Institution name</td>
<td>University of South Florida</td>
</tr>
<tr>
<td>Expected presentation date</td>
<td>Mar 2021</td>
</tr>
<tr>
<td>Portions</td>
<td>Table 1</td>
</tr>
<tr>
<td>Requestor Location</td>
<td>Mr. Jair Burgos 12029 USF Richard Beard Dr</td>
</tr>
</tbody>
</table>
Appendix B: Expansion Charts

Figure B.1 Expansion of sulfate optimized cement BB mixes with slag 8
Figure B.2 Expansion of sulfate optimized cement BB mixes with slag 10C

Figure B.3 Expansion of sulfate optimized cement BB mixes with slag 10F
Figure B.4 Expansion of sulfate optimized cement TIL mixes with slag 14B

Figure B.5 Expansion of sulfate optimized cement Z mixes with slag 14B
Appendix C: XRD Charts

Figure C.1 Phase assemblage of 40% cement BB mixes with (a) 60% S8 as-received, (b) 60% S8 1-day sulfate optimized, and (c) 60% S8 2-day sulfate optimized
Figure C.2 Phase assemblage of 40% cement BB mixes with (a) 60% S10C as-received, (b) 60% S10C 1-day sulfate optimized, and (c) 60% S10C 2-day sulfate optimized
Figure C.3 Phase assemblage of 40% cement BB mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized
Figure C.4 Phase assemblage of 40% cement C mixes as-received with (a) 60% S8, (b) 60% S10C, (c) 60% S14A, and (d) 60% S14B
Figure C.5 Phase assemblage of 40% cement C mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized
Figure C.6 Phase assemblage of 40% cement TIL as-received with 60% S14A
Figure C.7 Phase assemblage of 40% cement TIL mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized
Figure C.8 Phase assemblage of 40% cement THIL mixes as-received with (a) 60% S8, (b) 60% S10C, and (c) 60% S10F
Figure C.9 Phase assemblage of 40% cement Z mixes as-received with (a) 60% S8, (b) 60% S10C, and (c) 60% S14A.
Figure C.10 Phase assemblage of 40% cement Z mixes with (a) 60% S10F as-received, (b) 60% S10F 1-day sulfate optimized, and (c) 60% S10F 2-day sulfate optimized
Figure C.11 Phase assemblage of 40% cement Z mixes with (a) 60% S14B as-received, (b) 60% S14B 1-day sulfate optimized, and (c) 60% S14B 2-day sulfate optimized.