Role of Alkalis and Sulfates of Portland Cement on Durability of Florida Structures

BD544#22

FINAL REPORT

Prepared For

Florida Department of Transportation

State Project Number: BD544-RPWO22

February 2008

PREPARED BY

Dr. Abla M. Zayed, Ph.D.

zayed@eng.usf.edu

Department of Civil and Environmental Engineering
University of South Florida
4202 E Fowler Avenue
Tampa, FL 33620

DISCLAIMER

This document is disseminated under the sponsorship of the Florida Department of Transportation and the Federal Highway Administration in the interest of information exchange. The opinions, findings and conclusions expressed here are those of the authoress and not necessarily those of the Florida Department of Transportation or the Federal Highway Administration.

METRIC CONVERSION TABLE

APPROXIMATE CONVERSIONS TO SI UNITS

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
SYMBOL	**WHEN YOU KNOW**	**MULTIPLY BY**	**TO FIND**	**SYMBOL**
AREA				
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
SYMBOL	**WHEN YOU KNOW**	**MULTIPLY BY**	**TO FIND**	**SYMBOL**
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: volumes greater than 1000 L shall be shown in m^3				
SYMBOL	**WHEN YOU KNOW**	**MULTIPLY BY**	**TO FIND**	**SYMBOL**
TEMPERATURE (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
SYMBOL	**WHEN YOU KNOW**	**MULTIPLY BY**	**TO FIND**	**SYMBOL**
FORCE and PRESSURE or STRESS				
lbf	pound force	4.45	newtons	N
lbf/in^2	pound force per square inch	6.89	kilopascals	kPa

SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380. (Revised March 2003)

Reproduced from http://www.fhwa.dot.gov/aaa/metric.htm

Documentation Page Technical Report

1. Report No.

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Role of Alkalis and Sulfates of Portland Cement on Durability of Florida Structures

5. Report Date
February 2008

6. Performing Organization Code

7. Author's

Dr. Abla M. Zayed
Dr. M. Halawah and Troy Whitfield, M.Sc.

8. Performing Organization Report No.

9. Performing Organization Name and Address
Department of Civil and Environmental Engineering
University of South Florida
4202 East Fowler Avenue
Tampa, FL 33620-5350

10. Work Unit No. (TRAIS)

11. Contract or Grant No.
BD 544- RPWO#22

12. Sponsoring Agency Name and Address
Florida Department of Transportation
Research Center
605 Suwannee Street, MS 30
Tallahassee, FL 32399-0450

13. Type of Report and Period Covered
Final Report
December 2004- February 2008

14. Sponsoring Agency Code

15. Supplementary Notes
Prepared in cooperation with the Federal Highway Administration

6. Abstract

In this study, several ASTM Portland cements were used to address the effects of increasing alkali and sulfur trioxide content of cements on performance and durability of concrete. Several characterization techniques were used including: x-ray diffraction, x-ray spectroscopy, scanning electron microscopy, calorimetric studies, fineness, and porosomistry. Several curing regimes were employed that include ambient curing and elevated temperature curing. Two exposure environments were used; namely, lime and marine solution. The findings indicate that increasing sulfur trioxide content increases expansion in lime due to an increase in ettringite formation. Increasing the alkali content was well tolerated, in terms of expansion, if the curing temperature was at 23°C and the exposure solution was lime. Strength loss was found to occur on increasing the alkali content, under ambient conditions and lime exposure, for all sulfate levels. Strength loss accompanying increase in alkali content can be as high as 4,000 psi. Strength regression with increasing alkali content was found to depend on cement mineralogy. Increasing the curing temperature to 80º C increased expansion. The amount of expansion was found to depend on cement mineralogy with the highest expansion recorded for cements of high tricalcium silicate and aluminate content. Exposure conditions also affected durability of the mixes with continuous submersion in marine solution resulting in highest expansion. Incorporation of mineral admixtures, on replacement basis, was found to improve durability for mixes exposed to high temperature cure and marine environment. It is recommended that for structural elements exposed to elevated temperature and salt environment, the alkali content of cements has to be maintained at 0.60% and SO_3 content at the current specification limits. This is especially critical for cements with tricalcium silicate and aluminate above 58% (XRD) and 4% (XRD) respectively.

17. Key Words
Alkalis, sulfur trioxide content, durability in marine environment, strength, high temperature curing, hydrated gel quality, pore structure refinement, fly ash.

18. Distribution Statement
No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161

19. Security Classif.(of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages
93

22. Price

Form DOT F 1700.7 (8-72) **Reproduction of completed page authorized**

ACKNOWLEDGEMENT

This work has been supported by the Florida Department of Transportation. The principal investigator appreciates the technical assistance offered by Mr. M. Bergin, PE, Technical Project Manager and Mr. C. Ishee, PE during the course of the investigation.

EXECUTIVE SUMMARY

The findings of a previous study, conducted for the Florida Department of Transportation, on the effects of sulfur trioxide content of Portland cement did indicate that it has significant role on concrete durability. It was found that there is an optimum SO_3 content that is dependent on the alkali and tricalcium aluminate content of cements. Due to the intimate interaction and effect of those two compounds the present study was initiated.

A point of concern that currently exists is that increasing the alkali content of cement appears to increase the allowed amount of SO_3 that can generate expansion within the set limits of ASTM C1038. It is known that an increase in the latter can lead to delayed expansion in concrete. Increasing the alkali content can subsequently lead to possible alkali-aggregate reaction in concrete made with marginal aggregates.

Effects of higher sulfate or alkali content can also be exacerbated if concrete is exposed to elevated temperature. This is possible for different conditions that include, mass placement, precast elements or hot weather concreting. Other conditions that are known to be of significance to this problem are subjecting elements to wet/dry cycles or submersion in a salt environment.

The objective of the current research is to address the role of alkali and sulfate content in Portland cement on durability of Florida structural elements and infrastructure. In addressing the objectives of the current research, five Portland cements were selected after careful review of mill certificates. The selection of those cements was based on their mineralogy, fineness, alkali and sulfate content. The selected cements had wide variation in alkali, SO_3, Al_2O_3, tricalcium silicate and aluminate content.

As-received cements were analyzed for their oxide and mineralogical composition. Based on the findings, some of the cements were doped with Terra Alba gypsum and potassium hydroxide in order to establish a comparative base for data analysis. Additionally, physical tests and heat of hydration studies were conducted on cements.

Durability studies were conducted using mortar specimens. Strength and expansion measurements were conducted on more than 1,000 specimens. Several tools were used in assessing factors of significance to structural durability that include scanning electron microscopy (SEM) coupled with energy dispersive x-ray (EDX), x-ray diffraction (XRD)coupled with phase analysis and quantification software and optical microscopy. In addition to ambient curing, elevated temperature curing at 60°, 80° and 90°C was adopted in order to simulate precast and mass elements curing.

As exposure conditions have been reported in the literature to be of significance on structural elements durability, several exposure conditions were used in this study; namely, lime solution, salt solution continuous submersion, and wet/dry cycles in salt solution.

Results and Recommendations

The findings indicate that there is a need to maintain low SO_3 and alkali content for cements used in making structural elements that will be subjected during their service life to elevated temperatures and/or marine conditions. While increasing the alkali content of cements to 2.0% did not necessarily result in excessive expansion when mixes were cured at ambient temperatures and exposed to a lime solution, curing at elevated temperatures and exposure to marine conditions initiated excessive expansion at an alkali content of 1.5% and sulfate content as low as 3.07%. For a given sulfate content, alkali content and curing temperature, the degree of expansion was found to be dependent on tricalcium silicate and aluminate of cements.

Strength measurements indicated a strength loss of 2,000 psi when the alkali content of cements was increased to 1.5%. This loss was recorded independent of the sulfate content of cements. It was found that increasing alkalis results in a poor quality hydration gel that results in strength regression. The findings also indicate that incorporation of fly ash, on replacement basis, improved the expansion behavior of mortar mixes containing cements of high alkali content.

Since the findings of this study indicate that increasing alkalis and sulfates of cements have negative impact on durability for most of the cements considered here, it is recommended that the alkali content and sulfate maximum limit currently adopted in standards be sustained. Additionally, it is recommended to mandate incorporation of fly ash, on replacement basis, in concrete mixes used in mass structures or precast elements. It is also recommended that a study needs to be initiated with the objective of addressing the effectiveness of other mineral admixtures in alleviating the negative effects of high alkali and sulfate content on performance of concrete elements subjected to elevated temperature and/or marine exposure.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I
INTRODUCTION

As concrete becomes increasingly used as a construction material, durability issues become more and more important. Its availability and relative low cost compared to other building materials made it more versatile. With less skilled labor required as compared to other construction techniques, the improvement in workmanship and quality control can only go so far, if the quality of the material is compromised. One of the durability problems that may occur during the service life of concrete structures is sulfate attack. It may result in expansion, cracking, spalling and eventually strength reduction. These effects, may in turn, lead to other forms of attack.

Ordinary Portland cement used in making concrete consists mainly of calcium silicates and aluminates phases; namely, tricalcium silicates (C_3S), dicalcium silicates (C_2S), tricalcium aluminates (C_3A), tetracalcium aluminoferrites (C_4AF) and gypsum ($C\bar{S}H_2$) . Tricalcium silicate is responsible for early strength gain while dicalcium silicate contributes to later strength. Tricalcium aluminate is very reactive and in order to control its hydration, calcium sulfates (in one or more forms) are typically added. The reaction is presented in equation (1):

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \ldots\ldots\ldots\ldots\ldots 1$$

The hydration product given by the above equation is ettringite which is referred to as “primary” when it forms during the initial stages of hydration. Primary ettringite formed during the initial stages of hydration does not cause damage to concrete if its formation occurs during the plastic stage of hydration which can accommodate volume changes. However, if initial ettringite formation extends through the hardened stage, it might subsequently lead to structural damage. “Secondary” or “delayed” ettringite are typical terms adopted for ettringite formation beyond the onset of the hardening stage. It is typically accompanied by expansion that can prove detrimental to concrete elements.

In Type I Portland cement (ASTM specification), the Al_2O_3/SO_3 ratio is mostly equal to ~ 1.6 and contains a maximum of 3.5 to 4% SO_3 (US and European standards (1)). At the beginning of the hardening stage, primary ettringite will be converted to monosulfoaluminate according to equation (2) since ettringite requires a Al_2O_3/SO_3 ratio of 3 to remain stable.

$$C_6A\bar{S}_3H_{32} + 2\,C_3A + 4H \rightarrow 3C_4A\bar{S}H_{12} \text{ ……………}2$$

On subsequent exposure to a sulfate source, monophase may reconvert to ettringite according to equation (3)

$$3C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32} \text{ …………}3$$

Additionally, monosulfate hydrate ($C_4A\bar{S}H_{12}$) is known to be unstable at room temperature and lower temperatures (1,2). The transformation of monosulfate to ettringite is well known to cause 2.3 times increase in the solid volume.

The occurrence of the above reaction is not restricted to an external sulfate source but rather the availability of a sulfate source that can be for that matter internal. The latter phenomenon is what has been identified in the literature as internal sulfate attack (ISA) which occurs usually in heat treated concrete. The issue of internal sulfate attack started to receive more attention in the mid-eighties when damage was reported in heat-cured prestressed concrete railway ties. It was believed that this was due to elevated heat-cure followed by ambient cure. However, ISA is not limited to heat-cured concretes. ISA potential under ambient temperature cure exists under certain circumstances. This notion was emphasized by Collepardi (3) who proposed a model for ISA. Collepardi's model is based on a holistic approach where ISA could occur, under ambient conditions, if the following is present: microcracks, delayed release of sulfate and moisture. While microcracks in concrete exist whether due to loading effects, the delayed release of sulfates is definitely worth careful consideration. It is not necessarily due to slowly-soluble phases, but could rather be due to chemical changes occurring within the matrix. These changes do not require high temperature. One possible way to define the possibility of ISA (internal sulfate attack) due to DEF (delayed ettringite formation) is as follows: The formation of ettringite after the cementitious material has substantially hardened and in which none of the sulfate comes from outside the concrete or mortar.

From what has been reported in the literature, possible damage mechanisms due to ettringite formation in ambient cured as well as in heat treated concrete can be summarized through two major theories, crystal growth and swelling. In the latter, it is stated that if the formed ettringite, whether primary or delayed, is micro-crystalline in nature, then it may cause expansion pressure in hardened concrete on water adsorption. Mehta (4) reported that ettringite formed in the presence of calcium hydroxide is colloidal in nature; it has a high surface area and exhibit a net negative charge. On exposure to water, this type of ettringite attracts a large number of water molecules that would surround the ettringite crystals creating inter-particle repulsion that will eventually lead to expansion. Famy (5) expanded the theory by indicating that the high negative charge is due to a high pH (resulting from the presence of the calcium hydroxide), and in the absence of calcium hydroxide, ettringite is well-crystallized in nature and does not result in expansion. Min and Mingshu (6) stated that the concentration of the hydroxyl ions is what determines the nature of the formed ettringite rather than calcium hydroxide concentration in the pore solution. This implies that in presence of a high alkaline pore solution, low in calcium hydroxide, the same result would be expected due to high pH.

In the crystal growth theory, it is indicated that ettringite recrystallization in hardened concrete, due to the moisture changes and accumulation of reactants, may lead to damages due to crystallization pressures and volume increase. According to this theory, not all the formed ettringite could cause expansion, as portions are deposited in available voids and cracks. It is only the excess which could result in expansion. However, there are two different arguments regarding this theory (1). The first argument indicates that for an expansion pressure to occur, supersaturation must be achieved and this does not happen in hydrated cement solution. Another argument points out that this theory does not take into account the nature of concrete being a semi-brittle material and that partial saturation might be enough to exert pressure above the concrete tensile strength. A tensile stress applied at the tip of a crack might be magnified depending on the length and the geometry of the crack. Also, due to the heterogeneous nature of concrete a uniform expansion is not always likely, so preferential crystal formation and the heterogeneous nature may result in cracks due to non-uniform expansion.

Delayed ettringite formation can also occur from less-sulfate containing compounds either due to temperature gradients, which might occur in massive concrete or heat treatment. This can subsequently lead to nucleation and crystal growth that would be accompanied by volume increase and stresses that exceed the tensile strength of concrete. The expansive nature of ettringite, coupled with heterogeneous nature of concrete can result in non-uniform expansion.

1. Parameters of Significance in Internal Sulfate Attack

On reviewing the published literature, the following parameters have been identified as to have significant role on durability of concrete with respect to internal sulfate attack (ISA):

1.1 Cement Composition

1.1.1 Tricalcium Silicates (C_3S): This is the most abundant mineral in Portland cement, and mostly responsible for strength by forming C-S-H gel on hydration. C-S-H has an affinity to incorporate sulfates present in cement (5, 7). However, the affinity for sulfates increases with increasing temperature and/or alkali content. Sulfates are critical in ettringite formation and, if available at a later age, will participate in DEF (5). This could imply that increasing C_3S content may require higher sulfate content for proper retardation of cement hydration as there is competition for sulfate ions consumption between C_3A and C-S-H gel (8).Consequently, if conditions exist that favors the release of sulfates from C-S-H, more sulfates would be available to participate in DEF at a later age. It was reported in the literature (8) that C-S-H gel competes for SO_4^{-2} ions with C_3A. It was also reported that C-S-H gel incorporates sulfate ions in its crystal structure (5, 7). The impact of the adsorbed sulfate on the nature of the gel is unclear (5).

These ions may be released later to form late ettringite (7) as was shown by Divet et. al. (9). The uptake of sulfate ions by C-S-H gel is impacted by several parameters, the most investigated parameter in the literature being the curing temperature. The increase in curing temperature increases sulfate ions adsorption by the C-S-H gel (5). The desorption rate is typically slower as the curing temperature increases. The adsorption also increases with alkali content (10) for all curing temperatures. The desorption rate was slower than the adsorption rate; actually, desorption rate was half the adsorption.

1.1.2 Tricalcium Aluminate (C_3A): Regulating the hydration of tricalcium aluminate requires the addition of sulfates, higher C_3A content means higher sulfate requirement for proper retardation. Lerch (11) indicates that cements with higher C_3A require higher amounts of gypsum for proper setting. Odler et al (12) showed that expansion decreases with decreasing C_3A and increasing C_4AF, even with an increase in sulfate content. Their conclusion was ettringite formed in presence of high iron content has different morphology. Chengsheng Ouyang (13) showed that expansion due to internal sulfate attack increased with increasing C_3A at the same SO_3 level. The effect of increasing expansion due to increasing tricalcium aluminate content was also reported by Kantro (14). Taylor (15) seems to believe that there is no danger of DEF at ambient temperature cures in modern cements unless the SO_3 content exceeds 5-6%. The research also indicates that safe limits of SO_3 content increases with C_3A content. This is not exclusively true as there are other factors that need to be considered when discussing safe limits on sulfate content.

The primary concern regarding C_3A content is its availability to participate in the formation of ettringite, which could be expansive. Since the formation of ettringite requires both sulfate and aluminate ions, it is expected that for the same SO_3 content, expansion will decrease if there is an increase in C_3A content. This will be entirely true if all the aluminates and sulfates were available for reaction and formation of ettringite in the plastic stage, and whatever ettringite forms during this stage will remain stable. Unfortunately this is not the case. First, not all the aluminates and sulfates are released during early stages of hydration. Additionally, it was mentioned earlier that C-S-H gel competes for sulfate ions with C_3A. These sulfate ions, captured within the gel, could be released at a later age and become available to participate in the formation of delayed ettringite. Also, the presence of alkalis affects the rate of C_3A hydration, and it is known to increase the affinity of C-S-H gel for sulfate ions (8). In summary, it can be concluded that in addressing the role of C_3A on expansion in ISA phenomenon, the effects of C_3S, SO_3, and alkalis can not be ignored.

1.1.3 Alkali Content: Cement alkalis are known to influence the rate of hydration of C_3A and ettringite stability (1). This in turn may affect the sulfate requirement for proper placement. It also influences the nature of the hydration products including ettringite (morphology and stability) and C-S-H gel (morphology and composition). The presence of alkali hydroxide may increase the rate of sulfate ion release into solution, ettringite instability, and inclusion of these sulfates in the C-S-H gel (10). As has been indicated earlier, ettringite formed in high pH solutions has a morphology that renders it expansive (4,6). Additionally, pH directly affects the stability domain of ettringite.

Stark and Bollmann (1) presented a summary of what has been reported in the literature about the stability domain of ettringite. The domain covered a wide range of pH. The reason for this wide range is the dependence of this phenomenon on other factors, such as cement composition (SO_3 and C_3S). It appears that even at high pH values, if there is enough supply of sulfate ions, ettringite can still form. The implications are that in indicating whether ettringite will form or not, the pH of the pore solution can not be considered as the sole parameter.

Lerch (11) reported the necessity to increase the amount of sulfate needed to control the setting of cements with high alkali content. This was thought to be due to its effects on C_3A reactivity. An increase in rate of hydration of C_3A with alkali content was also reported by Sprung and Rechenberg (16). B. Osbaeck (17) also reported an increase in the reactivity of C_3A and C_3S with total alkali content of cement. Odler and Wonneman (18) also reported similar findings on doping clinker with K_2O. However, Na_2O did not affect tricalcium aluminate reactivity. Way and Shayan (19) reported an increase in the gel production with increasing alkali content; the increase was achieved through the addition of NaOH to the mixing water. Juenger and Jennings (20) reported that the addition of NaOH to the mixing water increases the initial hydration but retards the reaction beyond an age of one day. Similar findings were reported by Bentz (21). Mori (22) reported acceleration in C_3S hydration with NaOH solution compared to pure water.

There appears to be contradicting findings in the literature on the effects of adding alkalis as sulfates on cement hydration process. If alkalis are added as sulfates, the hydration of tricalcium silicate or aluminate did not show significant change (23). Others (24) reported an increase in the hydration rate on addition of alkali sulfates.

Generally, the evidence points to an increase in initial hydration with alkali content. Additionally, the literature appears to have reports of inconsistent findings on the effects of alkali sulfates and hydroxides. As an example, some researchers (18, 23) reported an increase in the rate of hydration when alkalis were increased as hydroxides but not as sulfates, while others (24) showed an increase in the rate of hydration when the alkalis were added as sulfates.

It is evident from the literature that the solubility of calcium hydroxide decreases with the increase of the concentration of alkali hydroxide. The effect of alkali sulfates on the solubility of lime is more complicated and depends on the concentration of each phase and the type of alkalis. This result was reported by Sprung and Rechenberg (16). Ghorab et al (25) reported an increase in the solubility of gypsum with the increase in NaOH concentration as well; this means higher sulfate availability in solution. The solubility of silica is known to increase with alkalinity and the respective pH value (26, 27). The high alkalinity was achieved through additions of NaOH to the mixing water. Alkali sulfates did not show the same effect (28).

Up to this point, it is very clear from the literature that alkalis impact the hydration and kinetics of hydration of Portland cements. This effect also extends to the nature of the hydration products formed, especially the C-S-H gel. The results reported in the literature are either incomplete or somewhat contradicting. This is believed to be due to the dependence of the hydration process on many factors, especially sulfate content; the dependence of sulfate content on alkali content as well as the cement composition appears not to be clearly considered.

Jawed et al (22) conducted a thorough literature review on the influence of the alkali on the properties of hardened concrete. Generally, the higher alkali content, present in the form of hydroxide or sulfate, results in quick setting. The alkali hydroxide favors the formation of crystalline monophase around the C_3A grains. Alkali sulfates, mostly as potassium, lead to the precipitation of syngenite. These effects are strongly dependent on the ions concentration.

For strength development, most of the evidence pointed to an increase in the early strength and a decrease in the 28-day strength. Other researchers, however, showed a positive effect on strength development (22). Alexander and Davis (29) showed a 56% decrease in 28-day strength in cement pastes on increasing alkali content from 0.15 to 2.8% (as Na_2O_e added as alkali hydroxides). The authors indicated that the decrease occurred regardless of the type of the alkali cation (sodium or potassium). The study was done on five different cements. The C_3S content of the cements varied from 31-51% (Bogue) and the C_3A content varied from 4-14% (Bogue). There was no mention of the sulfate content of these cements. The sulfate content is believed to impact the effect of the alkalis. The authors did not offer an explanation for strength reduction.

McCoy et al (30) reported that water-soluble alkalis constitute 10% to 60% of the total alkalis present in clinker. The data indicated that the amount of water-soluble alkalis has very little effect on the pH of the aqueous extract from cement pastes. This work was done using w/c ratios of 0.5 at ½ hour hydration and w/c ratio of 2 at ½ hour and 24 hours hydration. The pH ranged from 12.3-12.7 for cements with alkali contents ranging from .03%-1.19% Na_2O_e. It was also indicated that alkalis in clinker have a significant effect on compressive strength development. The absence of alkalis resulted in an abnormally low early strength, and the presence of alkalis resulted in higher early strength (1-3 days) and lower strength at 28 days.

Osabaeck (28) reported that increasing alkali content (through the addition of K_2SO_4) increased the early strength and decreased the later strength. The data reported showed a corresponding increase in air content with alkali. It was concluded that the effect of alkalis on later strength development is due to its impact on early hydration and not governed by the conditions of pore liquid at later ages. The study was done on one cement with a C_3S content of

75% (Bogue) and C_3A content of 4% (Bogue). No details were given about the hydration process or the hydration products. In another study by the same researcher (31), a negative effect of total and soluble alkali content on the 28 day strength was reported. The effect was dependent on SO_3 content. The study showed an increase in the rate of hydration of certain phases (C_3S, C_3A, and C_4AF) at early ages. This was not necessarily responsible for the increased strength. However, the general conclusion reflected on the nature of the hydration products. No specific details were given about the hydration products. Osbaeck (17) reported an increase in the early age strength and a decrease in the 28-day strength when soluble alkali content was increased through doping with potassium sulfates. Doping levels were 0.5% and 1.0% K_2O. It was indicated that the increase in early strength might diminish if a constant slump is maintained through increasing w/c ratio, as the addition of alkalis increased the water demand.

Sprung et al (16) reported higher reactivity of C_3A in higher alkali solutions. If gypsum was lacking, aluminate hydrates formed causing rapid setting. However, in presence of high sulfate supply, large amounts of ettringite formed which also resulted in rapid setting. The authors indicated that with higher amounts of alkalis in clinker, particularly alkali sulfates, lower calcium hydroxide concentration existed in solution. This in turn increases the rate of hydration of C_3A prior to the dormant period which may lead to rapid setting. They also added that the solution composition during early hydration, not only impacts the setting, but also strength development as well. The study, however, did not investigate the effect of alkalis on the rate of hydration of C_3S, which could have an effect on the setting behavior.

Johansen (24) indicated that the switch from wet to dry process, during clinkering, resulted in higher alkali content in cements. Also, the use of cheap sulfur-rich fuels, led to higher SO_3 content in clinker. The author suggested that this change is responsible for a decrease in the 28-day strength. The author also reported that an increase in K_2SO_4 results in 28- day strength decrease. The decrease occurred regardless of the source of alkali sulfates, whether coming from the clinker or externally added. It was shown that the 28-day strength correlated negatively with the amount of combined water after 3 minutes of hydration (chemically-bound water). This implies that the early hydration of C_3S and the nucleation of the gel early on is of significance.

Bhatty et al (32) reported that C-S-H gels with low C/S ratio retain more alkalis than high C/S hydrates when these hydrates come in contact with alkali solutions of various concentrations. The authors mentioned that this change, depending on the alkali concentration of the solution as well as the type of alkali cation, will change the nature of the C-S-H formed as indicated by XRD pattern. This change was attributed to a change in the crystal structure. The study did not mention the physical implications of this change.

Way et al (19) reported an increase in the rate of gel and CH formation on increasing the concentration of sodium hydroxide in mixing water from 0 to 1M. At a concentration of 2M and higher, the formation of aluminosulfates was retarded and sodium-substituted monosulfate formed instead of ettringite. It was also noted that the formation of a sodium-containing C-S-H gel at these higher concentration occurred. The study did not provide firm analytical data to support the increase in the rate of gel production. The cement used in the study had 52.7% C_3S and 5.9% C_3A (Bogue) and 3.3% SO_3.

Jelenic et al (33) studied the effect of gypsum on the strength development of two cements that had identical chemical composition except in their alkali content. The cements used in the study had 70% alite (XRD), 8-10% C3A (XRD), and alkali contents of 0.16 and 1.06%. The study showed an optimum sulfate content for strength gain. For a given age, an optimum occurred which was higher for low alkali cement. It was noted that the optimum for the high-alkali cement shifted to a higher value with age. The maximum strength was higher for the low alkali cement up to 47 days. However, at 90 days the difference in the strength was not noticeable. This was explained by the reaction of the adsorbed sulfate to form sulfoaluminate phases and the redistribution of the sulfates in the gel. Higher strength was attributed to better quality gel. Alite hydration was slightly higher for low alkali cement at all sulfate contents (1-5%) up to 47 days of hydration.

Gebauer et al (34) reported an increased reactivity in higher alkali clinkers. The alkalis were mainly sulfates. The early hydration rate increased with the clinker alkali-sulfates. Early compressive strength (2 days) increased while the 28 day strength decreased. There was no effect on the 28 days flexural strength. There was also no clear influence on the 28 day compressive strength of concrete.

Odler et al (18) conducted a study on the influence of the alkalis added to the raw feed of clinker preparation. Two clinkers were prepared through the addition of Na_2O and K_2O. In both cases, the alkalis were incorporated preferentially into the lattice structure of C_3A modifying it from cubic to orthorhombic. It was reported that the hydration of C_3A was accelerated in the potassium-doped clinker and slowed down in sodium-doped one. The hydration of C_3S was not altered. The strength development was not affected by the presence of alkalis, yet the setting time was moderately extended in the sodium case and shortened in the potassium case. In another study (23) conducted on the influence of alkalis added to the clinker as sulfates (the doping levels were 0.72% and 1.26% Na_2O as Na_2SO_4, and 0.88% and 1.48% K_2O as K_2SO_4), no significant effects on the hydration of C_3S or C_3A were noted. The setting time was shortened in both cases, but significantly in the case of potassium sulfates. This was attributed to the formation of syngenite, but there was no explanation for the case of the sodium sulfate doping. The compressive strength decreased in both cases at all hydration ages. Though the cause of this decrease was not obvious, it was postulated that changes in the structure and intrinsic properties of the hydrates occurred due to changes in the liquid phase caused by dissolution of the alkali sulfates. These two studies (18 and 23) were conducted on one laboratory-prepared clinker having the following mineralogical composition: C_3S=70%, C_2S=10%, C_3A=10%, C_4AF=10% (based on Bogue). The SO_3 content for the control case was maintained at 3.0% using interground gypsum, and the Blaine fineness was 300 m^2/kg.

Suzuki et al (35) reported a lower Ca/Si mole ratio for C-S-H in systems of Ca-SiO_2-NaCl-NaOH. The authors suggested adsorption of Na ions by the C-S-H gel which lowered the exothermal temperature in DTA. After dispersion with water, this temperature increased to the same value reported for pure C-S-H gel. Smaoui et al (36) reported a reduction in mechanical properties of concrete (compressive strength, splitting, direct tensile, and flexure, but not modulus of elasticity) on increasing Na_2O_e from 0.6% to 1.25% through the addition of NaOH. The authors attributed the findings to a more reticular porous cement paste as observed under SEM though the hydration products did not show significant differences in both cases. Both cases resisted freeze/thaw well. It was also concluded that additions of alkalis did not modify the air-void system.

Shayan et al (37) conducted a study on the influence of alkalis through the addition of NaOH in the mixing water. The alkali levels ranged from 0.8 to 10.5% Na_2O_e. An increase in expansion with alkali level was observed. The study also noted a delayed formation of ettringite and enhanced formation of calcium hydroxide. However, as the alkali level was increased (2 and 4.5 M NaOH), neither ettringite nor monosulfate were formed; rather, the formation of a new phase (sodium-substituted monosulfate, referred to as U-Phase) and a crystalline form of C-S-H gel were observed. There was also a decrease in the compressive strength as well as the modulus of rupture with an increase in alkali level. This change was attributed to the formation of the new phase and to the substitution of sodium in the C-S-H gel structure, a (Na_2O/SiO_2) ratio of 0.17 was reported. It was also observed, through SEM, that high-alkali cement pastes had a less dense microstructure as opposed to low-alkali cement pastes. This could possibly contribute to loss of strength. The study did not provide the cement mineralogical composition, or the sulfate content which may have influenced the effect of alkalis on strength and expansion.

Luxan et al (38) conducted a study on the potential expansion of Portland cement with the addition of alkali salts (Na_2CO_3 or K_2SO_4). Aside from the expansion results, it was found that the addition of these alkali salts at 1, 2, and 3 % by weight reduced the expansion of Portland cement mortars. The authors found that the addition of the sodium carbonate altered the hydration reaction by causing abnormal setting (false or quick set). This problem was corrected through additions of natural pozzolans. For the potassium sulfate, it was reported that additions of 1, 2 or 3% did not cause abnormal setting; however, it did accelerate cement setting. The addition of <1% of this salt delayed both initial and final set. The addition of this salt caused a decrease in compressive strength at early and late ages; the reduction was attributed to modifications in clinker hydration due to the presence of alkalis in the liquid phase.

Juenger et al (20) reported that increasing the alkali content through the addition of NaOH (1M) accelerated the initial hydration; however, after the first day high alkalinity retarded the hydration process. The total surface area, determined by nitrogen absorption, decreased due to a decrease in gel pores with radii of 1-4 nm. It was also noted that the presence of NaOH led to the preferential formation of denser C-S-H gel, which resulted in heterogeneous structure. A slower rate of drying shrinkage was also observed. The authors offered the following explanation: since NaOH-containing samples had heterogeneous structure, localized stresses caused larger cracks. These cracks helped reduce the measured shrinkage. Also the samples continued to shrink without water loss, suggesting that this is due to microstructural rearrangement. The total alkali content for this study was 1.2% as Na_2O_e. The study was done on one cement with 54% C_3S and 10% C_3A (Bogue). The SO_3 content was 2.84%, and the Blaine Fineness was 368 m^2/kg. This cement was used for all the results reported in the study except for the heat of hydration data which was done on similar cement having a C_3S content of 64%, and C_3A content of 8% (Bogue). Although the cements are similar, the higher C_3S content may impact the results of this test.

Bentz (21) reported that increasing alkali content (using both sodium and potassium sulfates and hydroxides) of cement paste increased the early age hydration and retarded the hydration at later ages. It was also concluded that the presence of alkalis results in depercolated capillary pores. The author attributed the findings to the nature of the gel formed, being plate lath–like with higher crystallinty rather than random. This morphology might result in slower diffusion rate and slower hydration at later ages. The depercolation may be advantageous since it results in less freezable water in the pores.

Shayan et al (37) reported an increase in the expansion of mortar bars using sodium hydroxide doping. The expansion was reported to be approximately 0.04% at 12 weeks at 3.8% Na_2O_e. This study did not provide details about the cement composition or the sulfate content.

Luxan et al (38) reported that incorporation of alkali carbonate and sulfate salts (Na_2CO_3 1 and 2% by weight; K_2SO_4 1.2 and 3% by weight) reduced the expansion of Portland cement mortars, mainly when C_3A content is low (<5%). It was concluded that there is an optimum concentration for the alkali salt for each cement. Again, this study did not provide any details about the hydration products, or any details on the Na_2O_e levels. Vivian (39) showed no significant expansion to occur when the alkali content of the cement was increased to 4.08% using NaOH in the mixing water. The study was done on mortar prisms (1 in x 1in x 10 in). The expansion did not exceed .007% at 196 days. The study did not show any details about cement composition.

1.1.4 Sulfate Content: As presented earlier in this document, sulfates are added mainly to control the hydration of C_3A. They participate in the formation of ettringite. Sulfate requirements are complicated, due to several factors presented earlier. Optimizing sulfate content for proper retardation, placement, strength development, shrinkage, expansion and durability is not an easy task. This is especially true with stricter environmental regulations, and the need for less expensive fuels. Cement producers are pushing and advocating relaxing the restrictions on sulfate contents. The complicated cement hydration mechanisms make it hard to just allow higher sulfate levels than currently acceptable without more understanding of the interaction of all involved phases and their impact on long term durability.

1.1.5 Sulfate form: The late formation of ettringite is indicative of a source(s) for delayed release of sulfates. Among possible sources that are offered in the literature are sulfates in some silicate phases of clinker such as dicalcium silicates, or due to the presence of sulfates in slowly soluble forms, such as anhydrite or even in some sulfate-rich aggregates. While the idea of slowly-released sulfates was supported by several researchers (3, 41, 41) it was opposed by others (42, 43, 44, 45, and 46). This should not be a point of controversy; even if all the sulfates were to be very soluble, the late release may occur due to the other factors mentioned above.

1.2 Cement Fineness

Fineness influences the rate of hydration; consequently, it will influence the sulfate requirement needed for proper placement and long term durability of concrete.

1.3 Curing Temperature

The temperature affects hydration rate and the nature of the gel formed. The higher temperature results in higher porosity and a coarser C-S-H structure (47). It also impacts the stability of ettringite (5).

It has established in the literature (1, 2, 5, 15) that ettringite decomposes to monosulfate hydrate on exposure to elevated temperature >80 ˚C. The monophase is further converted to the sulfate free calcium aluminate hydrate at a long exposure time to boiling water temperature. Other published data offers a maximum curing temperature of ~70 ˚C as a safe curing temperature. Because ettringite is the stable calcium sulfoaluminate hydrate phase at room temperature, it will then reform in concretes stored at ambient temperature following heat curing. While high temperature cure can be one source of temperature rise that triggers such transformation, temperature rise in concrete to levels where ettringite becomes unstable and decomposes, does not have to be due to heat-curing. It was reported in the literature (48) that in large concrete sections with high cement content, the internal temperature could rise up to 85 ˚C. The stability of ettringite depends on factors other than temperature. Heinz et. al. (10) detected the presence of ettringite after 12 hours of curing at 90 ˚C when cement had 8.6% by weight SO_3. This could be due to the fact that the density of the matrix and the exposure time were not sufficient for its decomposition. It can be concluded that the exposure time has an effect, in addition to SO_3 content as well as cement composition, especially C_3S. C-S-H is known to incorporate sulfate ions (5,7). The C-S-H gel affinity for sulfate increases with the increase in curing temperature (10).

High temperatures in concrete are known to lower pore solution pH (49, 50). It is not known whether this affects the stability of ettringite directly. However, the drop in the pH results from the precipitation of calcium hydroxide, which in a cement system will be supplied through the hydration of calcium silicate phases. The literature indicates that the solubility of calcium hydroxide decreases with increasing temperature. This implies less calcium hydroxide available for the formation of ettringite. However, the decisive factor seems to be the availability of the sulfate in solution according to the experiments conducted by Heinz (10). Researchers (5) assessed an increase in sulfate ion concentration with increasing the curing temperature; at the same time, no ettringite was detected under these conditions. Since high temperatures decrease the solubility of calcium hydroxide, it may result in less calcium available for the formation of C-S-H gel. This can result in a lower Ca/Si ratio. Also, it was reported in the literature that the nature of the gel formed at elevated temperature differs from that formed at ambient temperature (47). The gel formed at higher temperature has been reported as coarser with higher porosity. Many researchers (8-10, 15, 40-46, 49, 50, 61-69, 70-72) have tackled the issue of DEF due to heat-treatment offering different hypotheses on the mechanism of the attack. However, the published literature still offers conflicting theories. However, it appears that temperature rise in concrete elements will have a direct effect on sulfate availability in pore solution, CH availability, C-S-H morphology and ettringite stability. It is therefore a very important factor to be considered in studying ISA.

From the above presented review of the literature conducted on ISA it can be concluded that there are several parameters with specific contributions that need to be considered in addressing ISA. It is also quite evident that each factor has implications on the others. While there is ample of information regarding single parameters effect, there is a lack of identification and consideration of the effects of varying several parameters in the same study. In other words, if data are presented that address the effects of alkalis on ISA, cement composition and sulfate content might not be addressed or even recognized as of significance to the conclusions reached by the researchers.

This study was initiated in order to address primarily the effects of alkalis and sulfates on concrete durability. In pursuing this objective, cement composition, exposure conditions (cycling moisture, salt environment), fineness and curing conditions were all recognized in assessing alkalis and sulfate content on ISA durability issues in concrete elements.

2. Research Objective

Role of alkalis at ambient cure temperatures

As mentioned above, the cement composition greatly influences the phenomenon of the ettringite formation as well as its reformation. Increased fuel costs and tightened environmental regulations have led to increased levels of alkalis and sulfates in modern cements. The switch from wet to dry processes in order to conserve energy and the lack of low-alkali raw materials resulted in higher alkali levels (22 and 73). Since any attempt to remove the alkalis from the raw materials is not a cost-effective nor is a practical solution, the presence of alkalis in cements is inevitable. The ASTM specifications do not limit the alkali content of OPC where there is no potential for alkali-aggregate reaction. The limit imposed by ASTM C-150 is 0.6% Na_2O_e for potential ASR, however, the typical alkali content of Portland cements range from 0.3%-1.3% expressed as Na_2O_e (22). In fact, since high alkalinity is favorably viewed to prevent the initiation of corrosion, high alkali-cements are being used as a measure to prevent corrosion. Recently, some DOT's received requests from concrete suppliers to uses alkali-containing aggregates due to the lack of better aggregates in those localities.

Higher alkalis are believed to have a detrimental effect on the durability of Portland cement concrete. The effect of alkalis on cement hydration and mechanical properties of concrete has been studied by many authors. However, the effect on the expansion potential due to internal sulfate attack, which is believed to be impacted greatly by alkalis, has not been studied thoroughly. In recent years however, this topic received more attention. This is due to the emergence of delayed ettringite formation especially in heat-cured concrete elements. Most of the research conducted in this area considered the influence of alkalis on expansion of cementitious systems exposed to elevated temperatures.

The objective of this research is to study the effect of alkali content on the expansion potential of PC systems. While these compounds are not deliberately added to the cements, they may be present in the raw materials used in the manufacture of cement; namely, clays and limestone.

CHAPTER II

EXPERIMENTAL FINDINGS

1. Introduction

The objective of the current study is to address the roles of alkalis and sulfates in Portland cement on the properties and durability of concrete. Towards satisfying the above objective, five ASTM Portland cements were used in this investigation. The results of the study will be presented in this chapter.

2. Characterization of the As-Received Materials

2.1 Blaine Fineness

Cement reactivity and therefore its rate of hydration depends on its particle fineness and particle size distribution. Increasing particle fineness corresponds to an increase in the total surface area available for interaction when cement is in contact with water during hydration. The cements used in this investigation were selected to reflect similar fineness but variable mineralogical phase content. Blaine fineness assessed for the as –received cements are depicted in Table-1. The results indicate that the cements share similar fineness except of MH4 which has higher fineness.

Table 1. Blaine Fineness of As-Received Cements

Cement	C	E	ERD07	MH3	MH4
Blaine Fineness (m^2/kg)	384	380	408	395	427

2.2 Oxide Chemical Composition of As-Received Materials

Oxide chemical composition of as-received materials was determined using x-ray fluorescence spectroscopy. The results are presented in Tables 2 and 3 where it can be seen that cement ERD07 has the highest sulfur trioxide content. In addition, alkali content of cements C and E are lower compared to the other three cements. Cement C had the lowest alkali content among all cements. In addition, Cements ERD07 and MH3 share higher potassium oxide content while MH4 has higher sodium oxide and moderate potassium oxide.

Oxide chemical analysis on fly ash (Table 3) indicates that it can be classified as Class F in accordance with ASTM C-618.

Mineralogical phase content for the as-received cements determined through Bogue calculations and x-ray Rietveld analysis are depicted in Tables 4 and 5 respectively. The results indicate the discrepancy between both quantification techniques. This finding is not surprising as it is well established that cement compound content as determined through Bogue calculations are essentially an approximation. X-ray quantification of the as-received cements reveals differences in the phase content of the as-received cements. First, tricalcium silicate content for cements E and ERD07 is similar and at average of about 57 % approximately while for cements MH4, C and MH3 it is higher (65, 67 and 72% respectively). Also, Cements C, E and MH3 share similar tricalcium aluminate content in the crystalline cubic form of approximately 2% while cements ERD07 and MH4 are characterized by a higher aluminate content of about 10%. While MH4 has a total tricalcium aluminate content of 10%; it only contains 2% of its aluminate in a cubic form while 8% in a crystalline orthorhombic form. So, among all cements, ERD07 has the highest cubic tricalcium aluminate, with all other cements having approximately 2%, while MH4 is the cement with the highest tricalcium aluminate content that is predominately present in an orthorhombic form. Additional differences exist in the form and content of calcium sulfate as will be discussed later. Fly ash mineralogical analysis indicates the presence of four crystalline phases; namely, quartz, mullite, hematite and magnetite.

In conclusion it can said that cement E is an ideal cement in terms of its sulfate, alkali, tricalcium aluminate and tricalcium silicate content and fineness for sulfate durability. Additionally, the above cements were selected carefully to serve in data analysis as to the effect of different mineralogical phases in cements on the role of alkalis and sulfates in concrete durability. That is to say, if a comparison is desired to study the effect of higher alkali and aluminate content on moderate tricalcium silicate cements, it can be easily done through comparing Cement E and Cement ERD07. Similar comparison can be done for their role in high tricalcium silicate cements through considering Cement C which was introduced in this study due to its high tricalcium silicate content but low alkali and tricalcium aluminate content. Matching Cement C in its silicate content is Cement MH4 with the exception of its high alkali and high tricalcium aluminate content.

Table 2. Oxide Chemical Composition of As-received Cements

Analyte	C	E	ERD07	MH3	MH4
SiO_2	20.52	21.15	20.08	20.20	20.99
Al_2O_3	4.92	4.78	4.98	4.02	4.92
Fe_2O_3	3.70	3.76	2.22	2.78	2.24
CaO	64.31	64.41	62.21	64.02	63.93
MgO	1.71	0.95	3.65	2.47	2.14
SO_3	2.81	2.58	3.47	3.09	2.55
Na_2O	<001	0.18	0.3	0.21	0.43
K_2O	0.41	0.34	1.12	1.10	0.67
TiO_2	0.27	0.33	0.21	0.22	0.21
P_2O_5	0.03	0.07	0.2	0.15	0.16
Mn_2O_3	0.04	0.03	0.1	0.06	0.04
SrO	0.04	0.12	0.34	0.04	0.13
Cr_2O_3	<0.01	<0.01	0.01	<.01	<.01
ZnO	<0.01	0.02	0.01	0.04	<.01
L.O.I (950° C)	1.08	1.15	0.66	1.40	1.36
Total	99.83	99.84	99.57	99.79	99.77
Alkalis as Na_2O	0.27	0.4	1.03	0.93	0.87

Table 3. Oxide Chemical Composition of Class F Fly Ash

Chemical Oxide	Weight Percent (w/o)
SiO_2	53.34
Al_2O_3	19.71
Fe_2O_3	8.27
Sum of SiO_2 ,Al_2O_3 , Fe_2O_3	71.32
SO_3	0.60
CaO	11.18
Moisture Content	0.10
Loss On Ignition	0.13
Alkalies as Na_2O	0.72

Table 4. Phase Content of Cements (Bogue Formulae)

Compound (%)	Cement				
	C	E	ERD07	MH3	MH4
C_3S	60	57	54	67	57
C_2S	14	18	17	7	17
C_3A	17	6	9	6	9
C_4AF	11	11	7	8	7

Table 5. Rietveld X-Ray Mineralogical Analysis of Cements

Compound (%)		Cement				
		C	E	ERD07	MH3	MH4
C_3S		67	54	59	72	65
β-C_2S		15	25	15	12	14.5
C_3A	Cubic	2	4	9	2	2
	Ortho	-	-	-	-	8
C_4AF		14	13	4	9	3.3
Gypsum ($CaSO_4.2H_2O$)		-	2	-	0.3	1.0
Bassanite ($CaSO_4.0.5H_2O$)		1.5	1.6	2.4	1.4	1.6
Anhydrite ($CaSO_4$)		1.3	-	-		-
Potassium Sodium Sulfate		-	-	1.6	0.7	-
Syngenite					1.4	-
Arcanite (K_2SO_4)						1.0
MgO		0.6	-	4	1.0	1

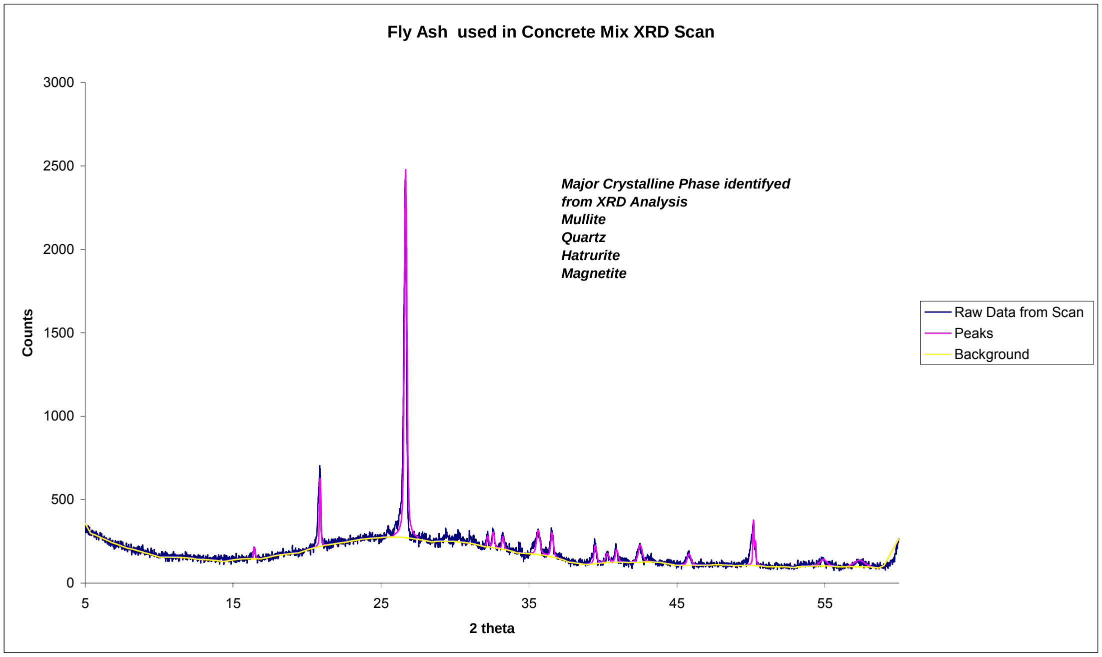


Figure 1. X-Ray Diffraction Pattern of Class F Fly Ash

3. Role of Sulfates

3.1 Expansion

In addressing the role of sulfur trioxide content mortar prisms and cubes were prepared for all cements. Each data point measurement reflects average reading for 4 bars or 3 cubes. For expansion measurements, the specimens were prepared and monitored in accordance with ASTM C1038. The results are presented in the Figures 2 through 6. It is to be noted that the condition defined by the symbols AR indicate the as-received content of the specific oxide. For example, 3.6%-AR set represents mortar with cement that has sulfur trioxide content doped to 3.6% and alkali oxide content that corresponds to the oxide content of the as-received cement with no additions.

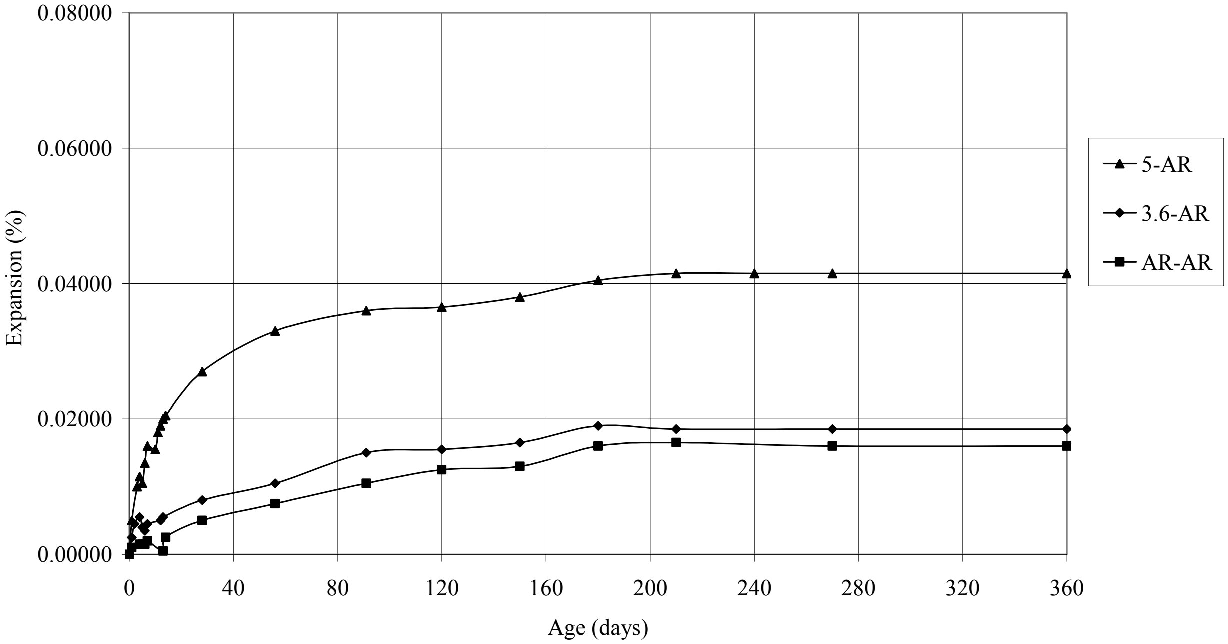


Figure 2: Effect of Sulfate Content on Expansion Behavior for Cement E

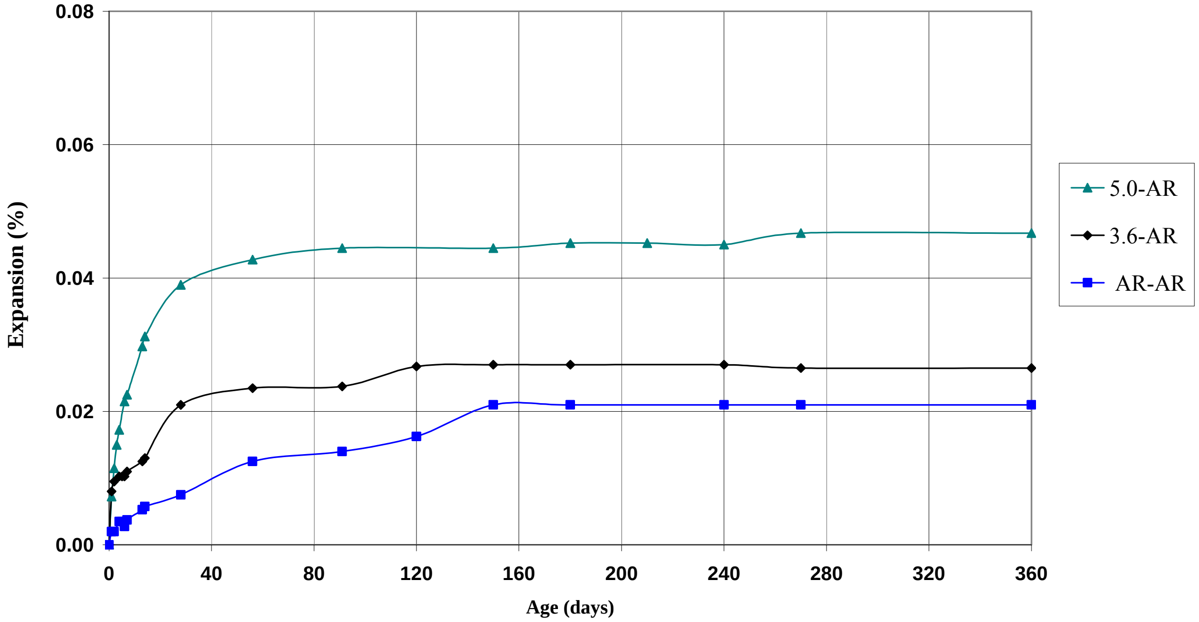


Figure 3: Effect of Sulfate Content on Expansion Behavior for Cement C

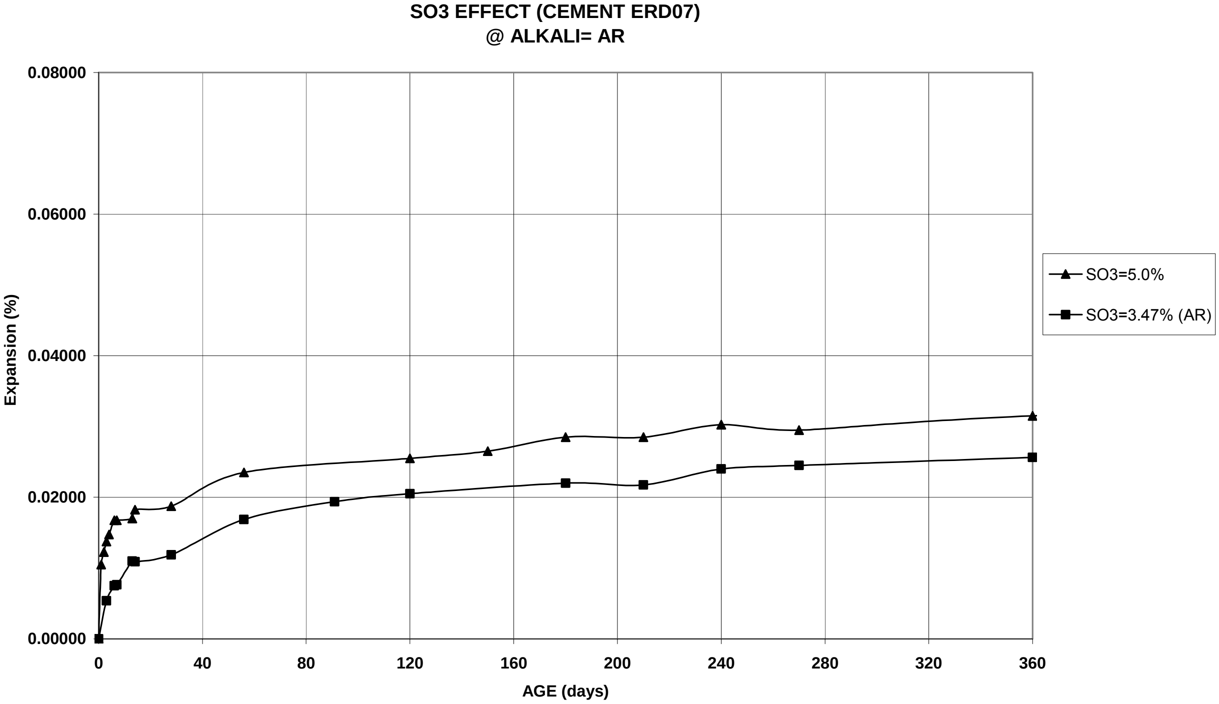


Figure 4: Effect of Sulfate Content on Expansion Behavior for Cement ERD07

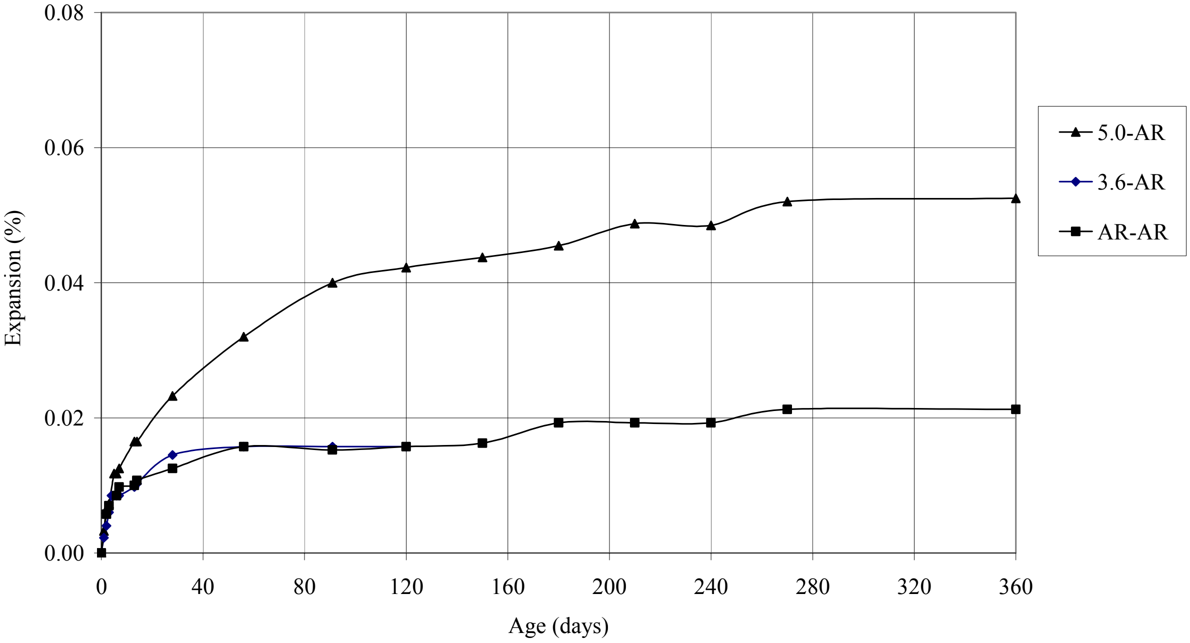


Figure 5: Effect of Sulfate Content on Expansion Behavior for Cement MH3

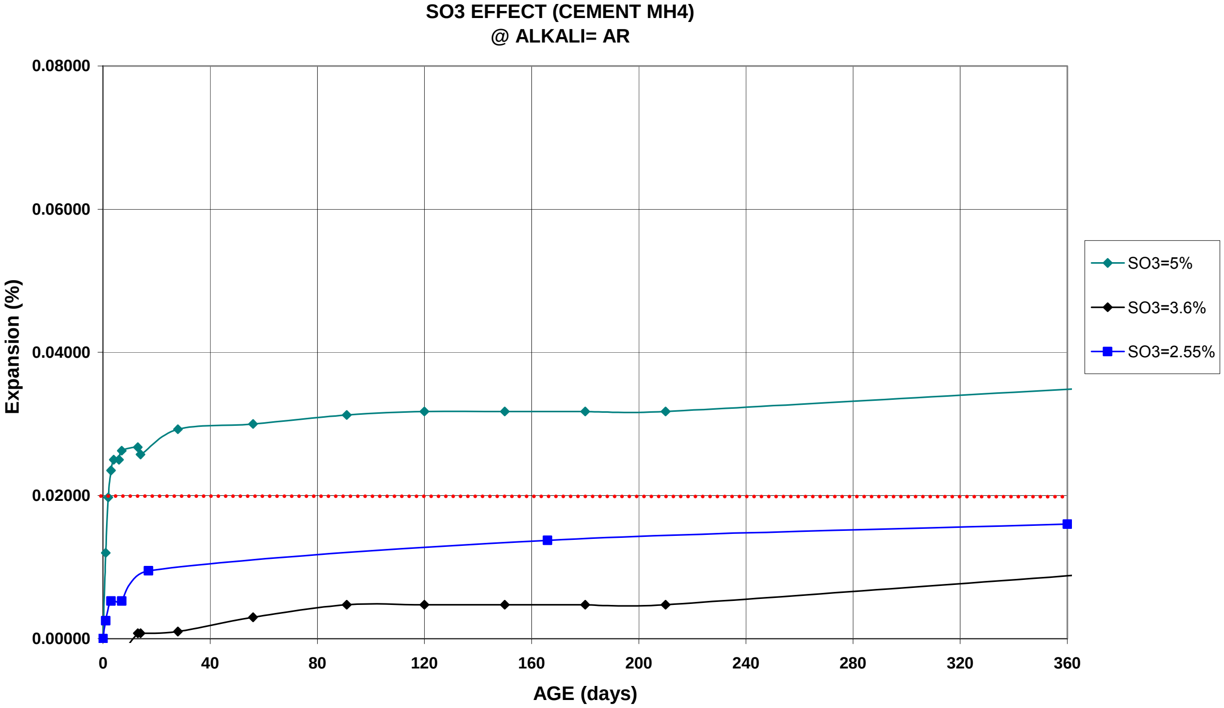


Figure 6: Effect of Sulfate Content on Expansion Behavior for Cement MH4

It is quite evident that there is an increase in expansion with the increasing sulfate content. For the AR cases, where sulfate content was between 2.58% and 3.47%, expansion did not exceed 0.03%, with the highest reported for cement ERD07. This could be due to the fact that cement ERD07 has the highest SO_3 content, although the values for all cements were within close range.

In order to assess the effects of varying cement composition and alkali content on the response of cements to increased levels of SO_3, all cements were doped to a constant SO_3 content of 3.6% and 5.0% using Terra Alba gypsum. The increase in the expansion values from the AR case to the 3.6% case was almost negligible. There was no 3.6% case for cement ERD07 since the AR-SO_3 content was close to that value. The increase in expansion values in the 5% case is clear; the values are almost double those of the AR case for cements C, E, MH3 and MH4. However, all the values were under .05%, up to the ages reported, in cases of C and E and ERD07, and just slightly above that in case of cement MH3. The increase from the AR case to the 5% case in cement ERD07 was not much; this could be due to the fact that the original cement has high sulfate content.

Cement MH3 recorded the highest expansion, followed by cement C. These two cements have high C_3S content and low C_3A content. Cement ERD07 showed the lowest expansion value at 5% sulfate followed by MH4. For the latter, C_3A content (in cubic form) was the highest among the cements studied here. MH4 has a high C_3A content as well, but it is predominately in the orthorhombic form. It appears that cements with high C_3A content expand less for the same sulfate contents.

In general, increasing sulfate content is expected to increase the expansion experienced by cements due to a corresponding increase in ettringite formation. This can be seen from quantification of ettringite that was conducted using x-ray diffraction and Rietvield analysis as depicted in Figure 7 and 8 for cements C and E. Ettringite was detected as early as 8 hours counted from mixing cement with water. This work also indicated the persistence of gypsum up to 24 hours for mixes with 5% sulfate. However, gypsum completely disappeared by an age of 3 days. This late persistence of gypsum is indicative of late ettringite formation beyond the plastic stage. This effect implies that the later formation into the hardened stage can generate more direct expansion than if ettringite formation was restricted to the plastic stage of concrete hardening. Though both of the examined cements are characterized by similar lower tricalcium aluminate content, they have a significant difference in their tricalcium silicate content. It appears from the data collected here that ettringite formation and expansion are more for Cement C that has higher tricalcium silicate content. Ettringite formation requires in addition to aluminates, calcium ions which is expected to be ample for cements higher in their tricalcium silicate content.

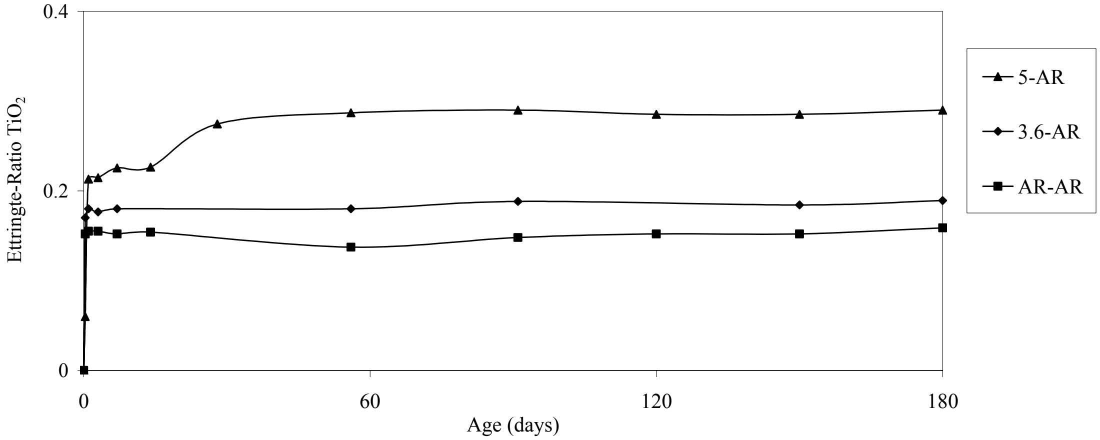


Figure 7: Effect of Sulfate Content on Ettringite Formation in Cement C

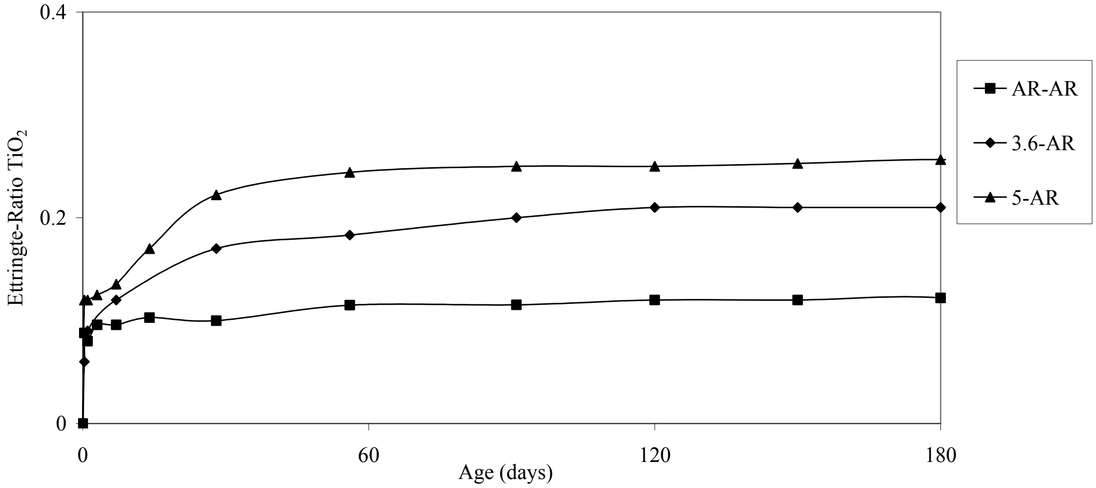


Figure 8: Effect of Sulfate Content on Ettringite Formation in Cement E

3.2 Compressive Strength

In addressing the role of sulfates on durability, mortar cubes were prepared. Each testing data point reflects an average for 3 mortar cubes. All specimens and testing procedures followed appropriate ASTM specifications. The results are depicted in Figures 9 through 13.

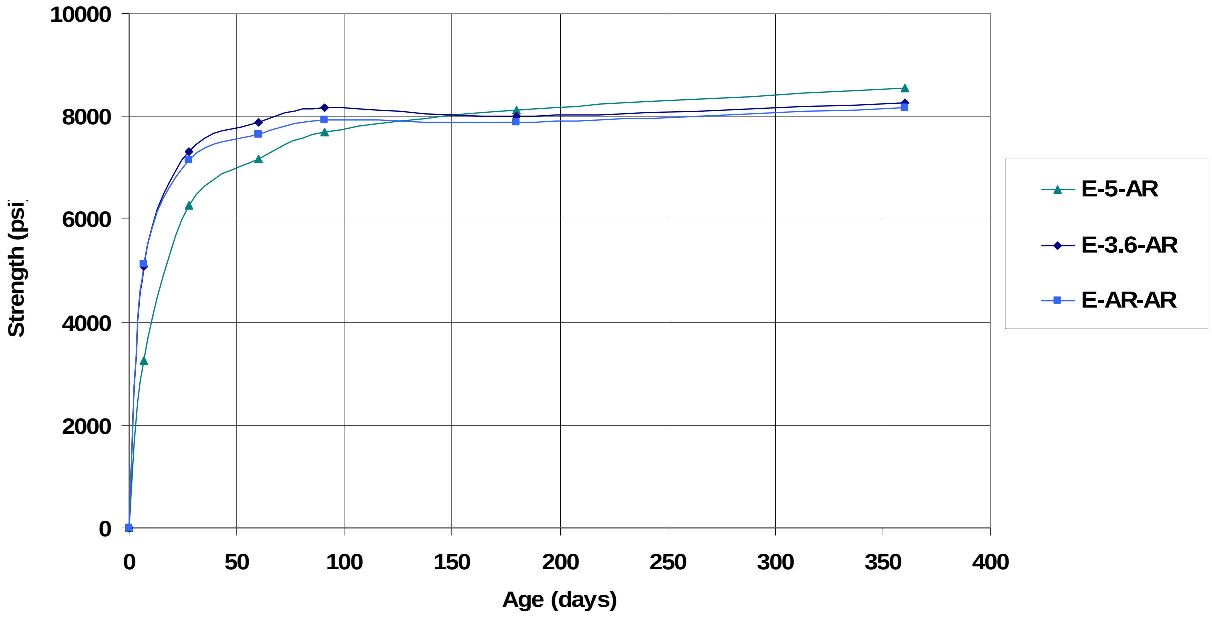


Figure 9: Effect of Sulfate Content on Strength Gain for Cement E

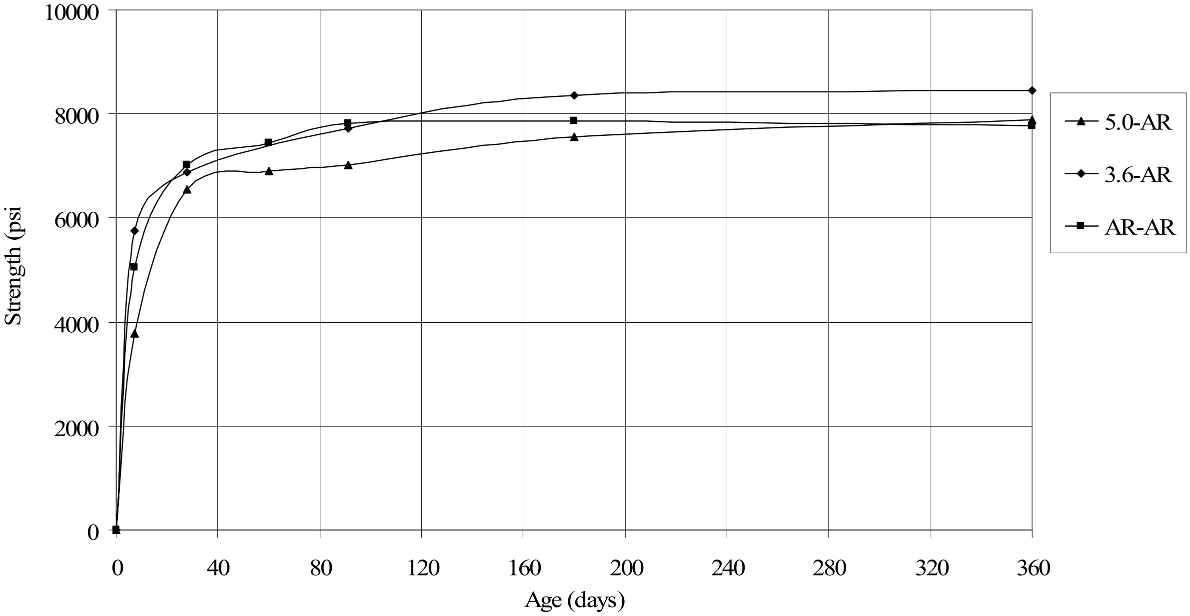


Figure 10: Effect of Sulfate Content on Strength Gain for Cement C

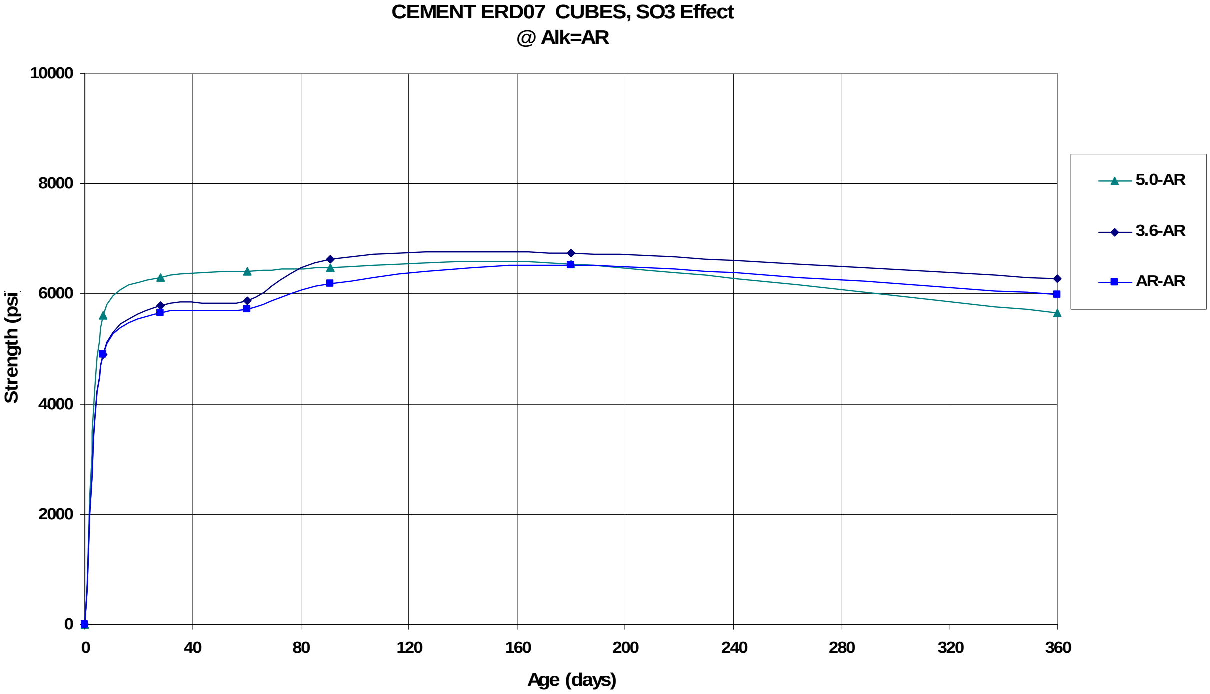


Figure 11: Effect of Sulfate Content on Strength Gain for Cement ERD07

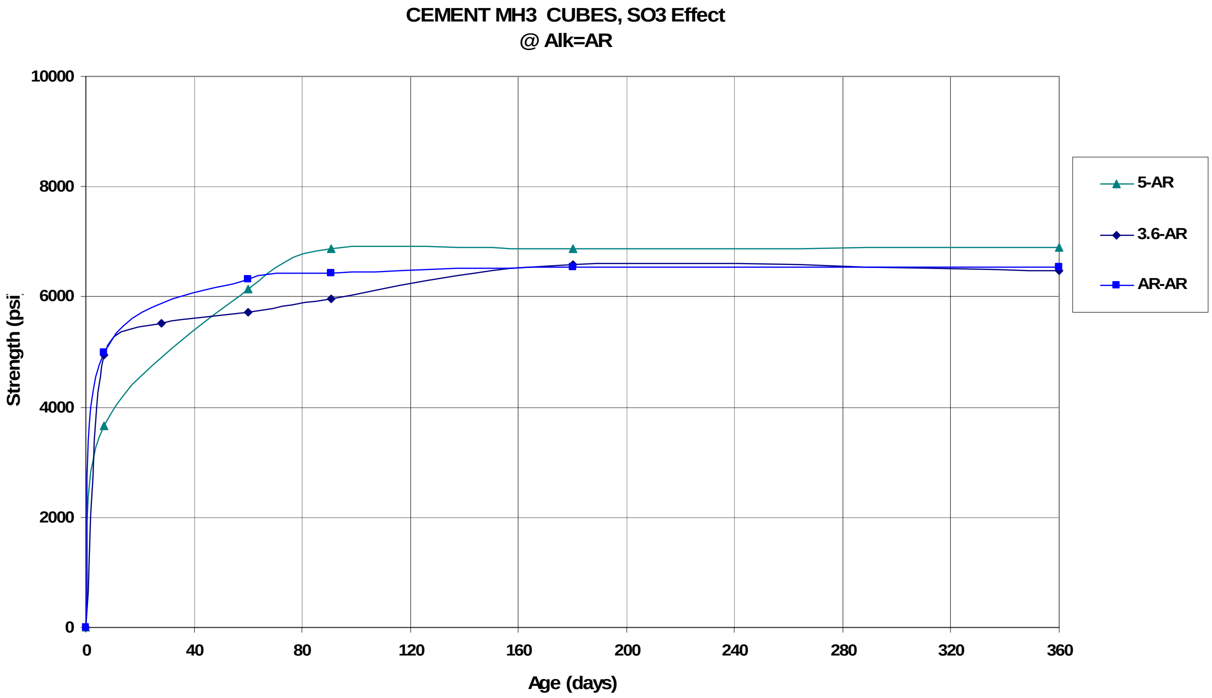


Figure 12: Effect of Sulfate Content on Strength Gain for Cement MH3

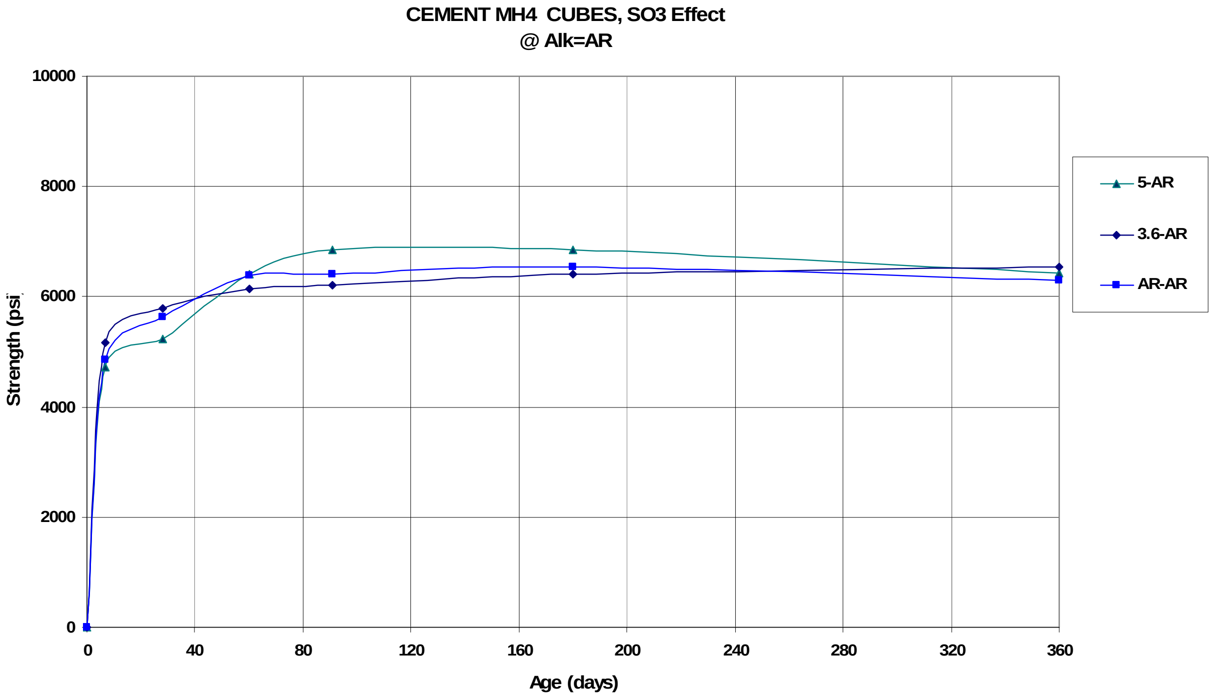


Figure 13: Effect of Sulfate Content on Strength Gain for Cement MH4

Strength data indicates that for cements with higher tricalcium aluminate content, increasing sulfates to 5% SO_3 did not have a positive contribution to long term strength at 360 days. This can be observed when considering the strength gain curves for cements ERD07 and MH4. Beyond 180 days, the both cements experienced strength loss at this level of sulfate. It is to be remembered that both cements have 9 and 10% tricalcium aluminate content respectively.

X-ray diffraction patterns collected for cements C and E depicted the effect of sulfate content on the rate of hydration of alite as can be seen from Figures 14 and 15. The effect of sulfate content on the rate of hydration of tricalcium silicate was appreciable within the first 24 hours with the rate decreasing with an increase in sulfate content. Beyond 7 days, differences in amounts of unreacted tricalcium silicates seem to be negligible.

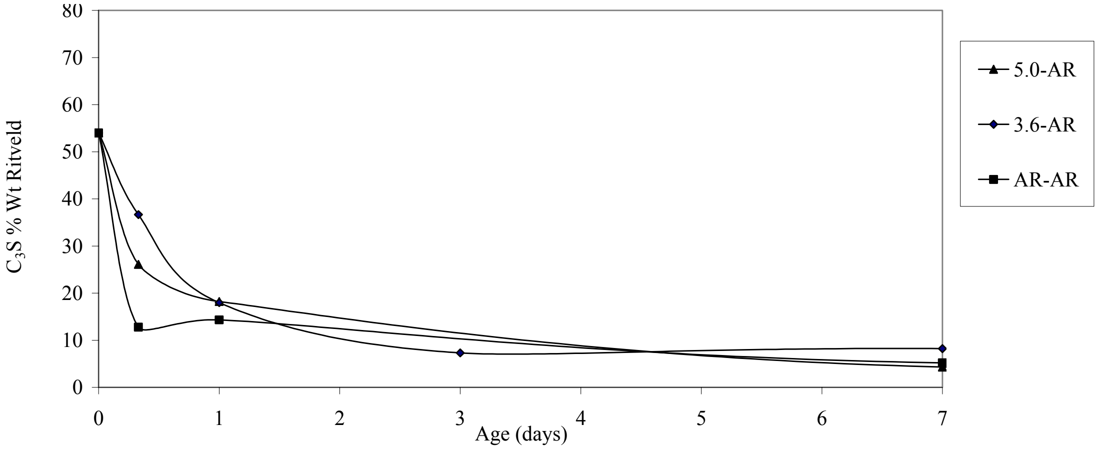


Figure 14: Effect of Sulfate Content on C_3S Hydration in Cement E

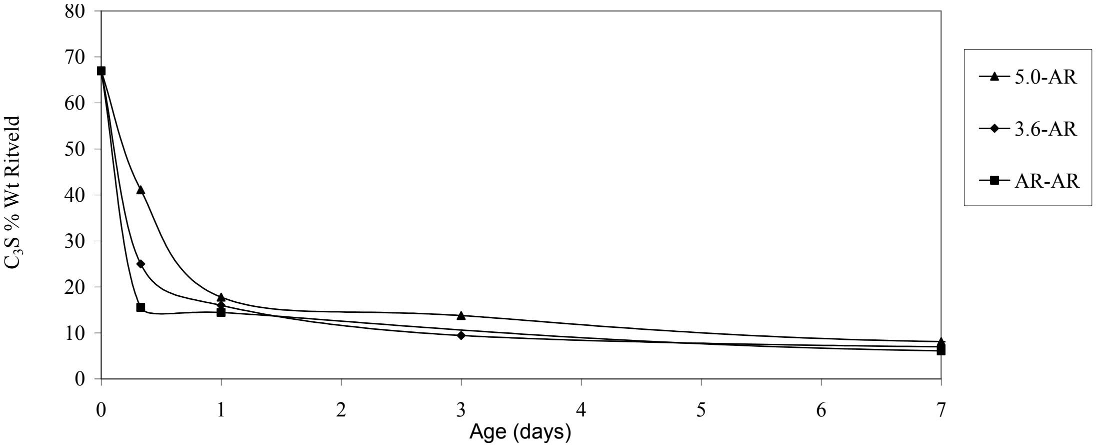


Figure 15: Effect of Sulfate Content on C_3S Hydration in Cement C

From diffraction data, the amorphous content of the hydration products could also be determined. Typically, it is attributed to C-S-H gel formations. The data indicate that increasing sulfate content of cements decreases the amorphous content or nature of the hydration products. This can possibly have an effect on mortar strength due to existence of weaker cleavage planes in gels with higher degree of crystallinity.

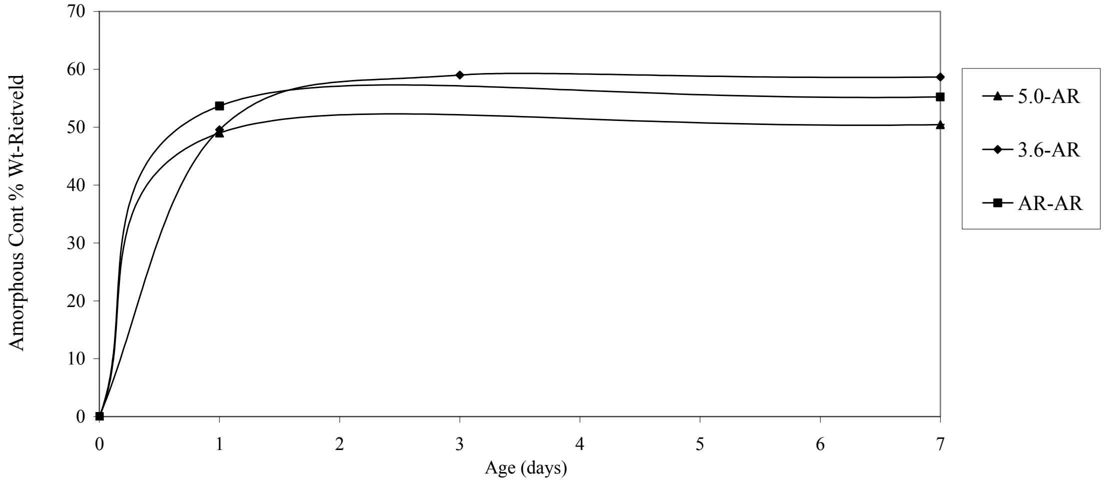


Figure 16: Effect of Sulfate Content on Formation of Amorphous Content for Cement E

Data analysis indicates that increasing sulfates in the as-received cements has a variable effect depending on cement mineralogy and oxides. To further our understanding of the effects of increasing cement sulfate content on its behavior, solution chemistry was also studied. Such study assists in addressing the effectiveness of sulfates on ion dissolution and phase formation. Figures 17 and 18 show the results collected on cements E and C sulfate ions concentration.

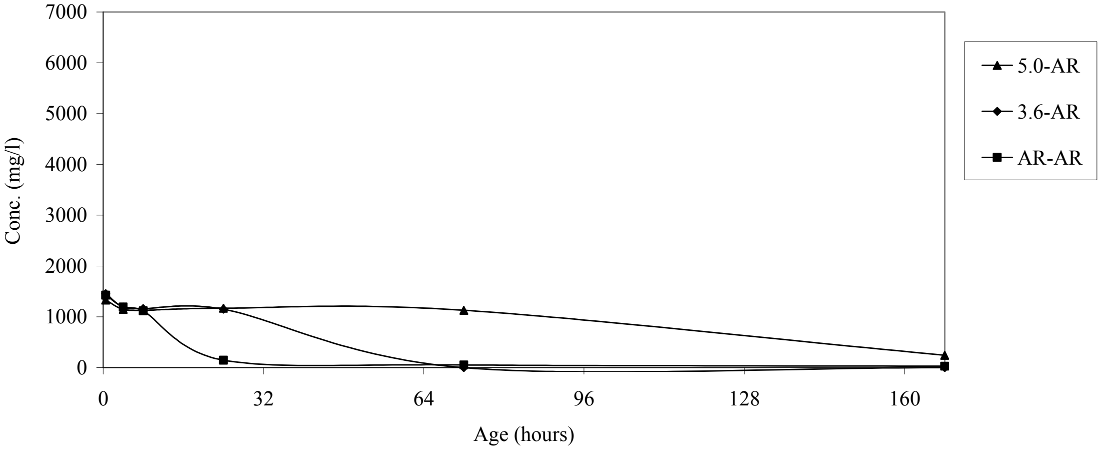


Figure 17: Effect of Sulfate Content on SO_4^{-2} Concentration for Cement E

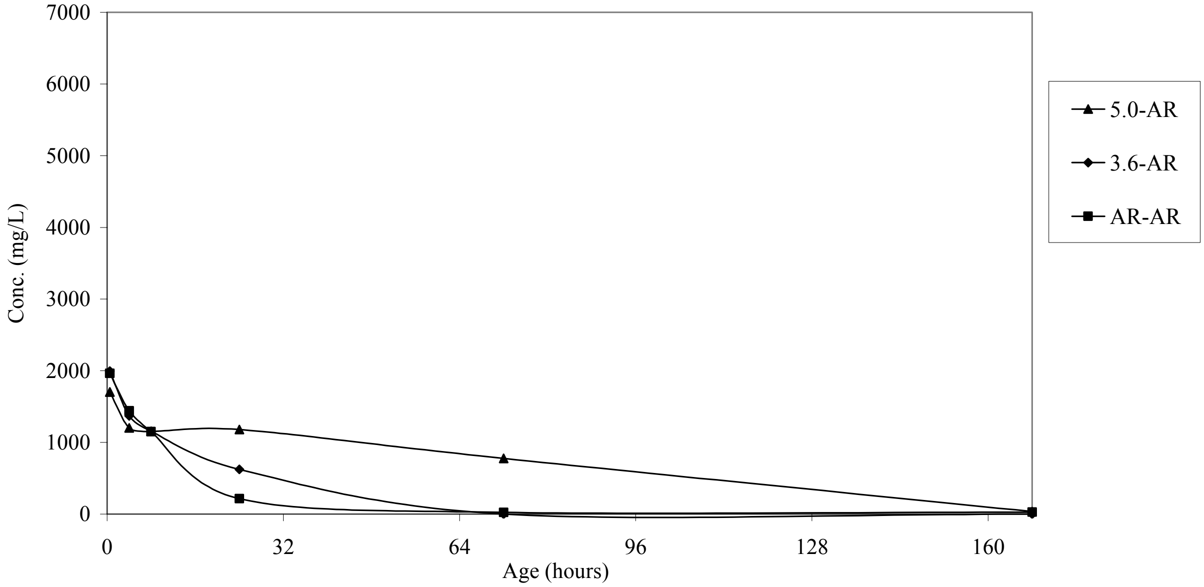


Figure 18: Effect of Sulfate Content on SO_4^{-2} Concentration for Cement C

Figures 17 and 18 show the variation of sulfate ion concentration within the first few days for Cements C and E. Both cements showed similar profiles for all sulfate levels for the first eight hours. The main distinction is the amount of dissolved sulfates for the 5% case. This is in agreement with the findings from diffraction analysis where it was indicated that there was a delay in sulfate dissolution as evident from the persisting gypsum peak up to 24 hours of age.

In regards to ettringite formation, x-ray data analysis and sulfate depletion studies indicate that ettringite formation continued after sulfates were depleted from solution. In accordance with XRD studies, ettringite continued to form up to 28 days while solution analysis indicates depletion of sulfates at 160 hours. This implies that sulfates required for further ettringite formation might come from another source, other than through solution. An example of such source can be C-S-H gel.

4. Role of Alkalis

In addressing the role of alkalis on structural elements durability, potassium hydroxide was used as a doping agent to vary the alkali content. In addition to studying the effects of variable alkali content on cement, sulfates were also varied to two concentrations: 3.6% and 5% in addition to the as-received content. The alkali content that was studied here for all specimens are: as-received, 1.5 and 2.0%. For selected cements, a higher alkali content of 3.8% was used in order to establish alkali effect at excessive high concentration within a period of one year. Mortar prisms and cubes were also prepared to assess the effect of alkali content on compressive strength and durability. In addition, paste specimens were also prepared for analytical work aimed to understand and interpret durability data. The results are depicted in Figures 19 through 24.

4.1 Expansion

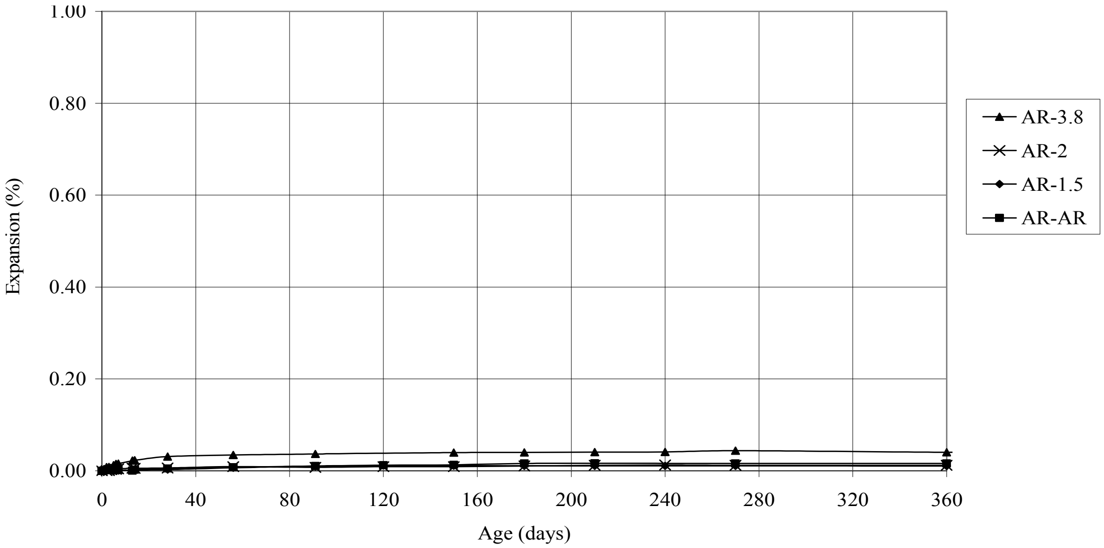


Figure 19: Effect of Alkali on Expansion Behavior for Cement E-SO_3=AR

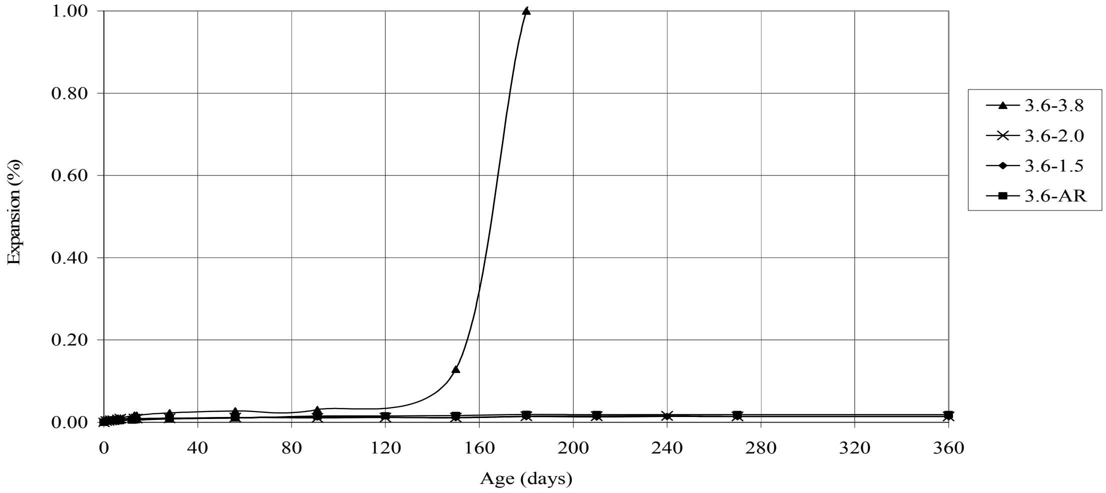


Figure 20: Effect of Alkali on Expansion Behavior for Cement E-SO_3=3.6%

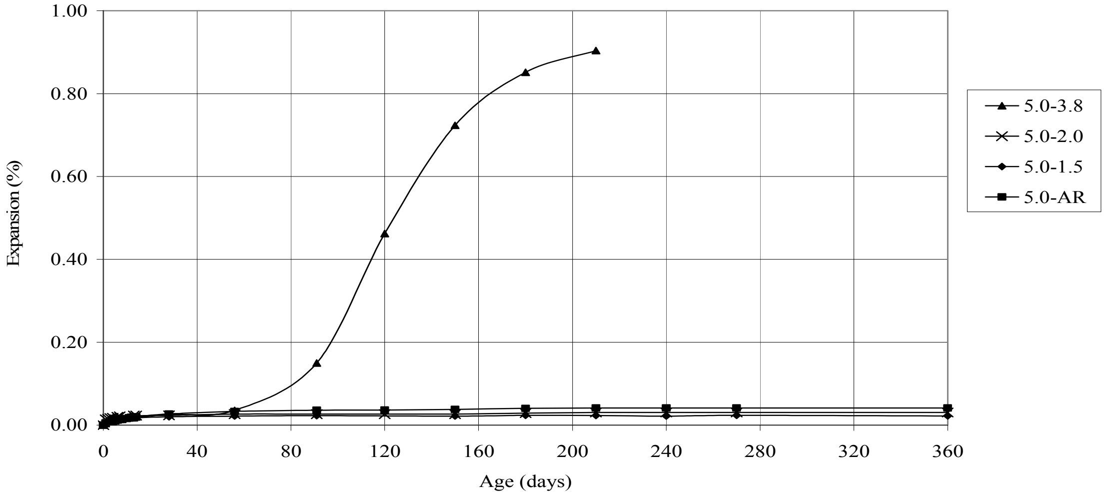


Figure 21: Effect of Alkali on Expansion Behavior for Cement E-SO_3=5.0%

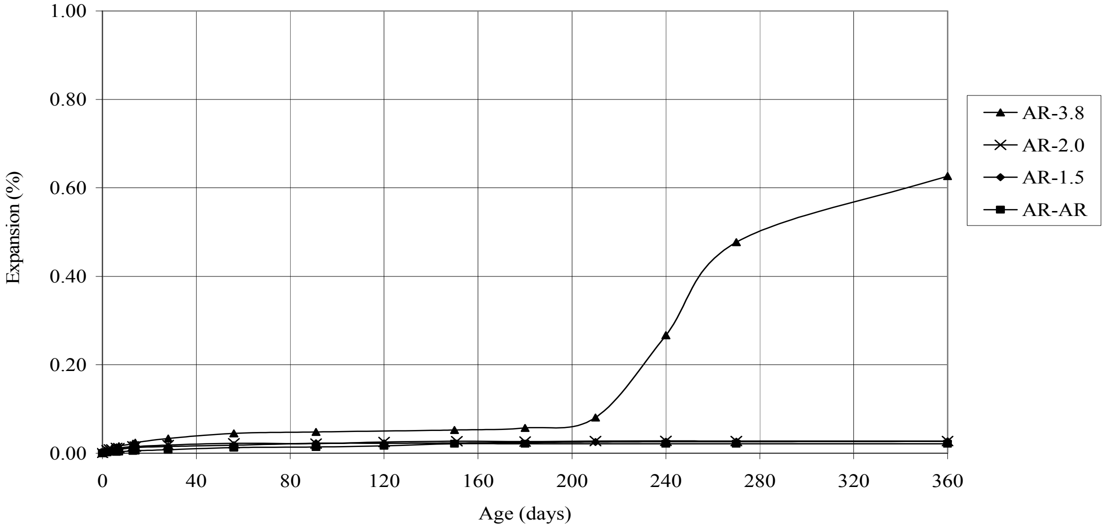


Figure 22: Effect of Alkali on Expansion Behavior for Cement C-SO_3=AR

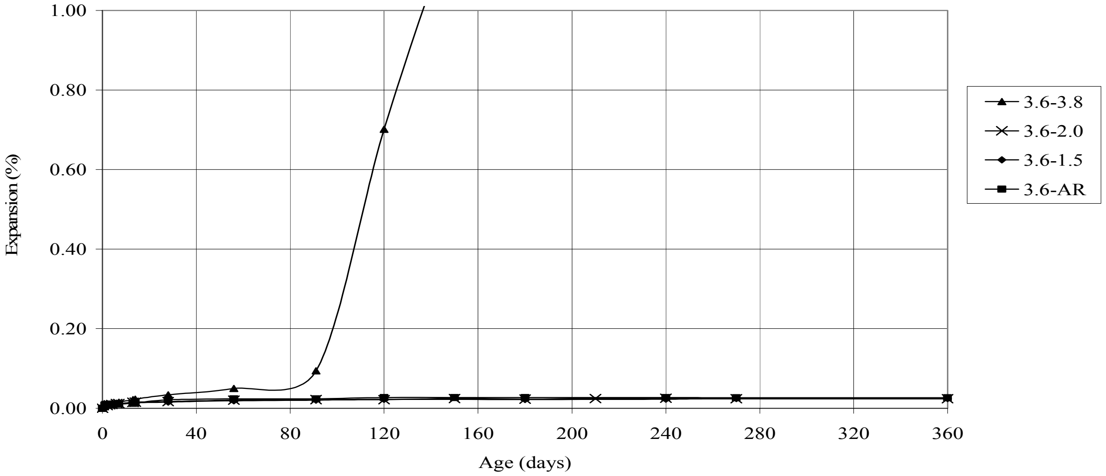


Figure 23: Effect of Alkali on Expansion Behavior for Cement C-SO_3=3.6%

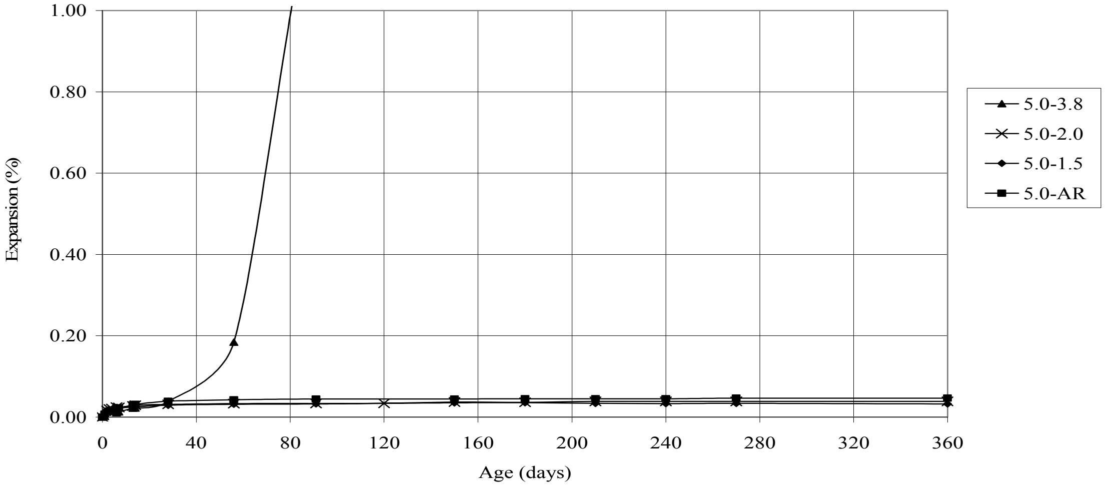


Figure 24: Effect of Alkali on Expansion Behavior for Cement C-SO_3=5.0%

Figures 19 through 24 show the expansion patterns for both cements E and C at all doping levels. As observed earlier where sulfates varied but and no alkali additions; that is as-received content, expansion increased with increasing sulfate content at the same alkali level. For cement E, the expansion for the 5-AR case was just above .04%, and about .016 for the AR-AR case, case 3.6-AR showed an expansion of just above .018%. Expansion behavior for cement C followed the same trends observed for cement E with the exception that numerical values were higher.

Increasing the alkali level to 1.5, and 2% did not show significant effect on the expansion behavior for the ages reported here, for all three sulfate levels, for both cements. However, at 3.8% alkali content, deterioration in specimens was quiet apparent as early as 56 days. During early measurements, differences due to variation in alkali content could not be detected until 56 days for cement E. However, beyond this age, the onset of deterioration was sudden and rapid as evident for the abrupt increase in the expansion rate. An expansion of approximately 1.0% was reported for Cement E at 56 days. Mortar prisms started to crack at 180 days, as can be seen in Figure 25. Similar behavior was observed for Cement C with the only significant difference being the timing of rapid deterioration initiation occurring at a shorter time; that is, 28 days.

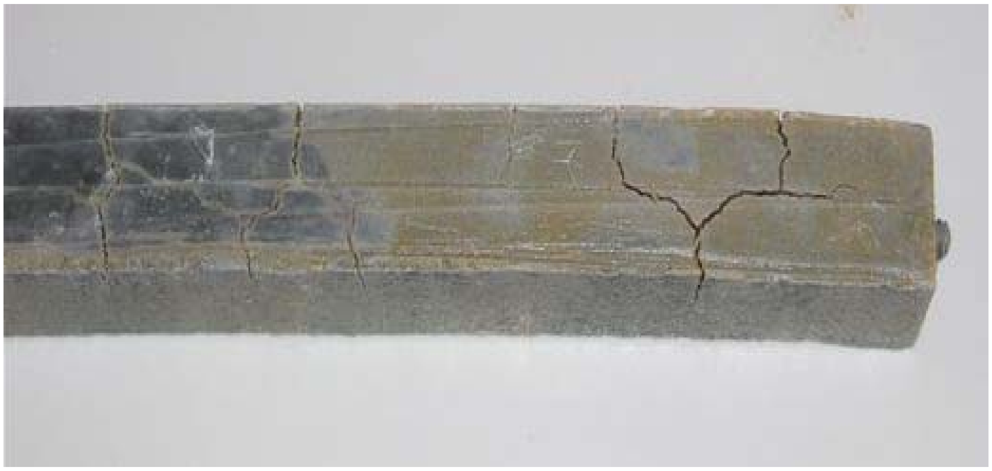


Figure 25**:** Mortar bar for cement E 5-3.8 at 180 days

The results presented here for both cements E and C indicates that expansion measurements using ASTM C1038 might not be sensitive to assessing alkali effects for durability considerations. Additionally, the results indicate that the alkali effect on durability is impacted by the sulfate and mineralogical composition of the cement. Increasing sulfate content increased expansion for the same alkali content. Expansion data indicates that the significance of alkalis on durability at 3 different sulfate levels appears to increase expansion. The increase is of significance only at an alkali level of 3.8% at all sulfate levels; that is, as-received, 3.6% and 5%. Increasing the alkalis or sulfate content had the effect of initiating rapid expansion in shorter time. Expansion data for cements MH3, MH4 and ERD07 are presented in Figures 26 through where it can be seen that no significant effect was observed for the alkali levels of 1.5 and 2%.

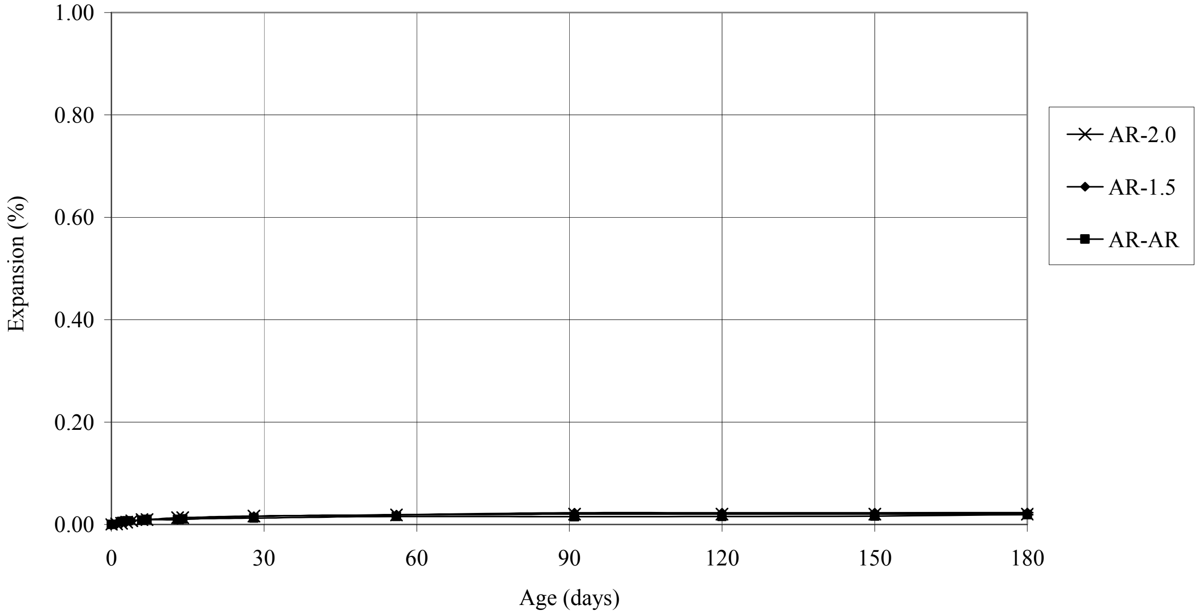


Figure 26: Effect of Alkali on Expansion Behavior for Cement MH3-SO_3=AR

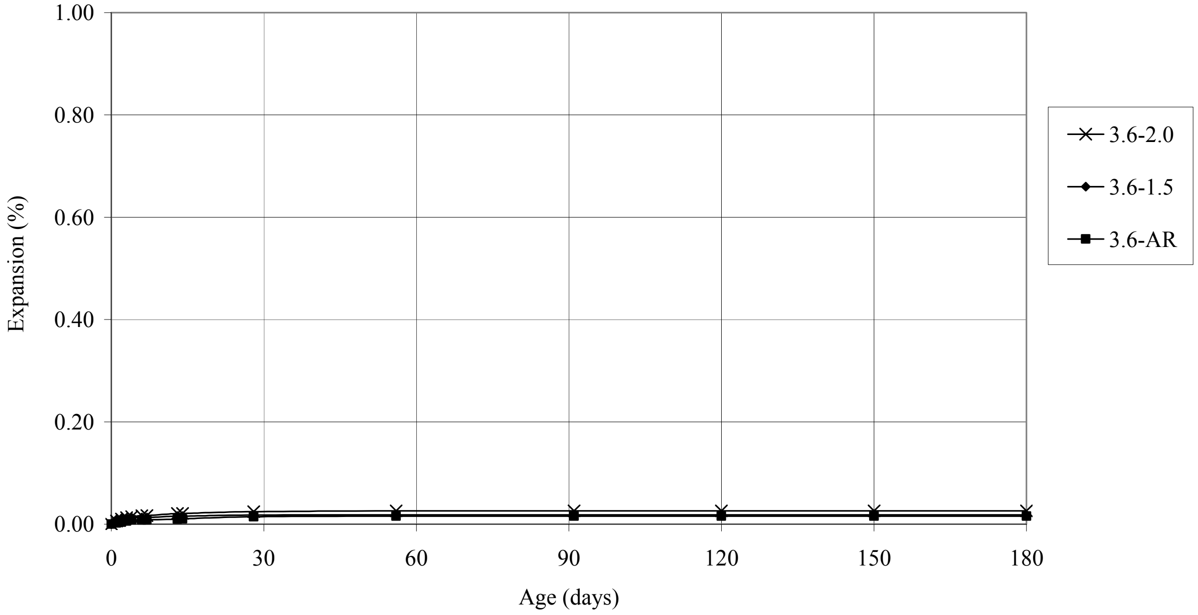


Figure 27: Effect of Alkali on Expansion Behavior for Cement MH3-SO_3=3.6%

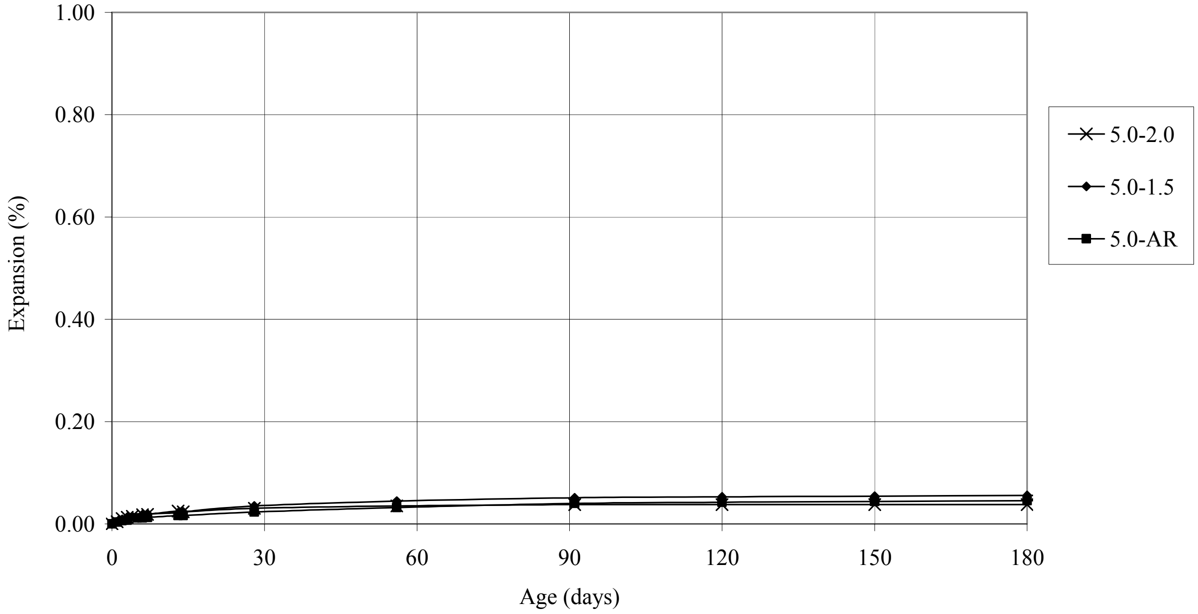


Figure 28: Effect of Alkali on Expansion Behavior for Cement MH3-SO_3=5.0%

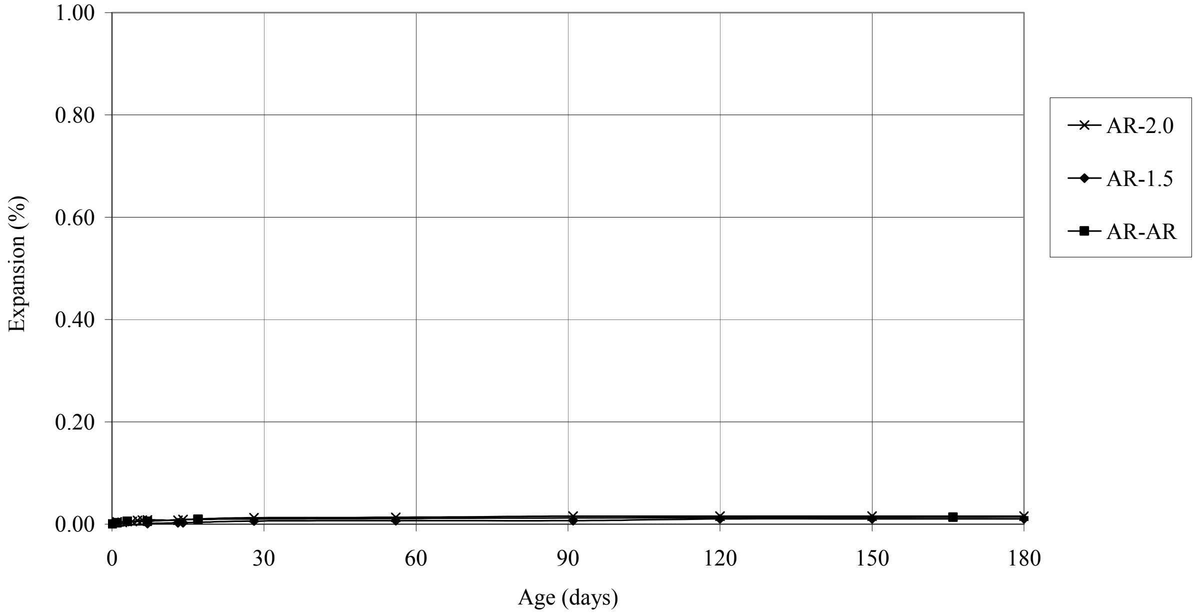


Figure 29: Effect of Alkali on Expansion Behavior for Cement MH4-SO_3=AR

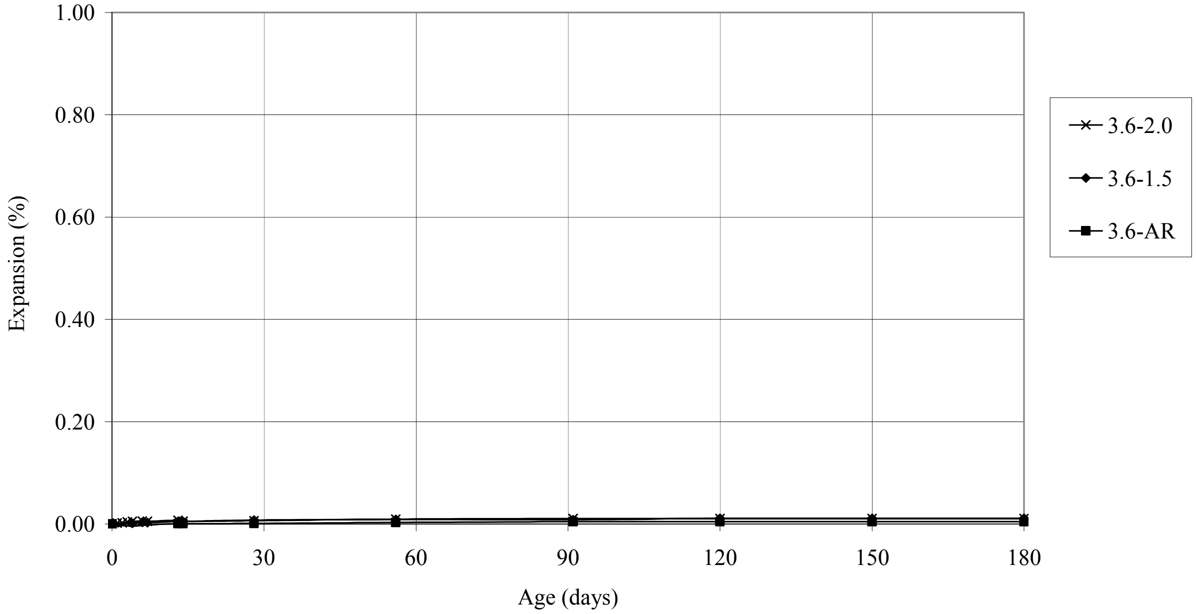


Figure 30: Effect of Alkali on Expansion Behavior for Cement MH4-SO_3=3.6%

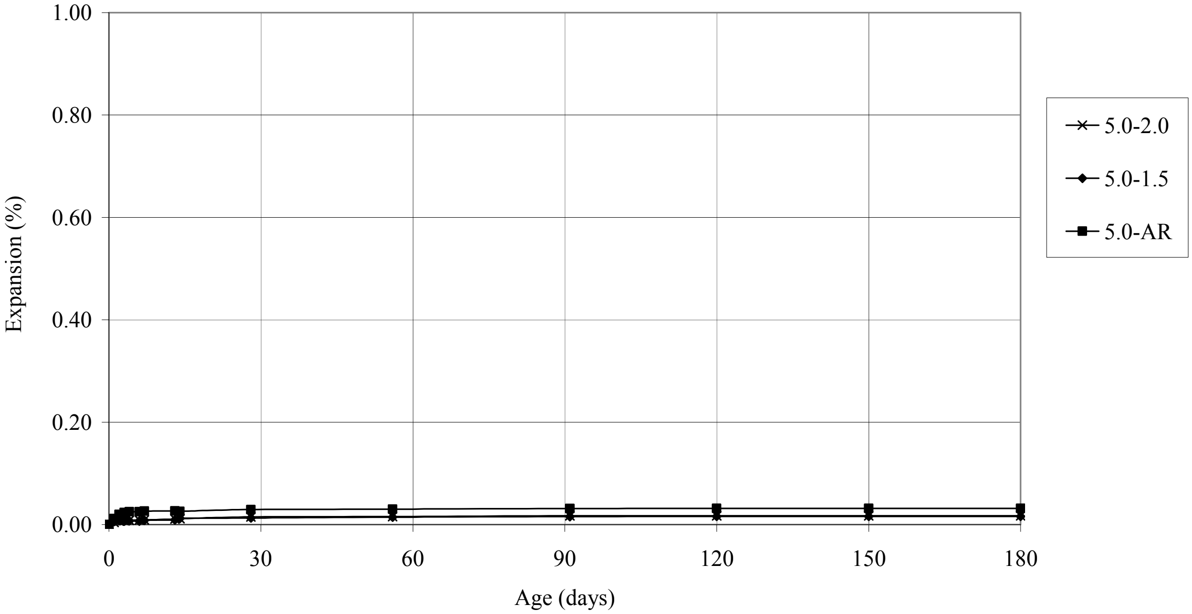


Figure 31: Effect of Alkali on Expansion Behavior for Cement MH4-SO_3=5.0%

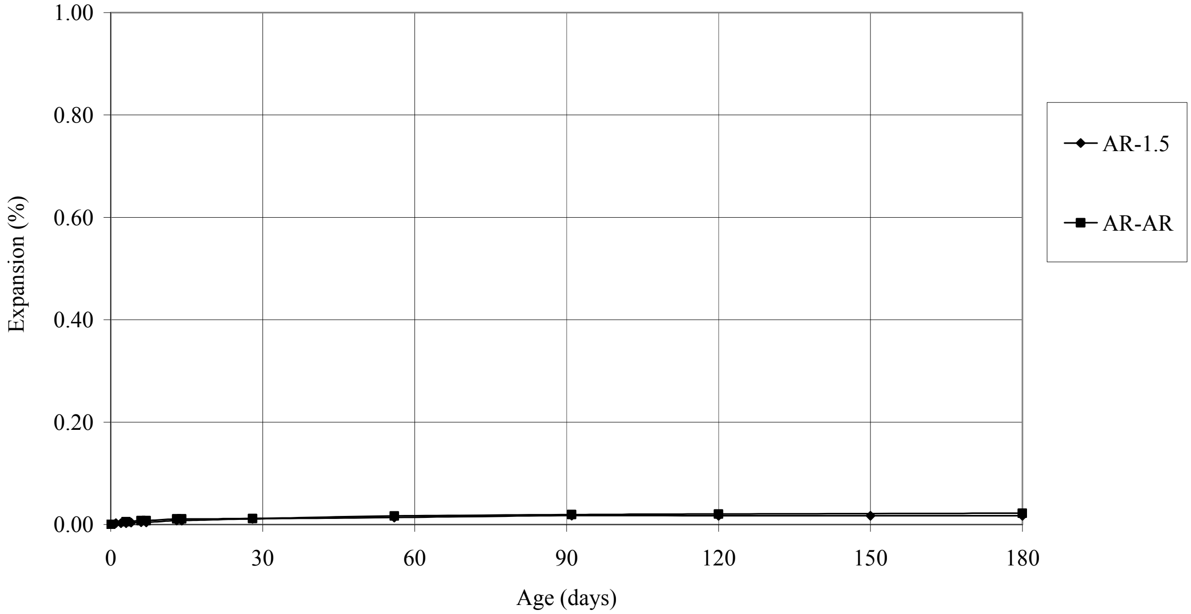


Figure 32: Effect of Alkali on Expansion Behavior for Cement ERD07-SO_3=AR

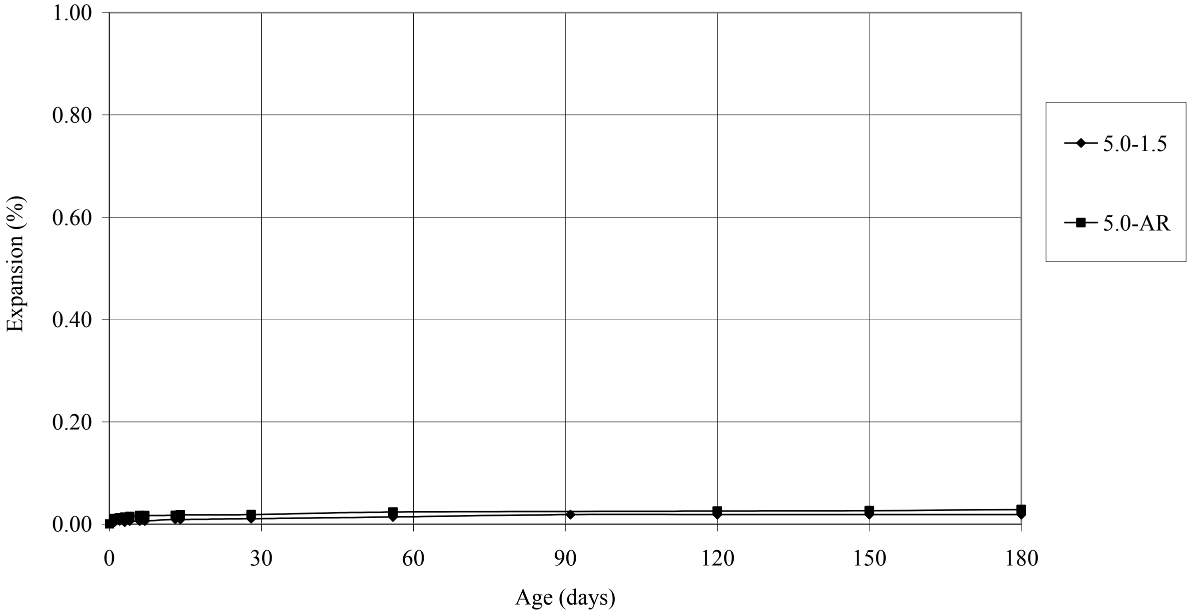


Figure 33: Effect of Alkali on Expansion Behavior for Cement ERD07-SO_3=5.0%

4.2 Compressive Strength

In addressing the role of alkalis on the durability of structural elements, compressive strength measurements were conducted for a period of a year at three different sulfate levels and several alkali content. The results are shown in Figures 34 through 46.

For cements C and E that share similar low alkali and triclaicum aluminate content, the alkali was varied from as-received to 1.5, 2.0 and 3.8%. It can be seen from Figures 34 through 39 that for all sulfate levels considered here, increasing the alkali content for constant sulfate content results in strength regression that can be as high as 4,000 psi (28 MPa) for cement E at an alkali content of 3.8% and sulfate content of 2.58% (AR) and 3.6% and 5,000 psi (35 MPa) for cement C. However, at an alkali content of 3.8% and sulfate content of 5%, the strength decreased from approximately 8,000 psi to approximately 2000 psi at an age of 180 days for both cements. Increasing the alkali content from the as-received condition for cements C and E results in similar trends. The significant difference between the trends observed here for those two cements is that for cement C regression started at an earlier age and at lower sulfate content. Cement C has significantly higher tricalcium silicate content in comparison to cement E (67% versus 54%).

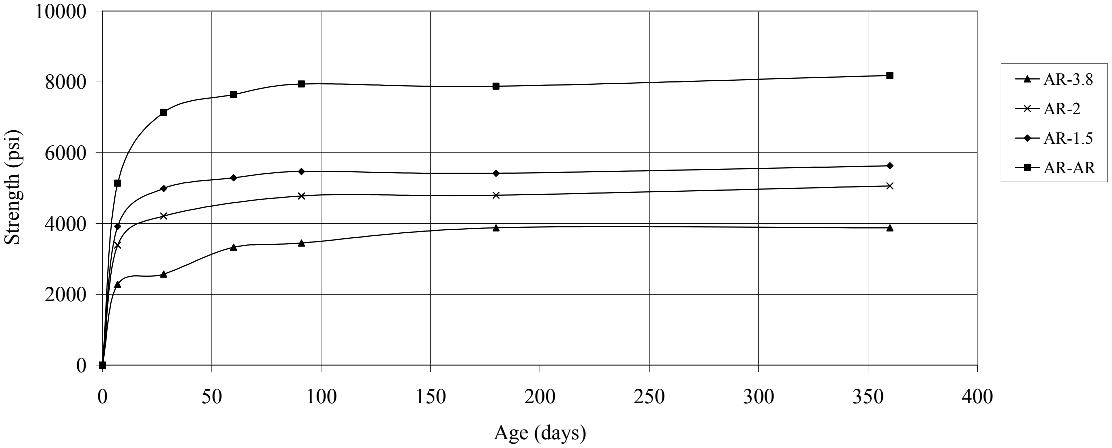


Figure 34: Effect of Alkali on Strength Gain for Cement E-SO_3=AR

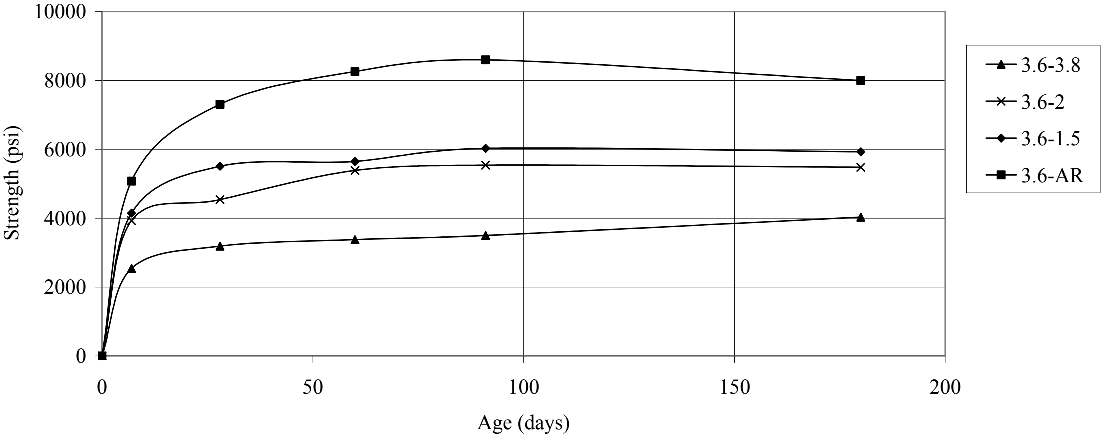


Figure 35: Effect of Alkali on Strength Gain for Cement E-SO_3=3.6%

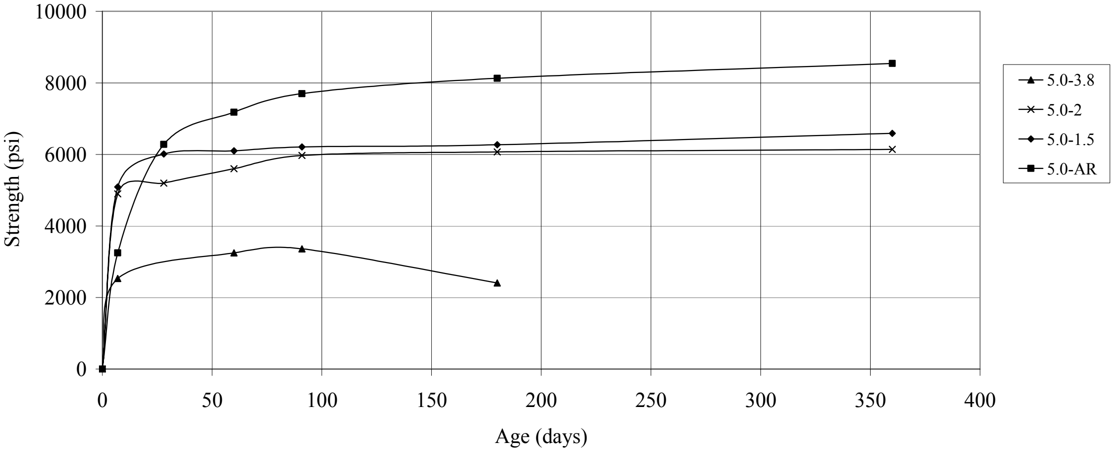


Figure 36: Effect of Alkali on Strength Gain for Cement E-SO_3=5.0%

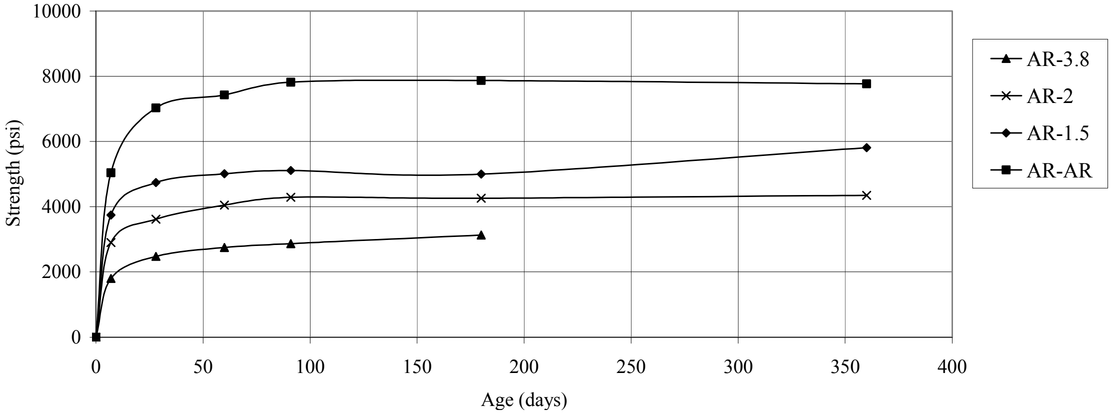


Figure 37: Effect of Alkali on Strength Gain for Cement C-SO_3=AR

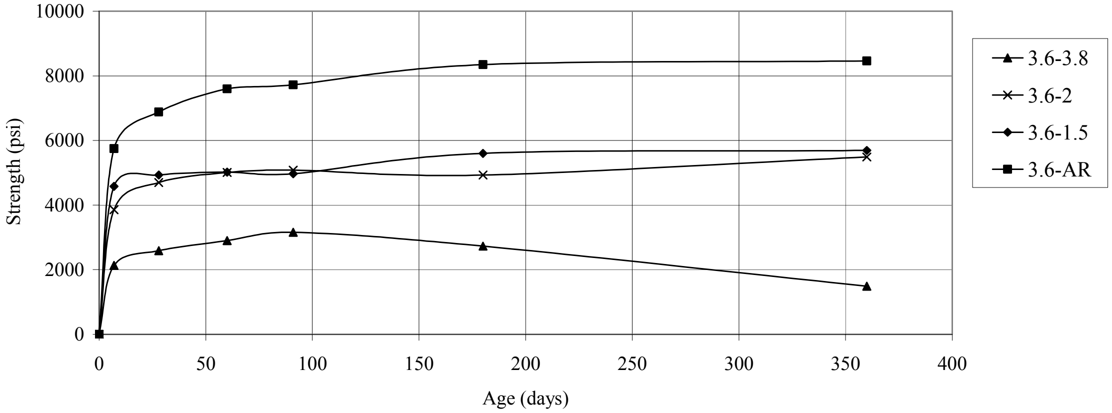


Figure 38: Effect of Alkali on Strength Gain for Cement C-SO_3=3.6%

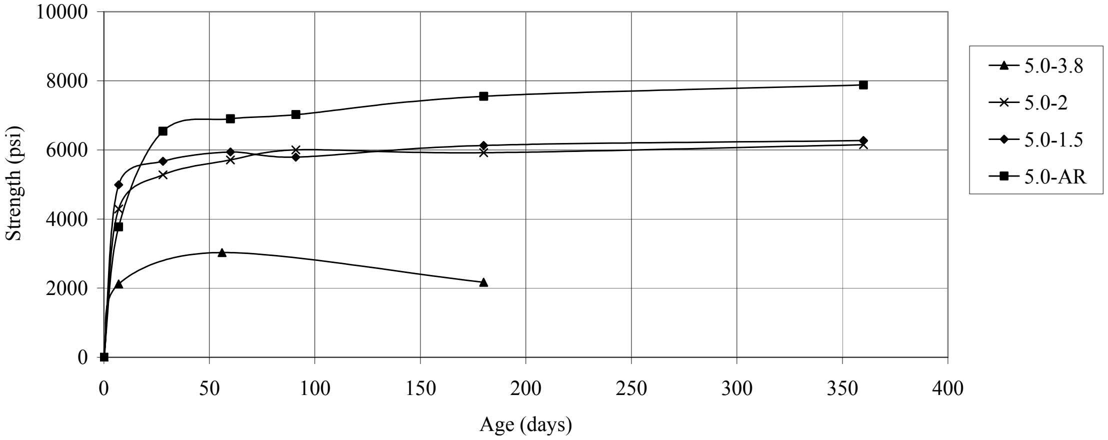


Figure 39: Effect of Alkali on Strength Gain for Cement C-SO_3=5.0%

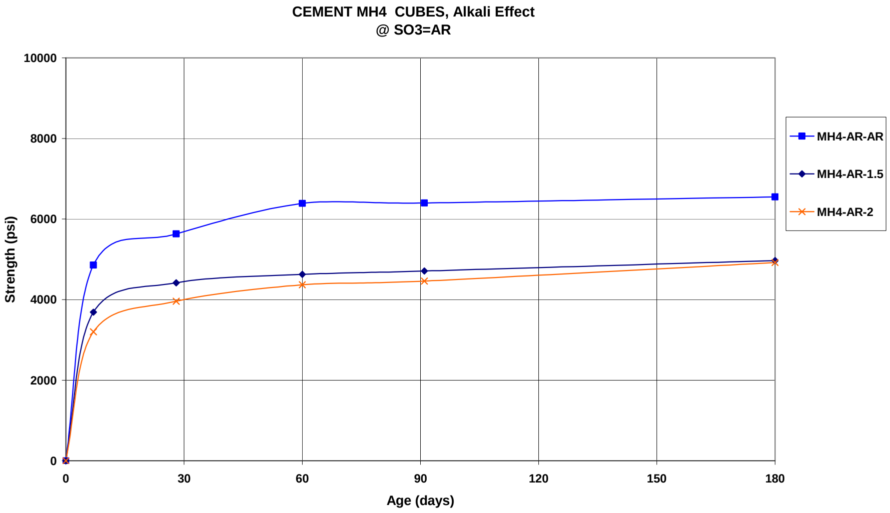


Figure 40: Effect of Alkali on Strength Gain for Cement MH4-SO_3=AR

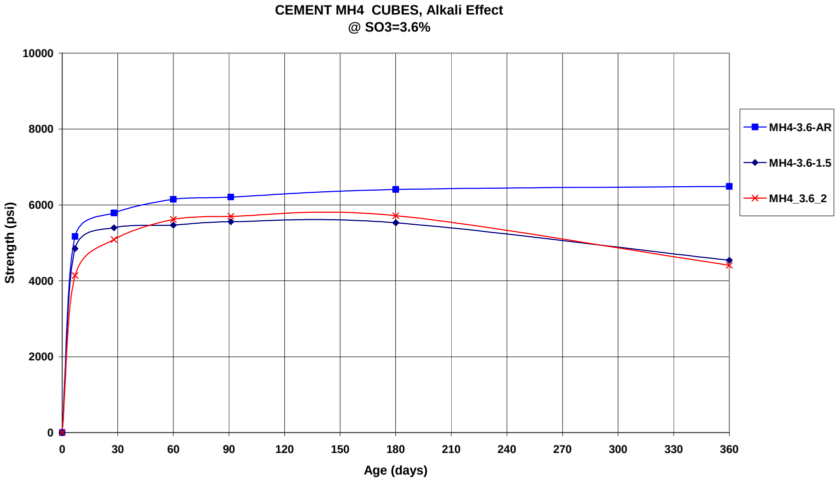


Figure 41: Effect of Alkali on Strength Gain for Cement MH4-SO_3=3.6%

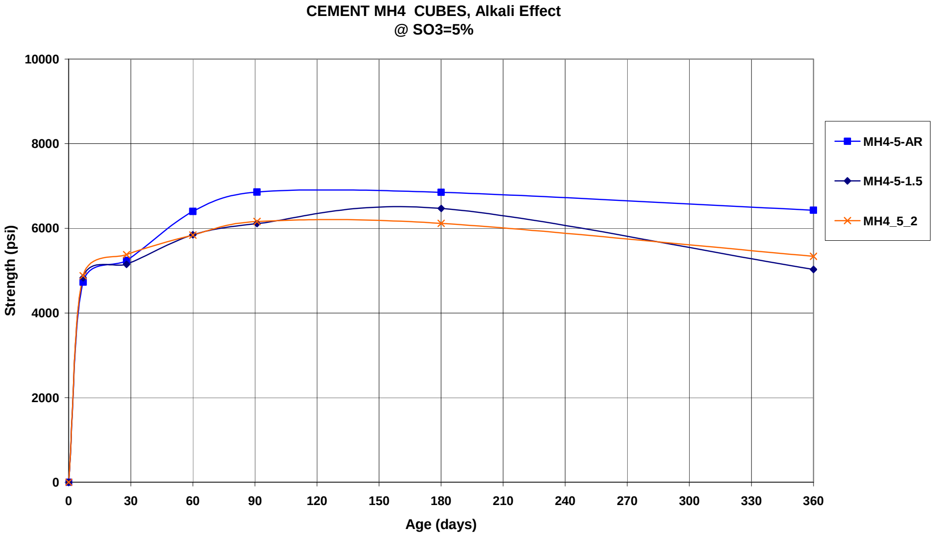


Figure 42: Effect of Alkali on Strength Gain for Cement MH4-SO_3=5.0%

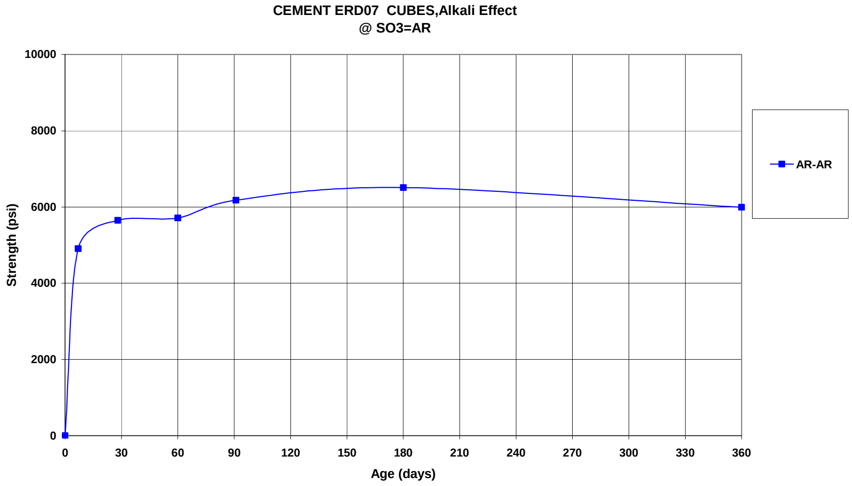


Figure 43: Effect of Alkali on Strength Gain for Cement ERD07-SO_3=AR

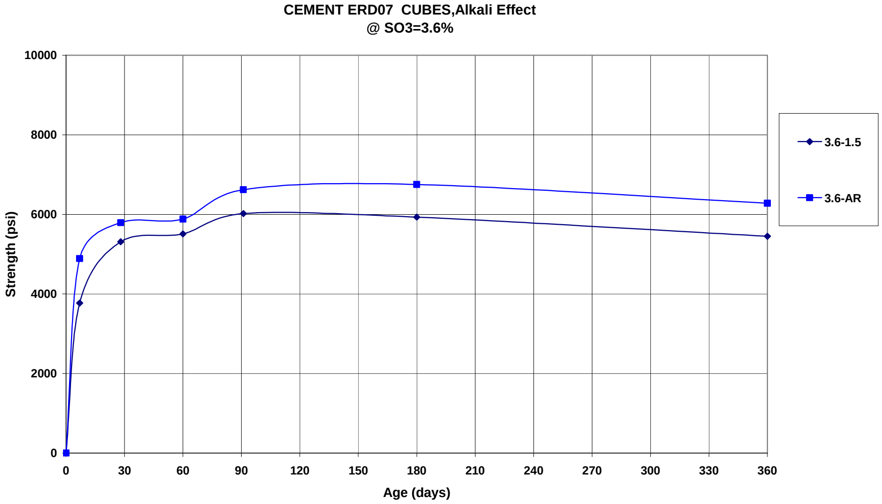


Figure 44: Effect of Alkali on Strength Gain for Cement ERD07-SO_3=3.6%

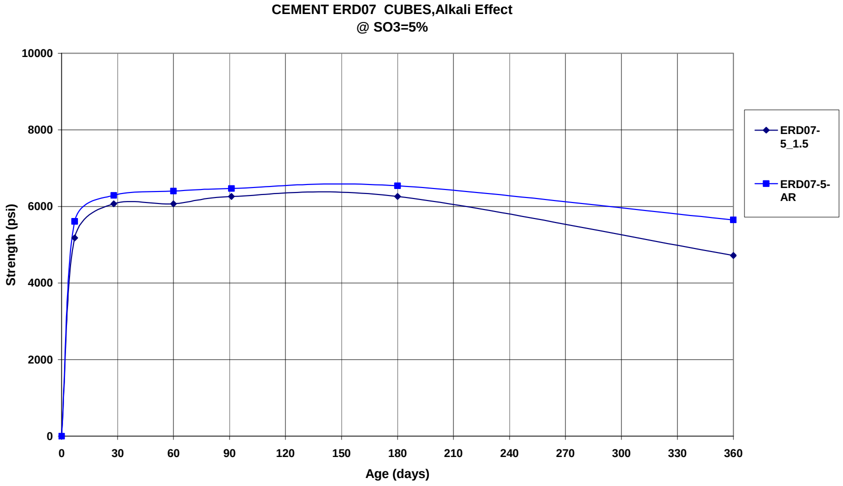


Figure 45: Effect of Alkali on Strength Gain for Cement ERD07-SO_3=5%

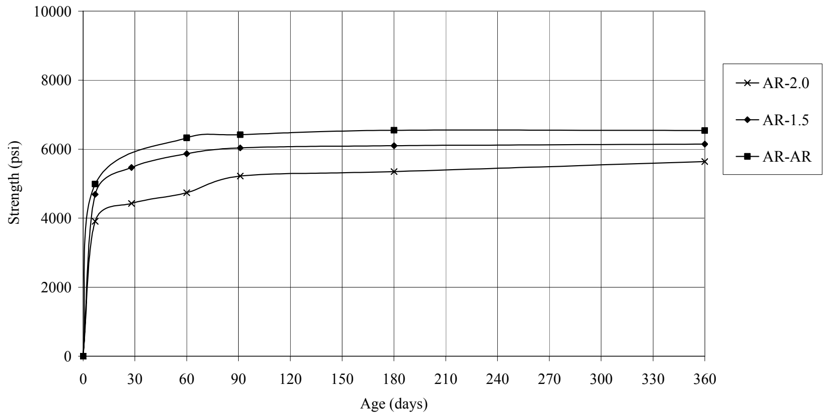


Figure 46: Effect of Alkali on Strength Gain for Cement MH3-SO_3=AR

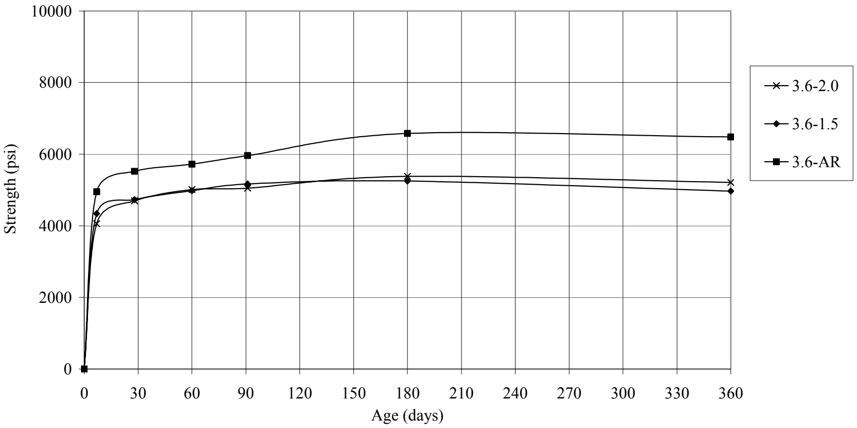


Figure 47: Effect of Alkali on Strength Gain for Cement MH3-SO_3=3.6%

Considering cements with high tricalcium aluminate and alkali oxides; that is cements MH4 and ERD07, it can be observed that increasing the alkali content at lower sulfate content results in a similar lower strength at all ages. Also, strength for both cements is significantly lower than cements E and C for all ages. Comparing Figures 34 and 37 for E and C cements with Figure 40 for MH4 cement, it can be concluded that the behavior of cements is quiet similar. However, this is not true for higher sulfate contents. In those cases, when alkali content was increased to 1.5 and 2% for MH4, at sulfate content of 3.6 and 5%, the effect of increasing alkali content on strength values beyond 180 days was noted as a strength drop of approximately 1,000 psi at 360 days compared to 90 days strength. Similar observations were noted for cement ERD07 with an as-received alkali and sulfate content of 1.03% and 3.47%, respectively. Such drop was only observed for cements E and C at an alkali content of 3.8%.

The effect of alkali content on compressive strength does not appear to be positive. Increasing the alkali content, at a constant sulfate level, results in a decrease in the compressive strength of mortar. Strength deterioration trends appear to be dependent on cement composition. For cements with higher tricalcium aluminates, the effect is more pronounced at sulfate levels of 3.6% and 5% and alkali content as low as 0.83%. For cements with low tricalcium aluminate content, increasing the alkali content results in an immediate decrease in strength. Additional regression was only reported at much higher alkali level, 3.8%.

It is rather interesting to note that while strength data indicate the significance of alkali content on durability, expansion measurements in accordance with ASTM C1038 showed no significant effects of higher alkali content on durability.

4.3 X-Ray Diffraction

X-ray diffraction was used to follow phase formation and transformation during different stages of hydration. Results [Figures 48 through 51] indicate that while increasing sulfates results in an increase in the amount of ettringite, addition of alkalis did not. The main effect of increasing the alkali content was in delaying ettringite formation. This is in agreement with the findings in the literature where it is indicated that ettringite is unstable at high pH [1]. The timing of formation appears to be dependent on the sulfate content of the cement. Increasing the sulfate content of as-received cement appears to alleviate the effects of alkalis on delaying ettringite formation as can be seen in Figures 50 and 51 for cement C. The effect of pH on ettringite formation will subsequently affect sulfate distribution in other phases. Additionally it will have its consequences on durability especially if conditions become favorable for its formation at later age, beyond the plastic stage of concrete hardening.

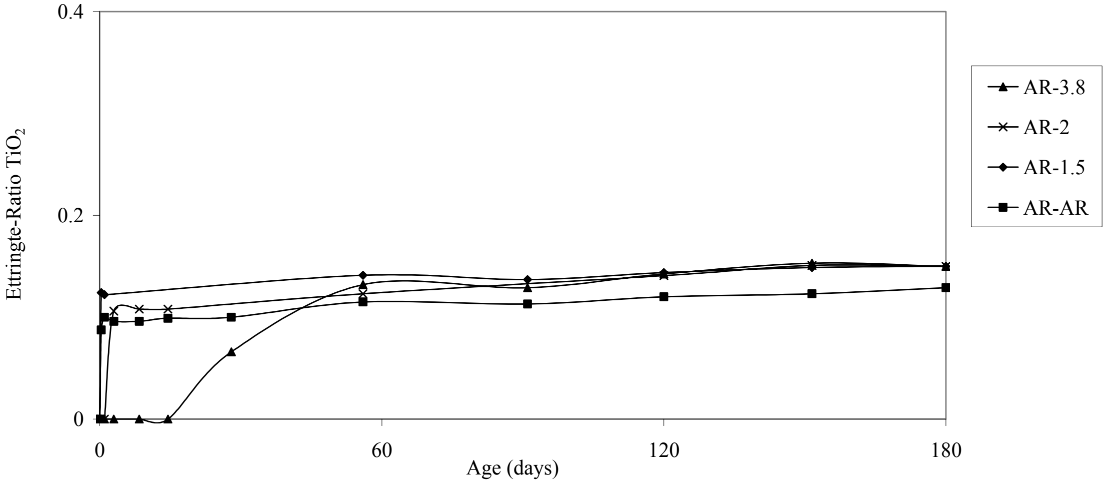


Figure 48: Effect of Alkali on Ettringite Formation for Cement E-SO_3=AR

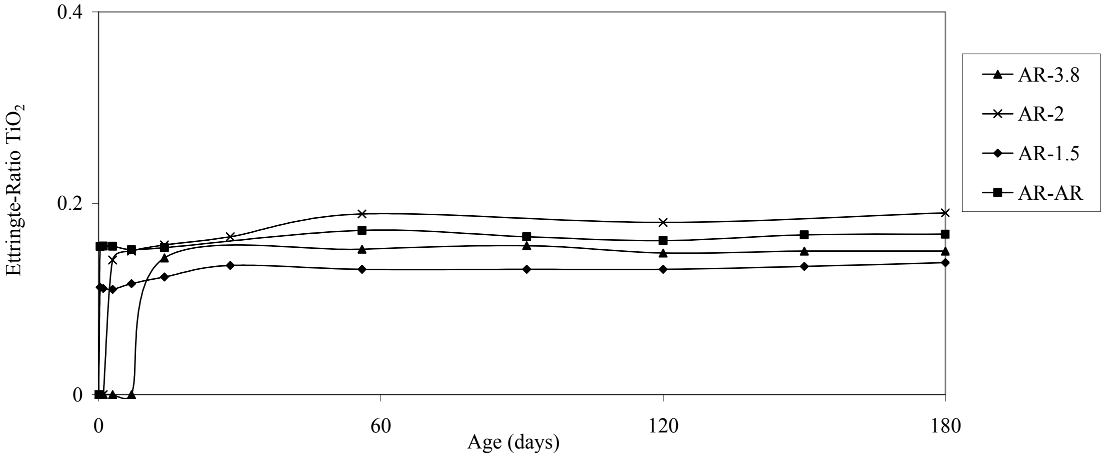


Figure 49: Effect of Alkali on Ettringite Formation for Cement C-SO_3=AR

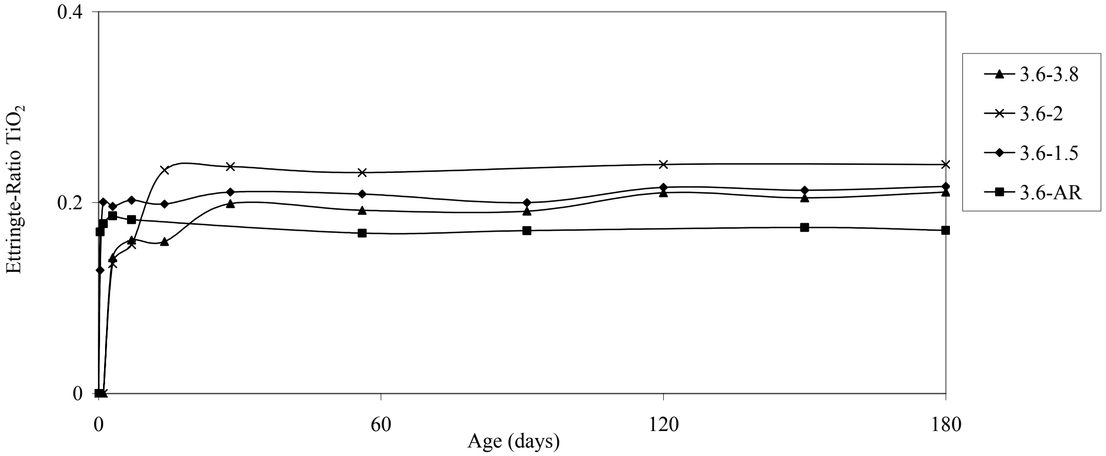


Figure 50: Effect of Alkali on Ettringite Formation for Cement C-SO_3=3.6%

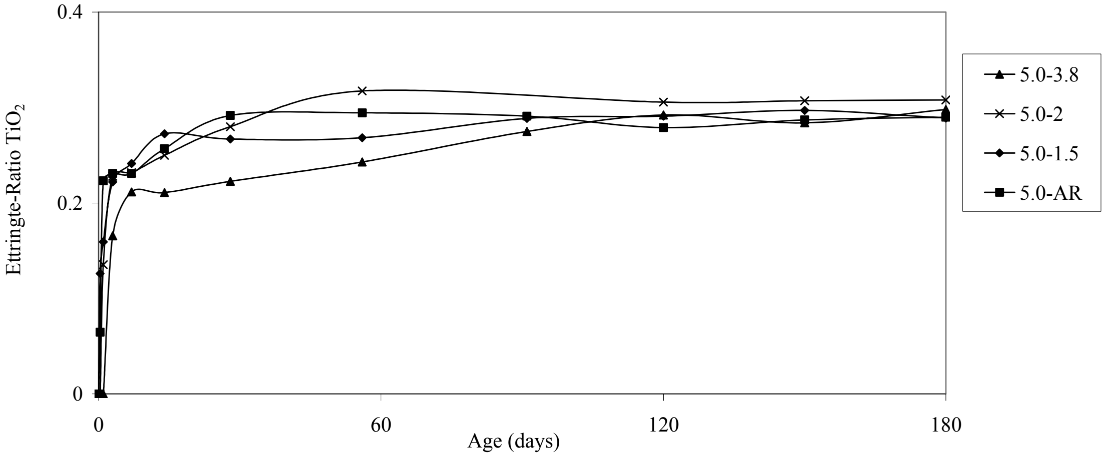


Figure 51: Effect of Alkali on Ettringite Formation for Cement C-SO_3=5.0%

Diffraction patterns and Rietveld analysis on hydration phases indicates that increasing the alkali content, increases the amount of calcium hydroxide. The results are depicted in Figures 52 through 57 for cements C and E at several sulfate and alkali concentrations. The findings do not necessarily indicate a faster rate of hydration for tricalcium silicate. Previous research [49] indicates the effectiveness of higher alkalinity on reducing the solubility of calcium hydroxide.

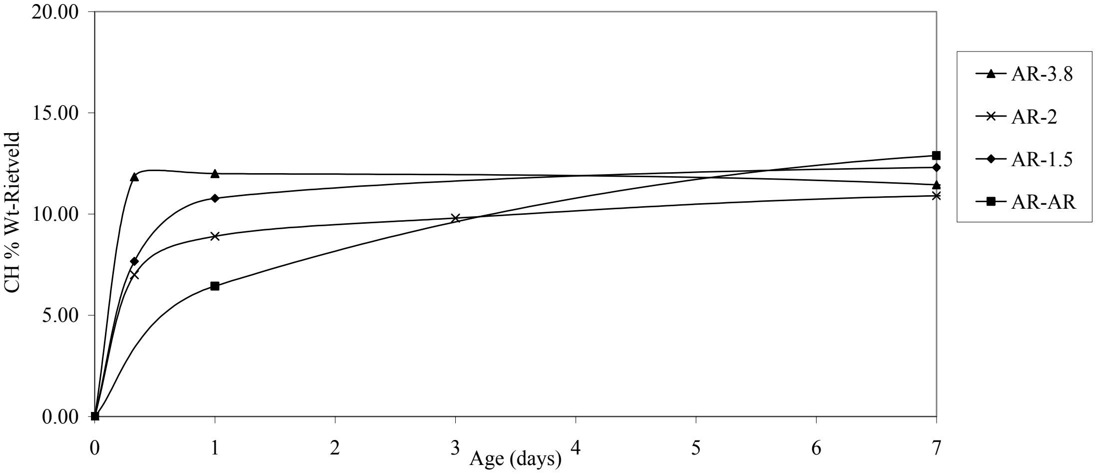


Figure 52: Effect of Alkali on Calcium Hydroxide Formation for Cement E-SO_3=AR

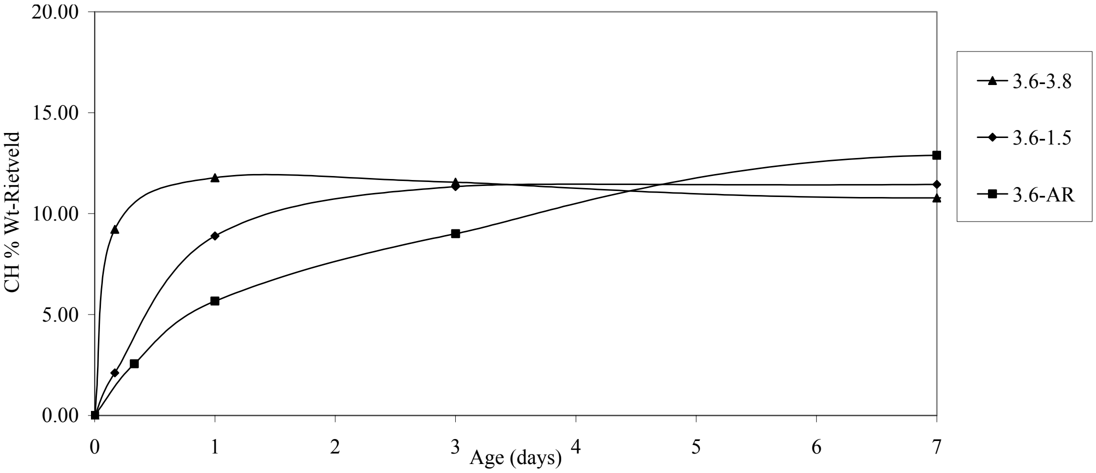


Figure 53: Effect of Alkali on Calcium Hydroxide Formation for Cement E-SO_3=3.6%

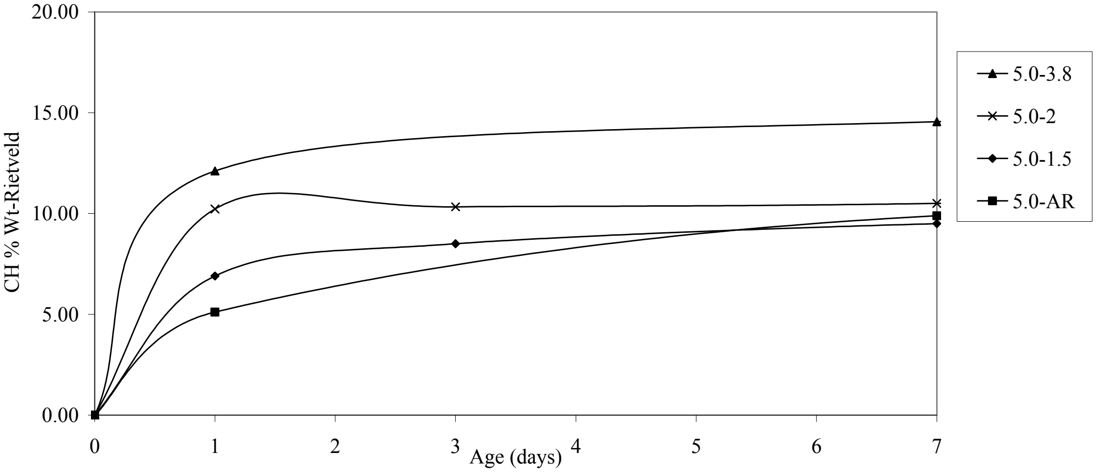


Figure 54: Effect of Alkali on Calcium Hydroxide Formation for Cement E-SO_3=5.0%

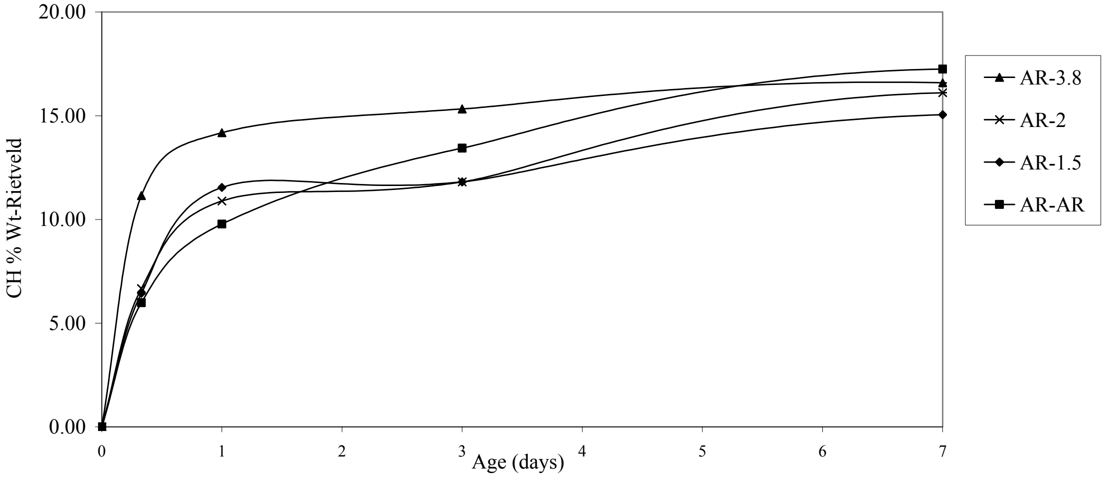


Figure 55: Effect of Alkali on Calcium Hydroxide Formation for Cement C-SO_3=AR

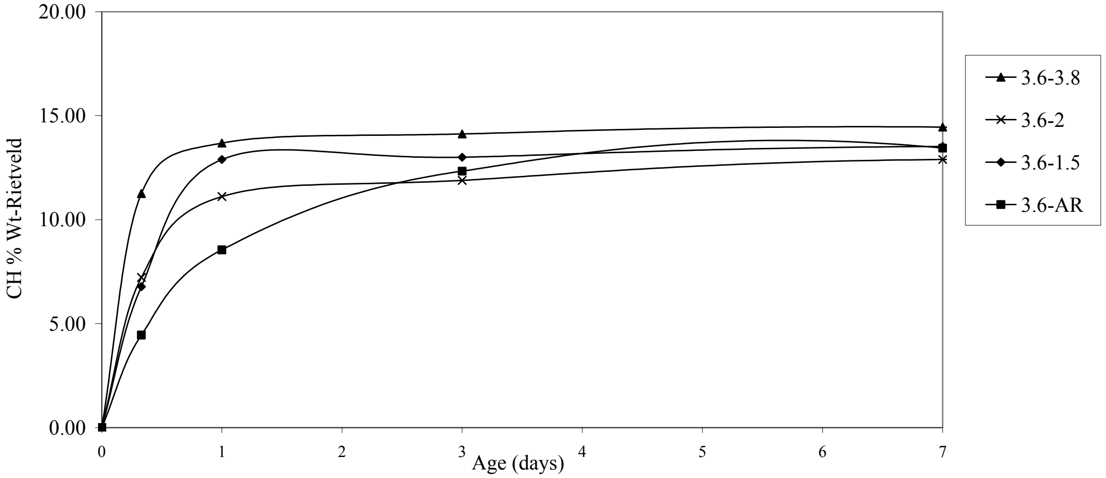


Figure 56: Effect of Alkali on Calcium Hydroxide Formation for Cement C-SO_3=3.6%

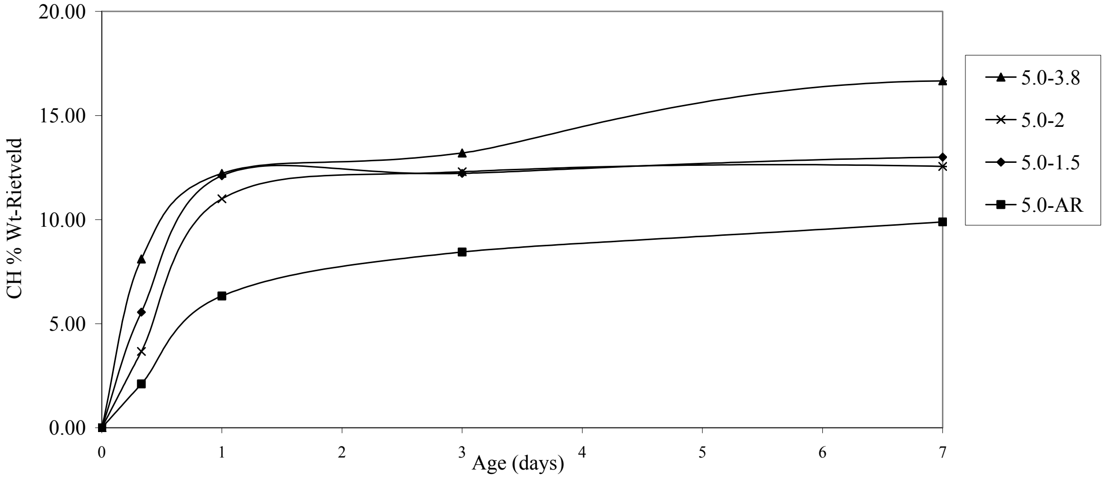


Figure 57: Effect of Alkali on Calcium Hydroxide Formation for Cement C-SO_3=5.0%

4.4 Heat of Hydration

To further our understanding to the role of alkalis and sulfates on durability, heat of hydration measurements were conducted on cements doped with alkalis and sulfates. The results are depicted in Figures 58 through 61. The results indicate that increasing sulfates results in retardation of the first exothermic peak that occurs due to the rapid initial hydration of tricalcium silicates and aluminates as can be seen from comparing the 5-AR with AR-AR cases for both cements. Increasing the alkali content while maintaining the sulfate content in the as-received condition, results in an increase in the rate of hydration of C_3A as clearly depicted in Figures 59 and 61. The first peak occurred at 2.5 minutes for AR-3.8 case versus 4.5 minutes for AR-AR. Another significant difference is the rate of heat generation was doubled on increasing the alkali content.

The results revealed by calorimetric measurements are consistent with mortar flow measurements depicted in Table 14 where mortar flow appears to decrease with increasing the alkali content at all sulfate levels.

While heat of hydration measurements indicate higher hydration reaction rates for tricalcium aluminate with increasing alkali content, XRD data indicates that ettringite is not the persistent phase during early stages of hydration. It was previously mentioned that ettringite is not stable at high pH pore solution.

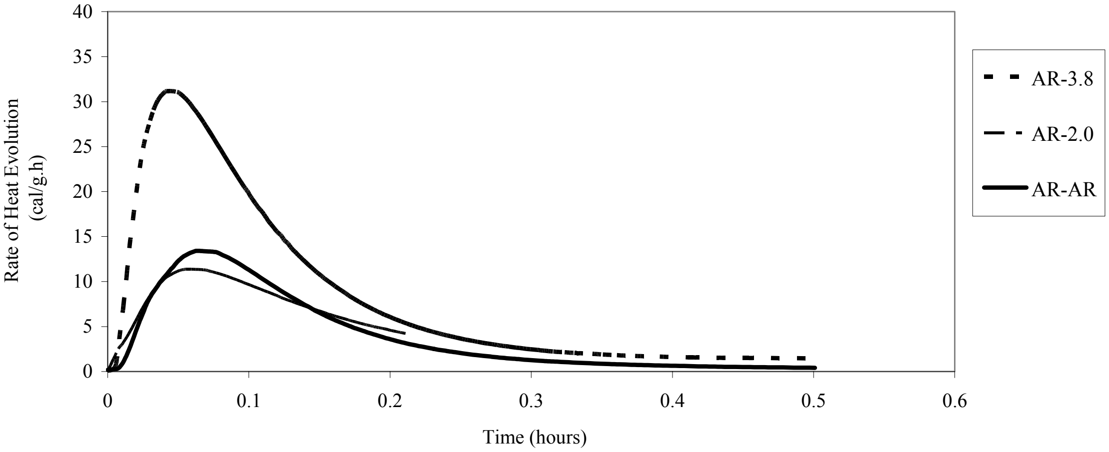


Figure 58: Effect of Alkali on Heat of Hydration for Cement E-SO_3=AR

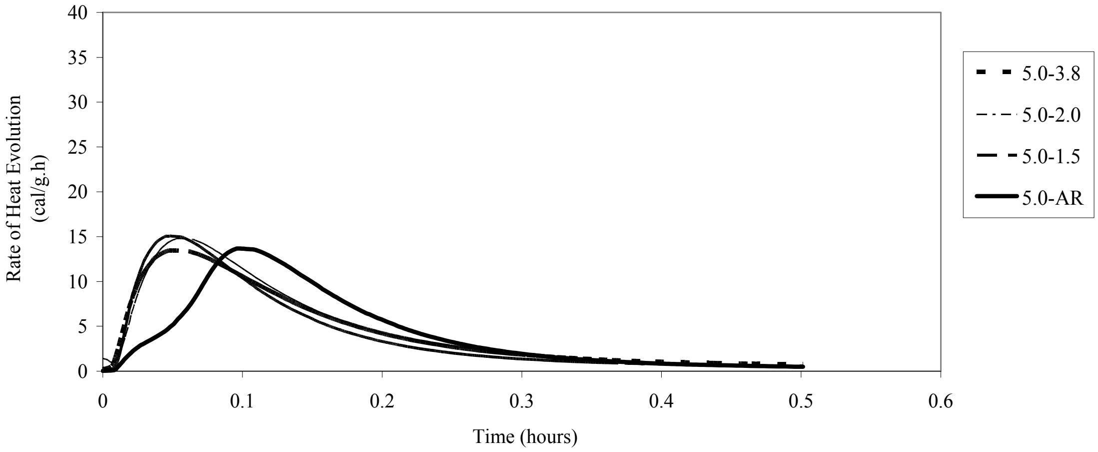


Figure 59: Effect of Alkali on Heat of Hydration for Cement E-SO_3=5.0%

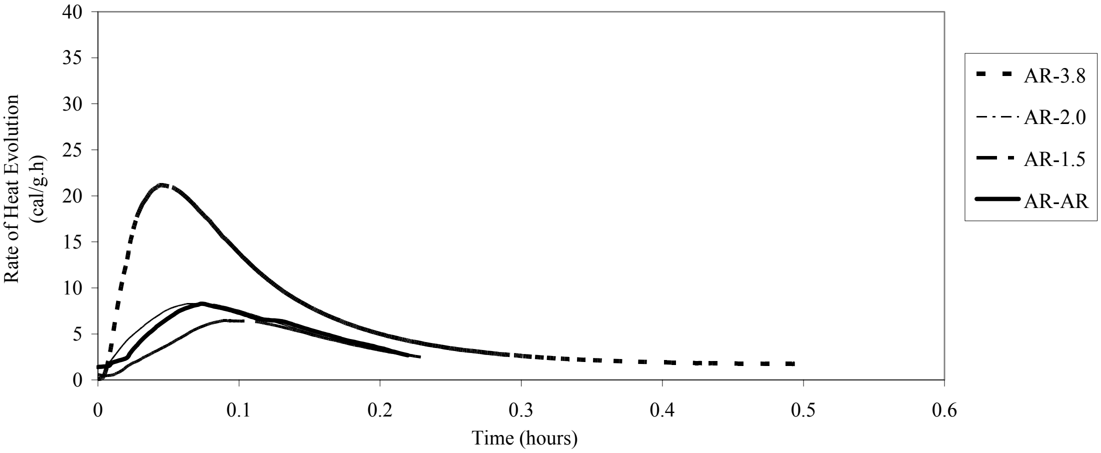


Figure 60: Effect of Alkali on Heat of Hydration for Cement C-SO_3=AR

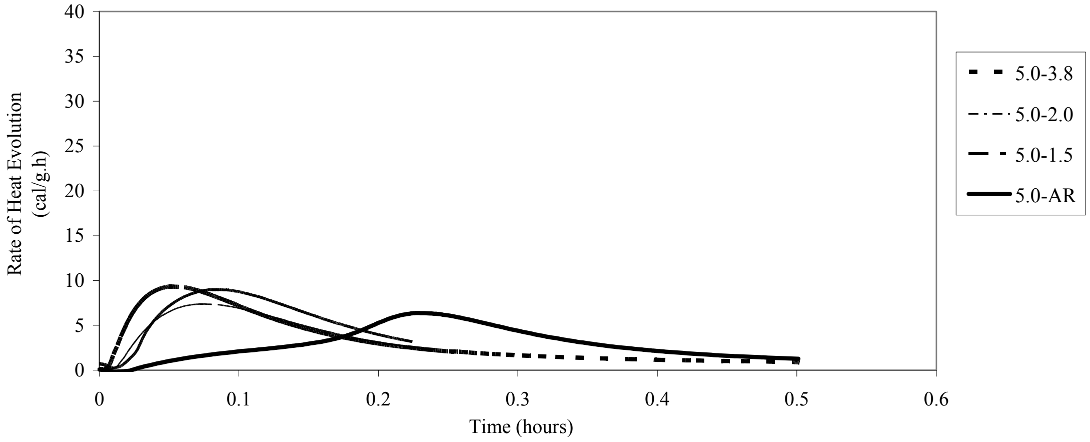


Figure 61: Effect of Alkali on Heat of Hydration for Cement C-SO_3=5.0%

Table 6. Mortar Flow Values for Cements C and E

	Cement C			Cement E		
Alk / SO_3	AR	2	3.8	AR	2	3.8
AR	111	110	92	103.5	90.5	63
3.6	115.5	104	90	113	96	87.5
5	116	79	106.5	104.5	102	96

4.5 Pore Solution Chemistry

Analysis of pore solution chemistry is critical in understanding the role of alkalis on durability. Profiles for sulfates and calcium ions were assessed and the results are depicted in Figures 62 through 73. From sulfate ion concentration measurements it was found that increasing alkali content of cement results in two effects. First, sulfate ions persisted longer in solution. Second, for the same age, the ion concentration was higher for higher alkali content.

Diffraction studies (section 4.3) on AR-3.8 did not indicate any ettringite formation for up to 14 days in cement E and 28 days for cement C. These results together with solution analysis might indicate that sulfate ion concentrations available for AR-3.8 cases were below the solubility limit of ettringite. Though solubility limits of ettringite was not addressed in this study, the formation of ettringite in case 3.6-3.8 and 5-3.8 at 8 hours of hydration corroborate the proposed explanation. Furthermore, sulfate concentration in 5-3.8 case was almost double what has been determined for 5.0-AR, yet the same amount of ettringite was determined by XRD for both cases. In addition to the high sulfate ion concentration, for higher alkali content, sulfates persisted for longer periods in higher alkali content. This finding again indicates the persistence of sulfates in solution at high alkali content. This makes sulfates unavailable to participate in ettringite formation or their incorporation in C-S-H gel formation.

Calcium ion concentration measurements indicate that increasing alkali content results in a decrease in the ion concentration. The results are in agreement with diffraction pattern analysis on calcium hydroxide presented earlier. Increasing the alkali content of cement appears to lower the solubility of calcium hydroxide and enhances its precipitation and nucleation in available space. Consequently, this might interfere with the nucleation and bridging of C-S-H gel. This might ultimately compromise the quality of the gel which is the main strength contributing binder in the cement hydrated paste. Additionally, a high calcium ion concentration in solution may also result in a lower Ca/Si ratio in C-S-H gel.

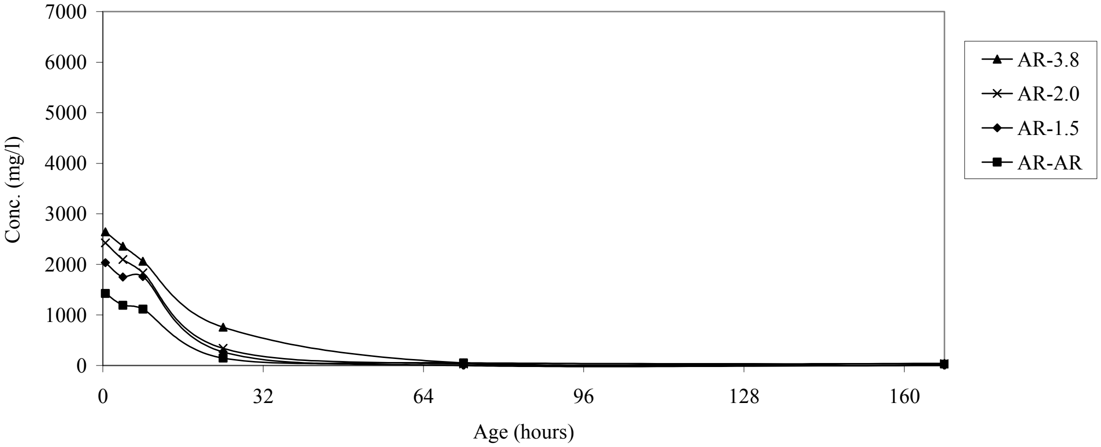


Figure 62: Effect of Alkali on SO_4^{-2} Concentration for Cement E-SO_3 =AR

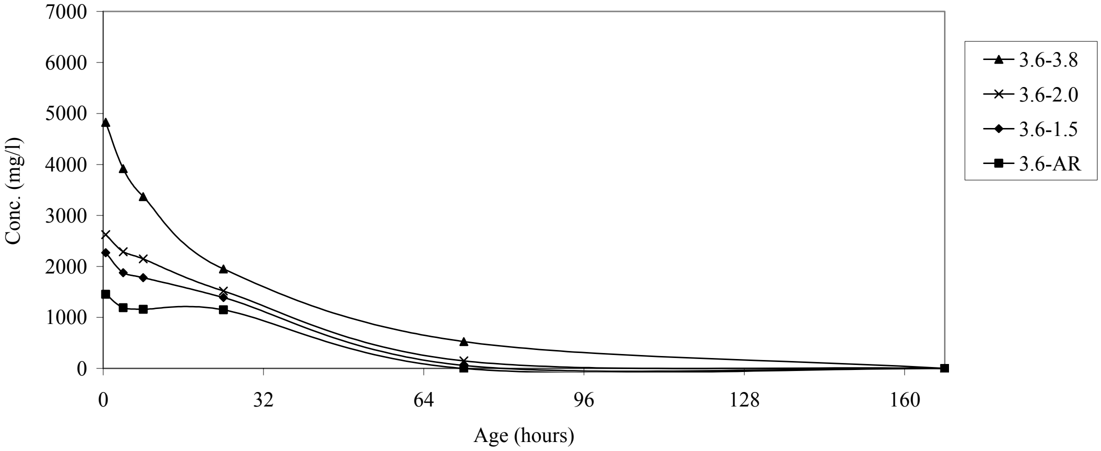


Figure 63: Effect of Alkali on SO_4^{-2} Concentration for Cement E-SO_3 =3.6%

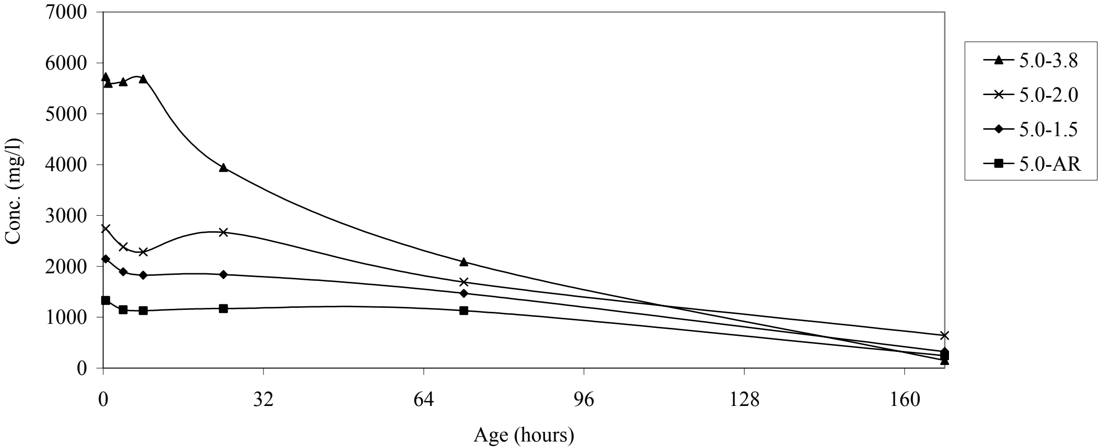


Figure 64: Effect of Alkali on SO_4^{-2} Concentration for Cement E-SO_3 =5.0%

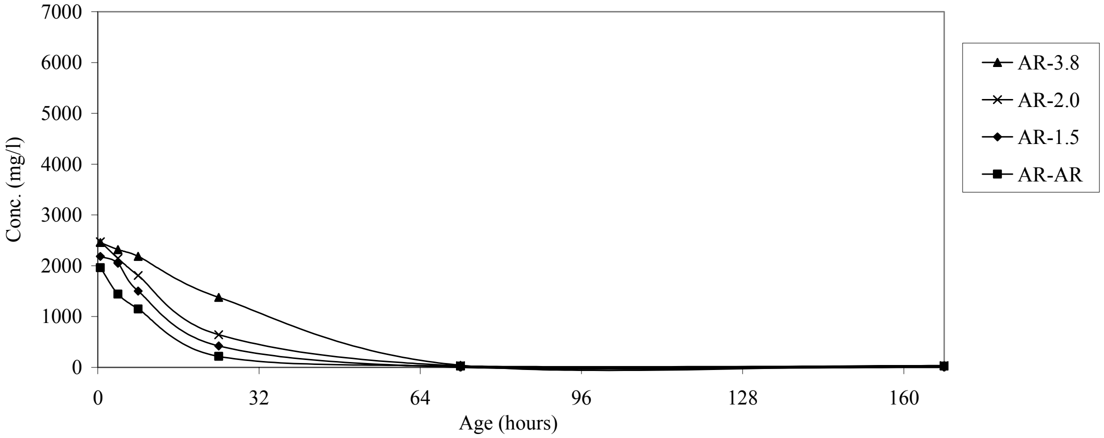


Figure 65: Effect of Alkali on SO_4^{-2} Concentration for Cement C-SO_3 =AR

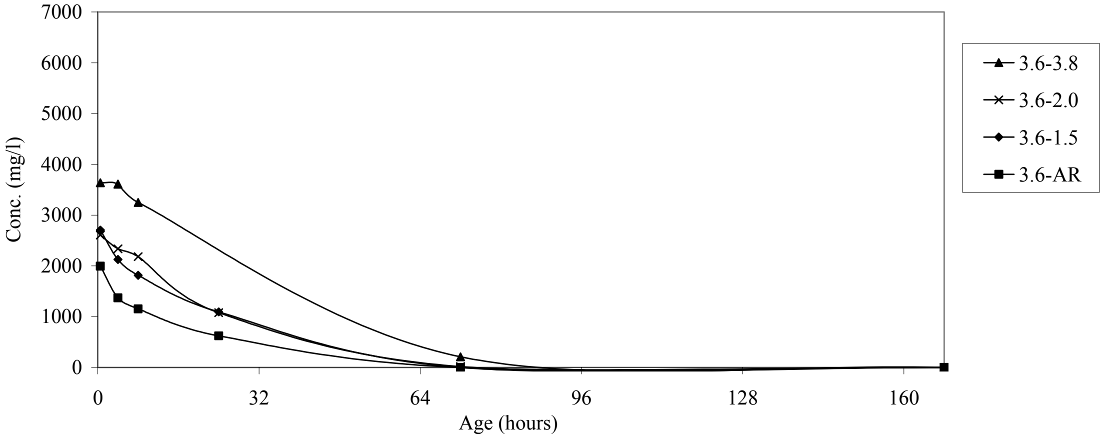


Figure 66: Effect of Alkali on SO_4^{-2} Concentration for Cement C-SO_3 =3.6%

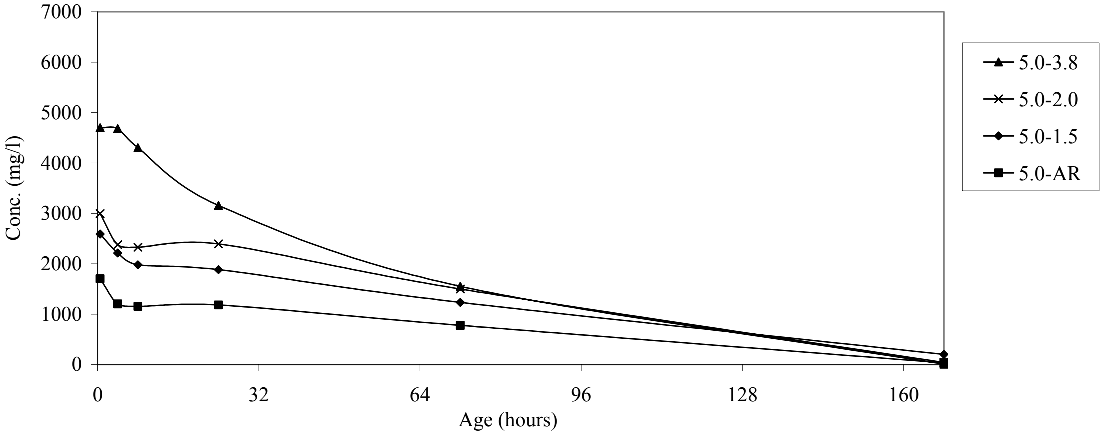


Figure 67: Effect of Alkali on SO_4^{-2} Concentration for Cement C-SO_3 =5.0%

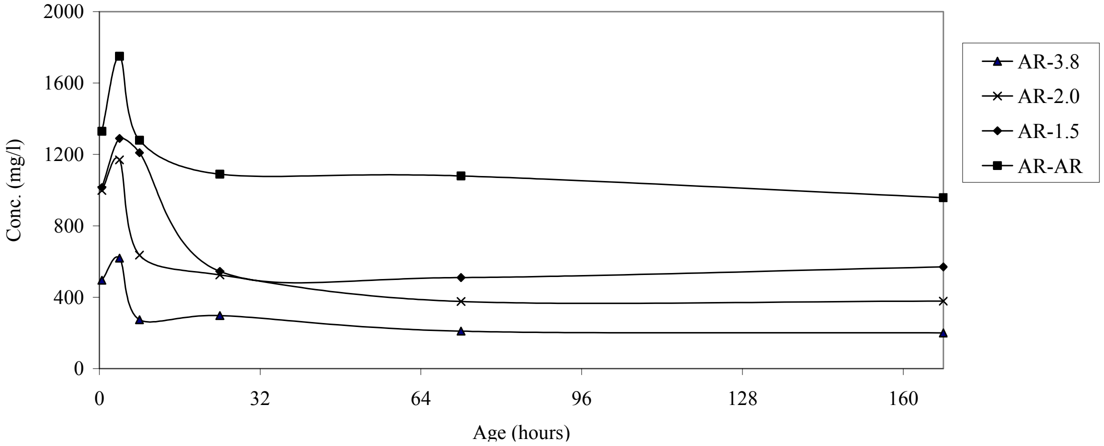


Figure 68: Effect of Alkali on Calcium Ions Concentration for Cement E-SO_3=AR

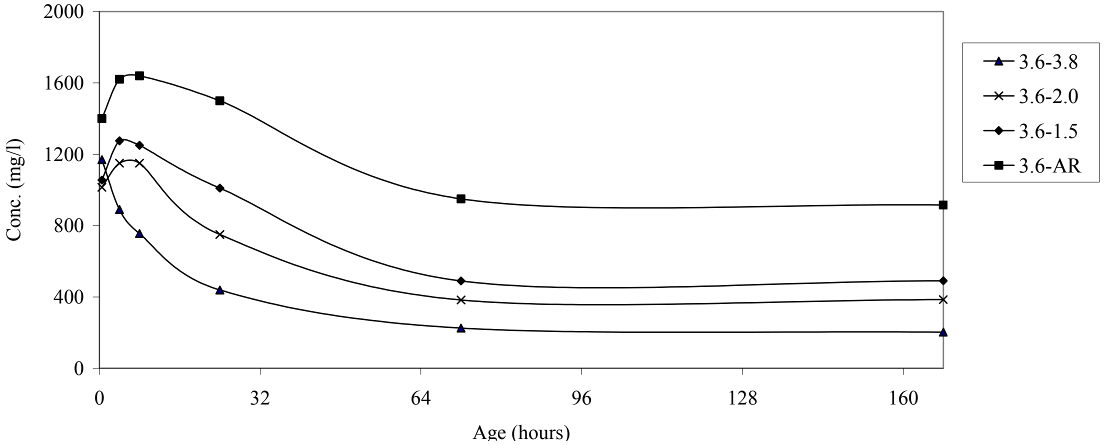


Figure 69: Effect of Alkali on Calcium Ions Concentration for Cement E-SO_3=3.6%

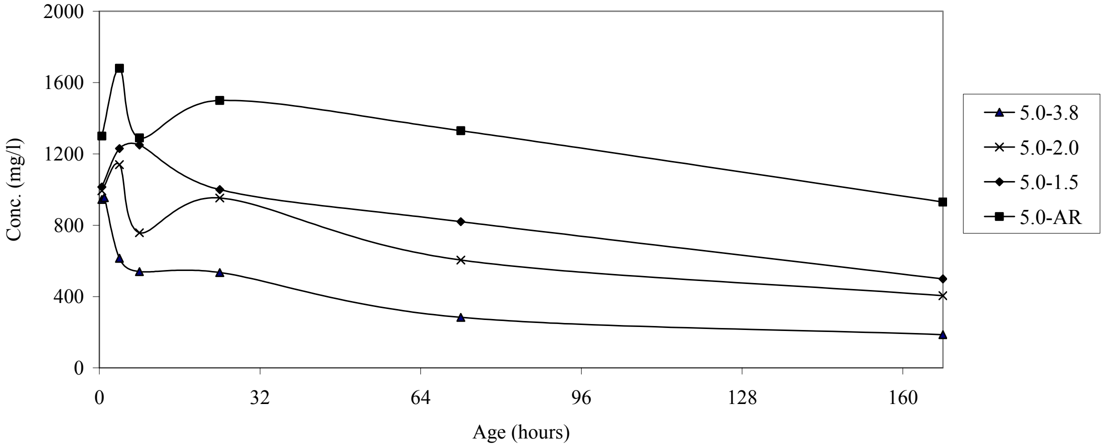


Figure 70: Effect of Alkali on Calcium Ions Concentration for Cement E-SO_3=5.0%

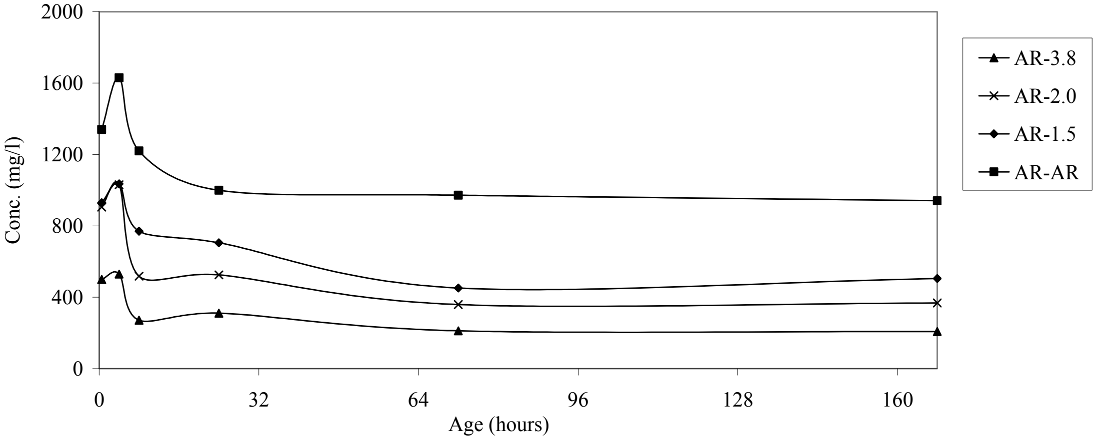


Figure 71: Effect of Alkali on Calcium Ions Concentration for Cement C-SO_3=AR

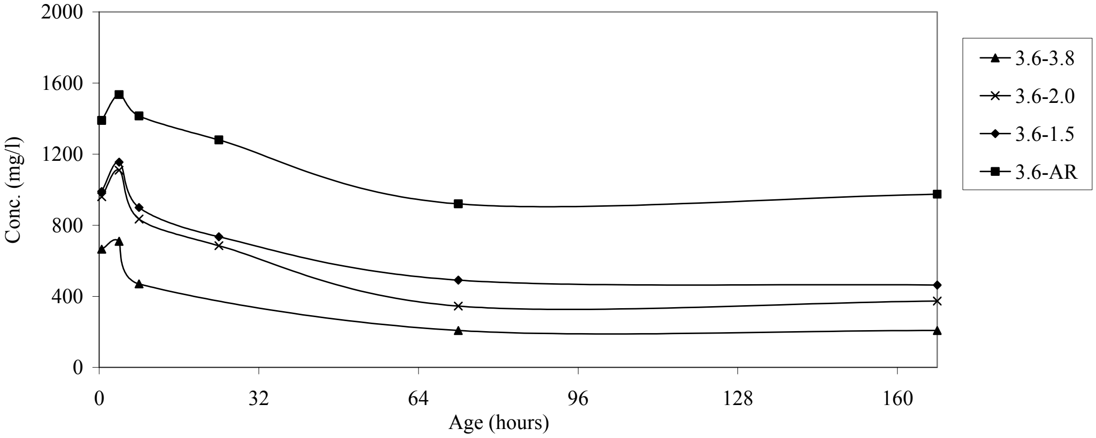


Figure 72: Effect of Alkali on Calcium Ions Concentration for Cement C-SO_3=3.6%

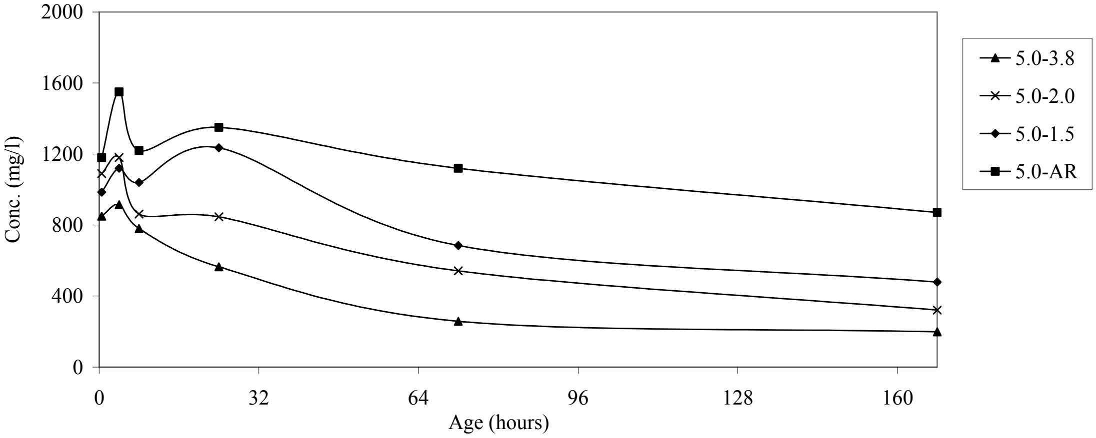


Figure 73: Effect of Alkali on Calcium Ions Concentration for Cement C-SO_3=5.0%

5. Role of Elevated Temperatures and Service Conditions

The effect of sulfates and alkalis on structural durability, at ambient conditions, was presented in the previous sections. The findings indicate that increasing alkali content of cements up to 2% was accompanied by strength loss but not significant expansion. However, increasing alkali content to 3.8% resulted in strength loss and excessive expansion. The curing regime adopted for this part of the study was at room temperature and mortars were maintained in a lime solution tank for the duration of the experiments. In order to address temperature rise effects on structural durability, another set of experiments were conducted. The main focus of those experiments was to simulate encounters in precast concrete and massive structural elements where temperature can be as high as 90° C. Three temperatures were selected for this set; namely, 60°, 80° and 90° C. For heat curing, mortar bars were placed in a humidity chamber for one hour following mixing. They were then placed in plastic sealed bags and moved to an oven with the set point adjusted to the specific curing temperature. The rate of heating was such that the oven reached the selected temperature in 1.25 hours. The soaking time for all selected temperatures was 12 hours, following which the oven was turned off. The specimens were allowed to cool to ambient temperature while in the oven so that the time to reach ambient temperature was approximately 4 hours. Once the bars reached ambient temperatures, they were placed in distilled water and allowed to soak for an hour. Following that, the initial bar length was collected. The bars were then placed in a lime solution for the duration reported in this study. Specific alkali and sulfate doping levels were selected. The selection criterion was based on conditions that did not initiate deterioration under ambient conditions. Based on that, alkali content of 3.8% was not selected for any of the heat curing experiments. Expansion measurements collected for cements C and E are depicted in Figures 74 through 90.

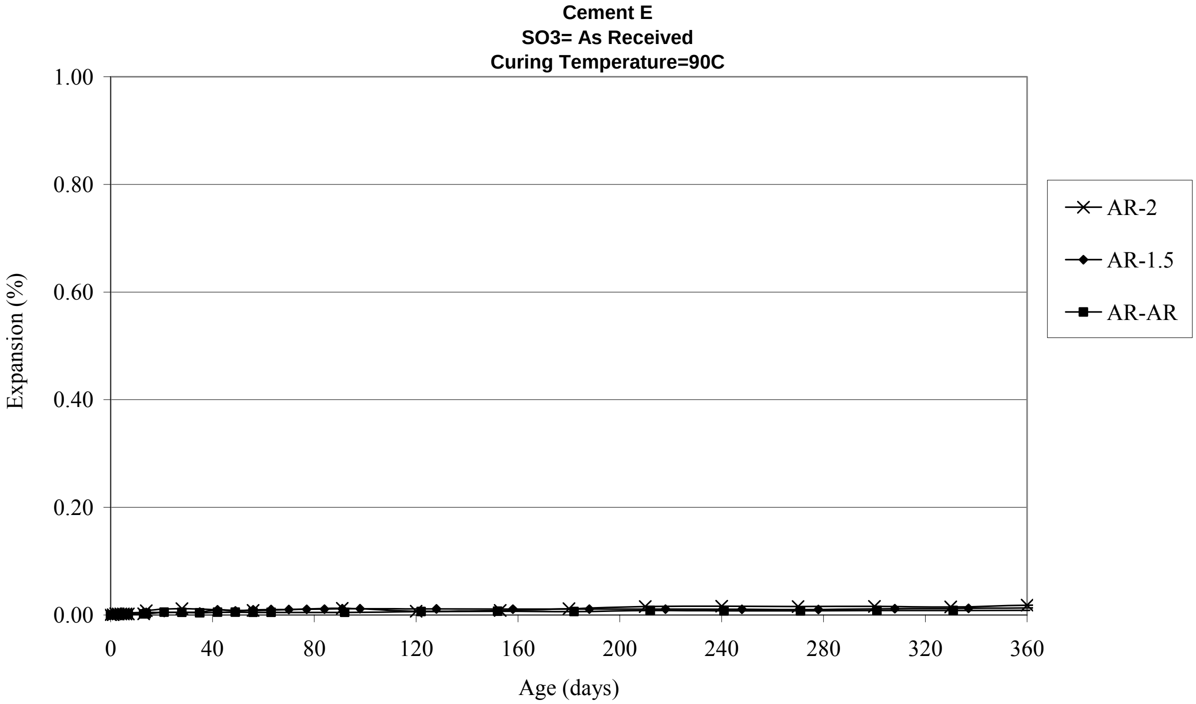


Figure 74: Expansion for Cement E

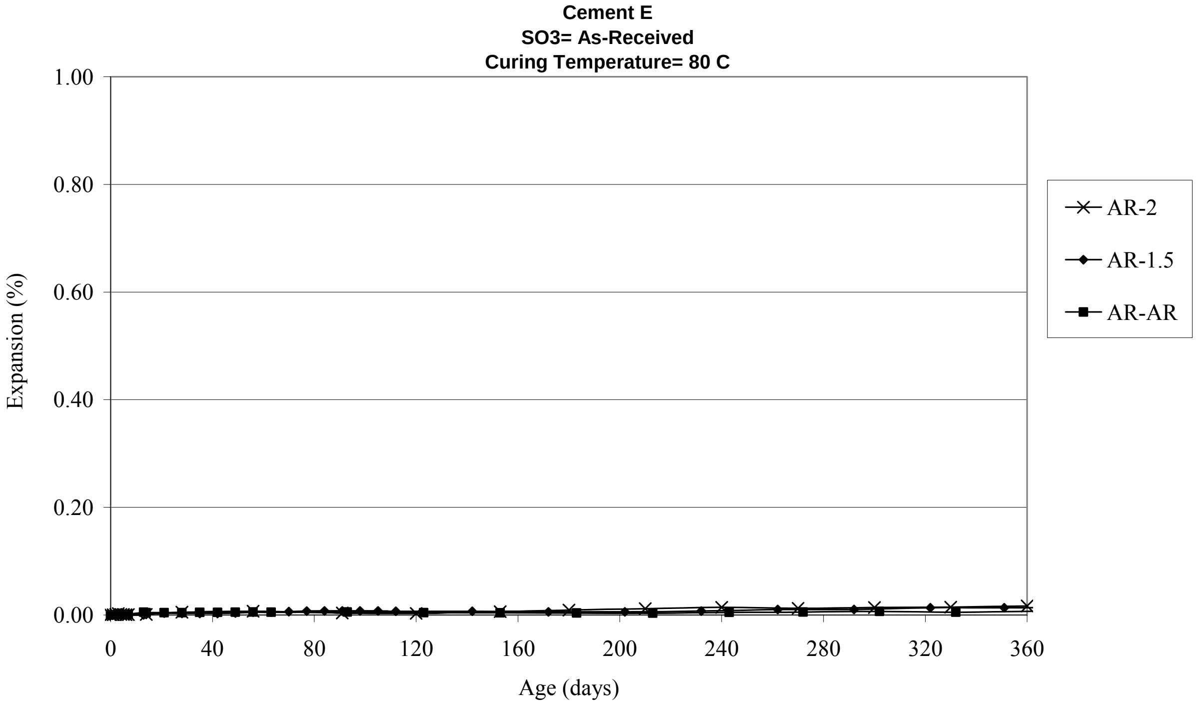


Figure 75: Expansion for Cement E

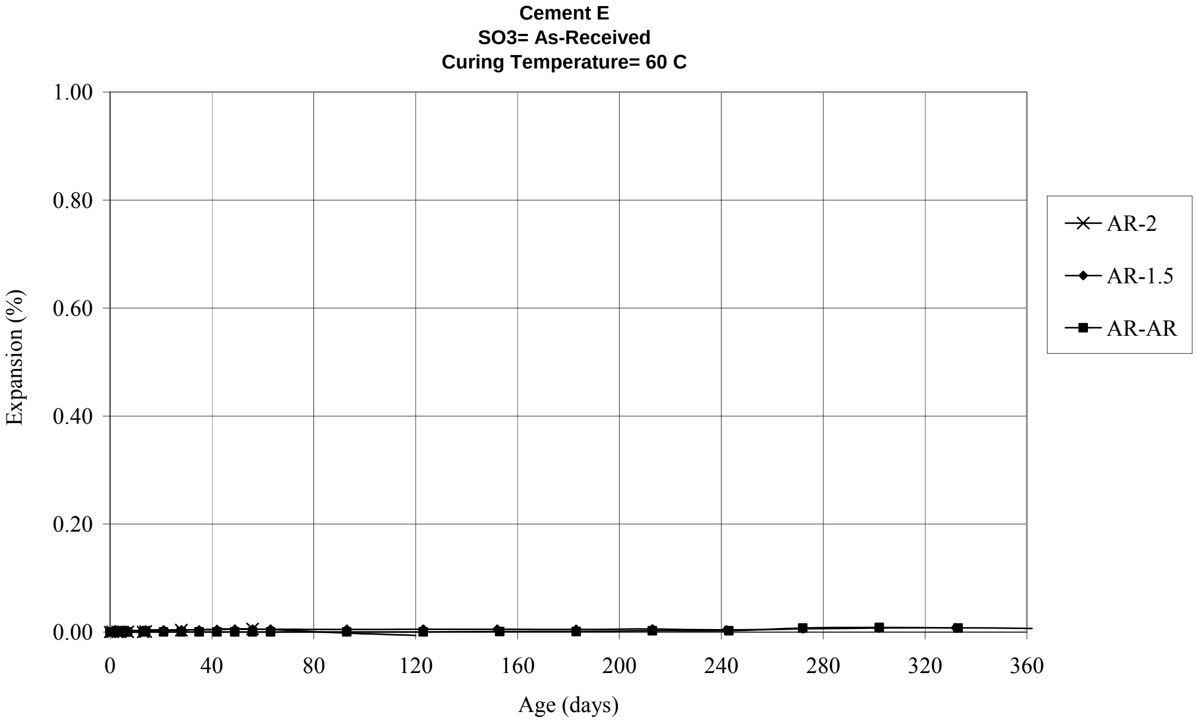


Figure 76: Expansion for Cement E

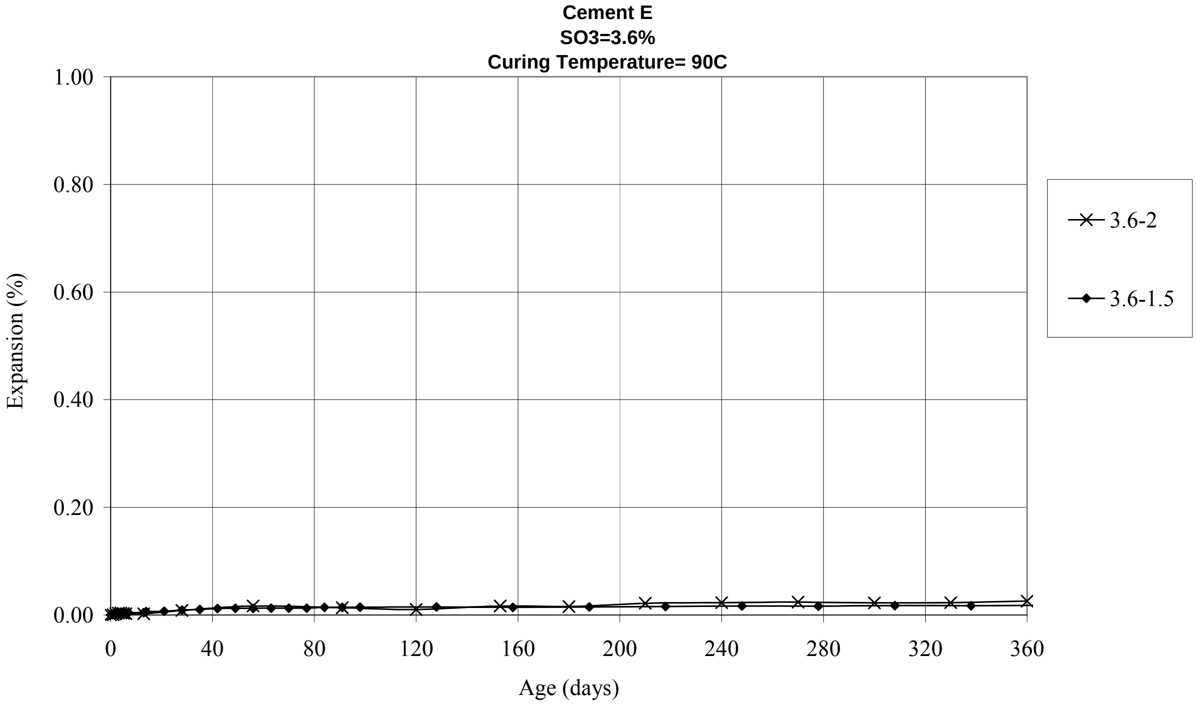


Figure 77: Expansion for Cement E

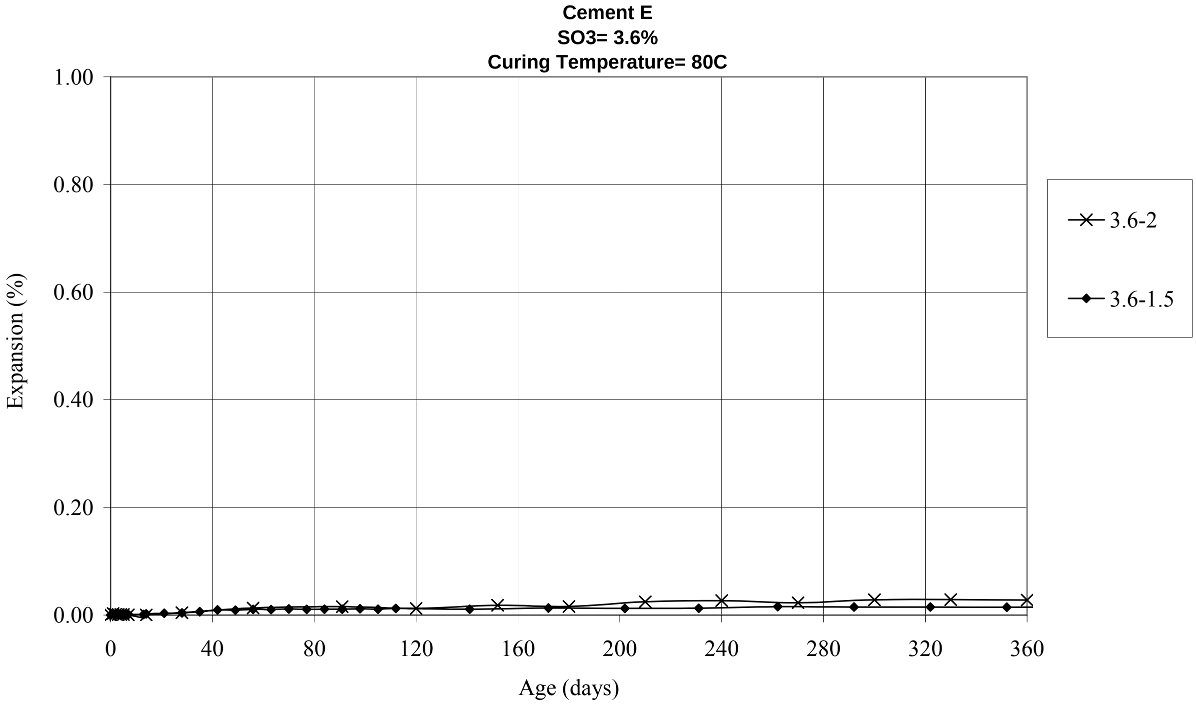


Figure 78: Expansion for Cement E

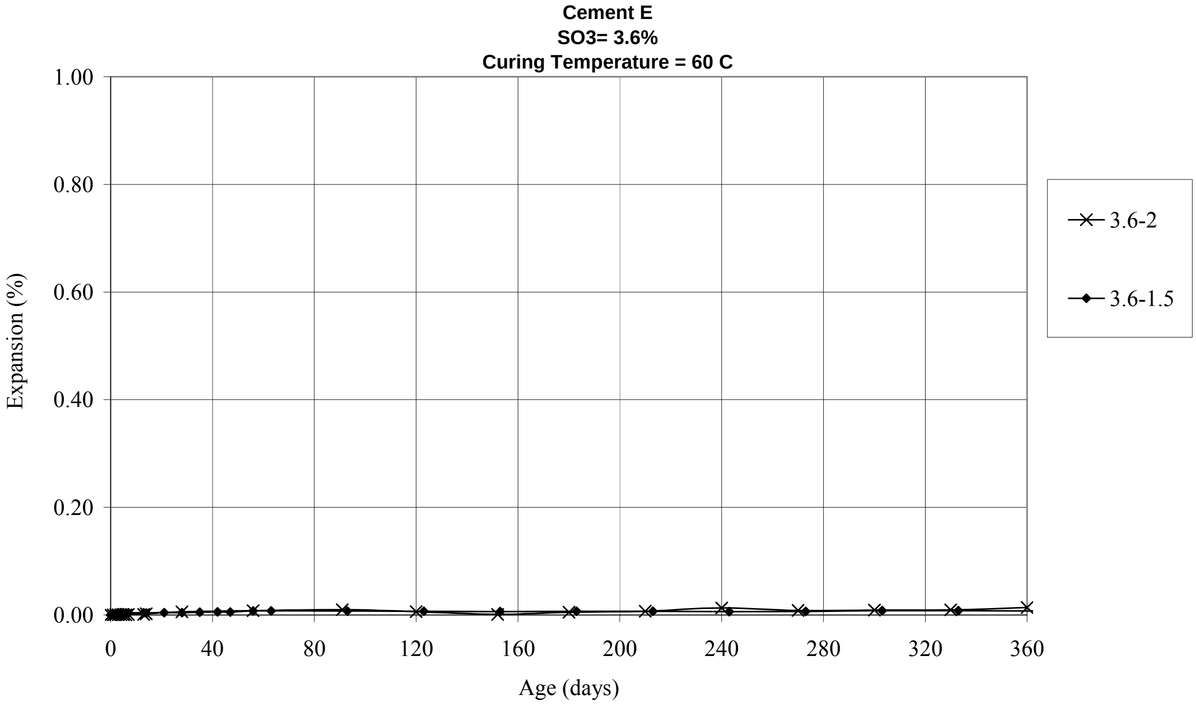


Figure 79: Expansion for Cement E

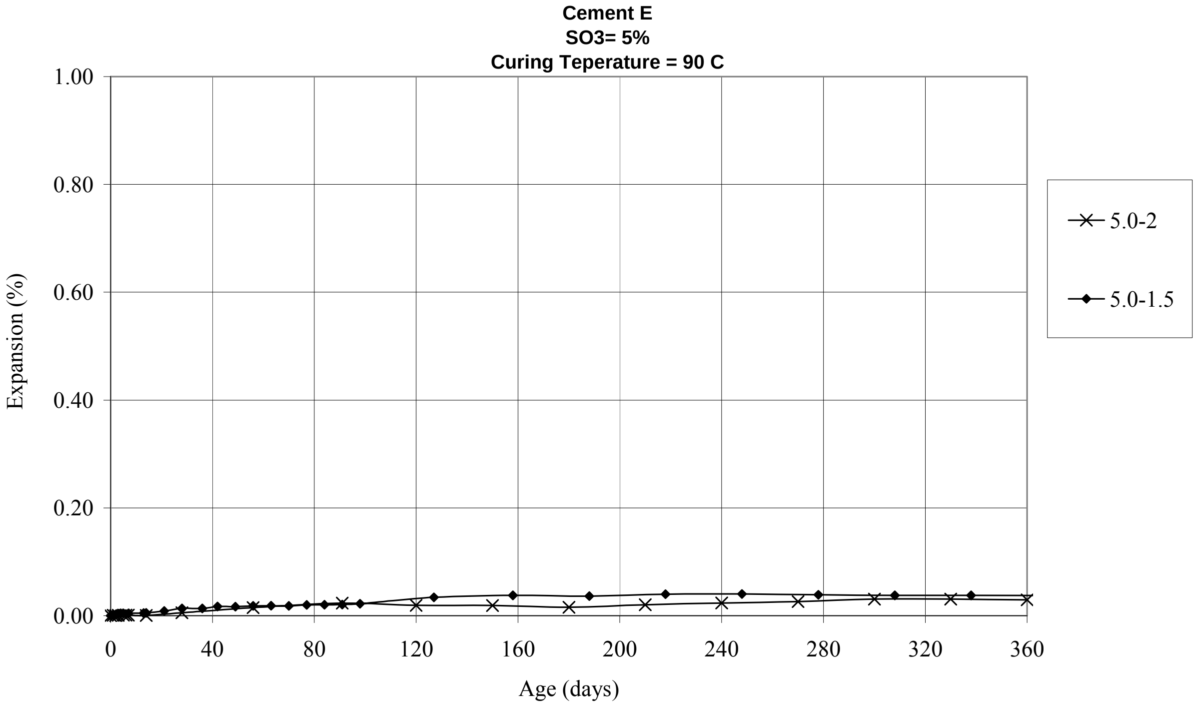


Figure 80: Expansion for Cement E

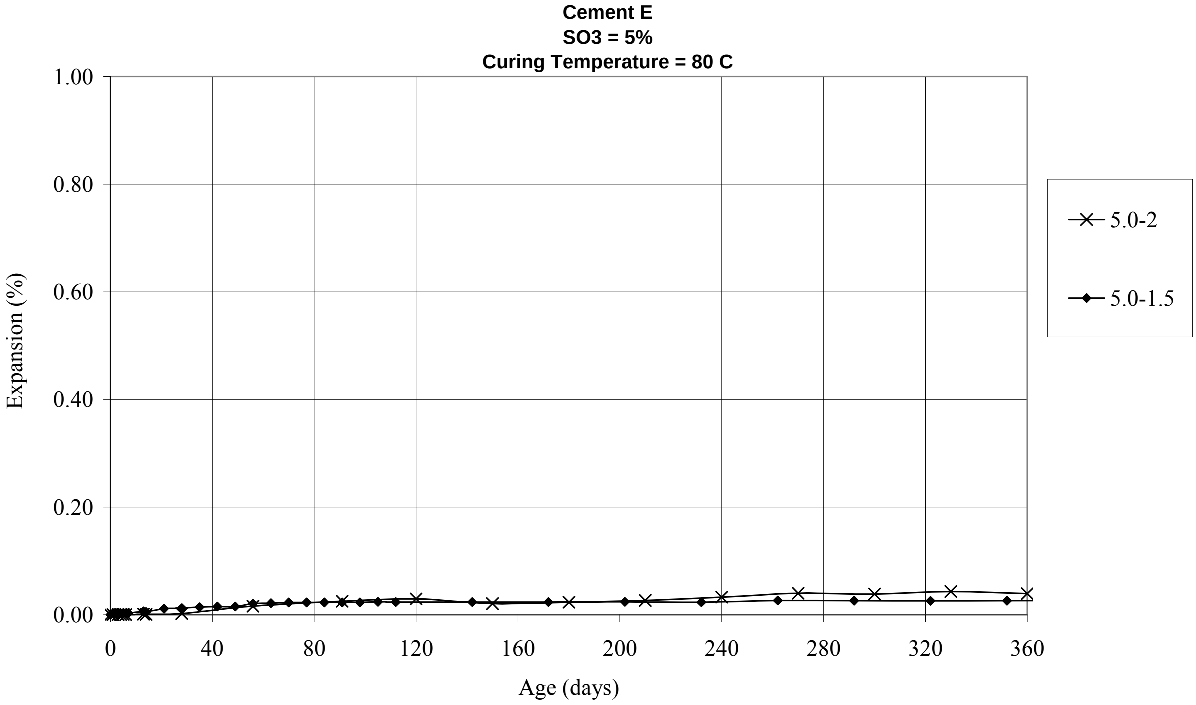


Figure 81: Expansion for Cement E

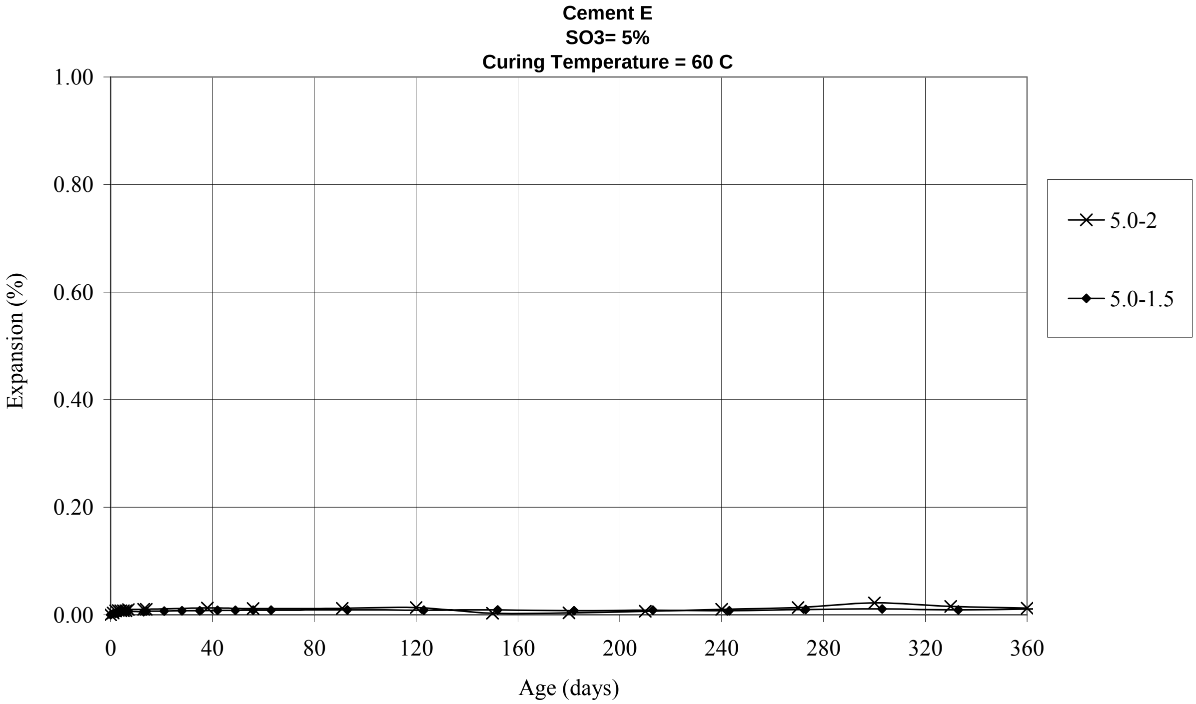


Figure 82: Expansion for Cement E

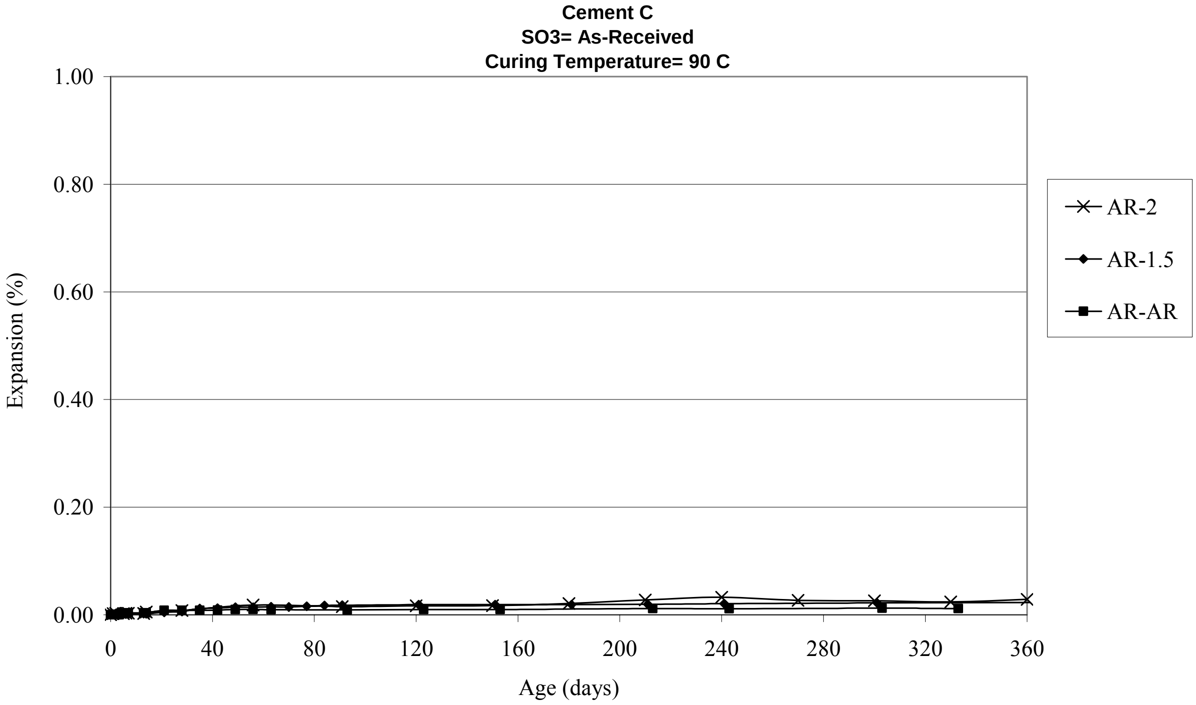


Figure 83: Expansion for Cement C

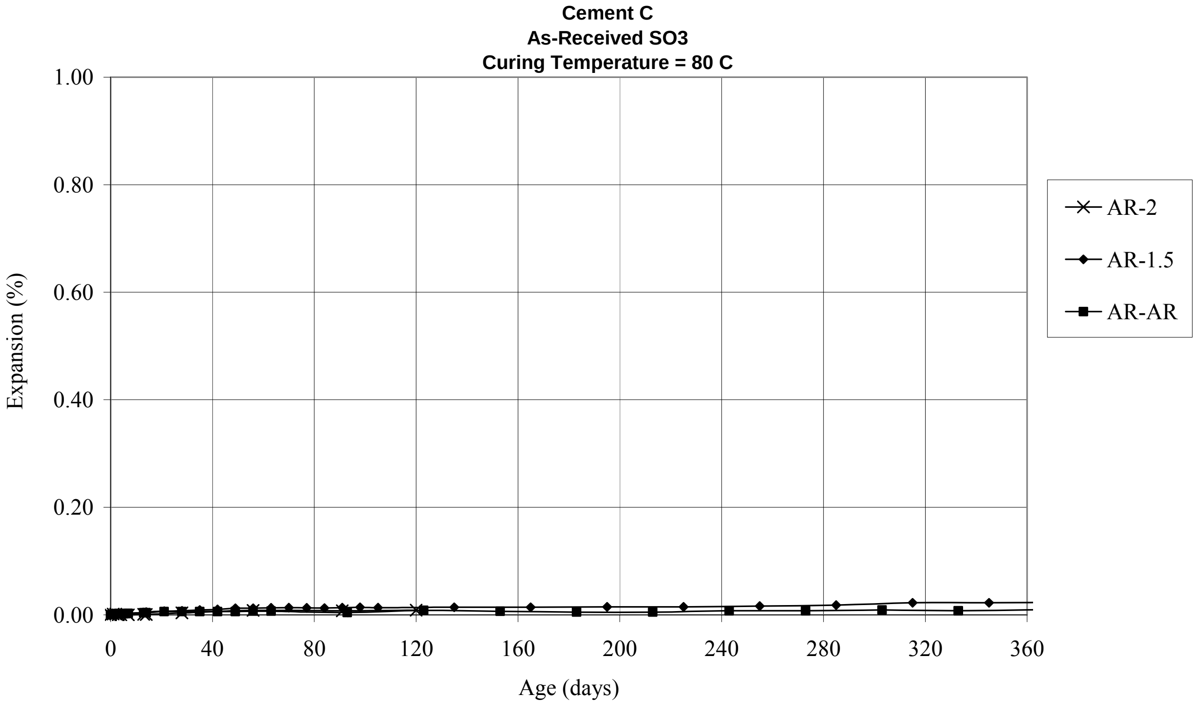


Figure 84: Expansion for Cement C

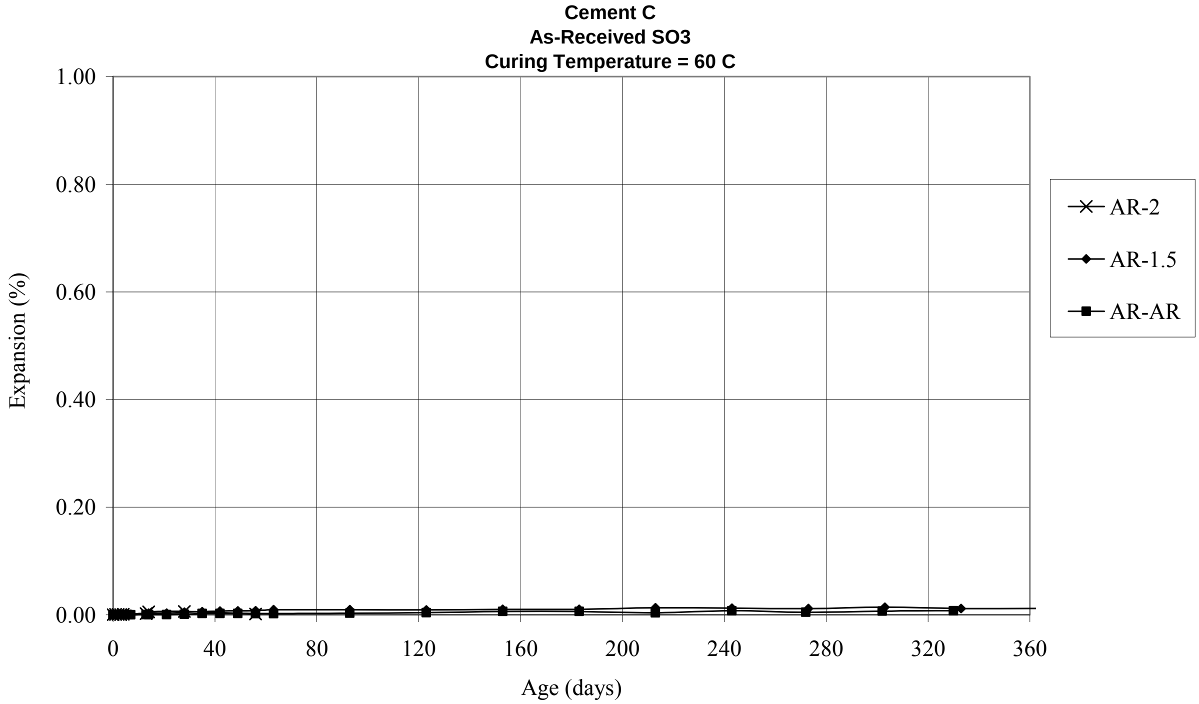


Figure 85: Expansion for Cement C

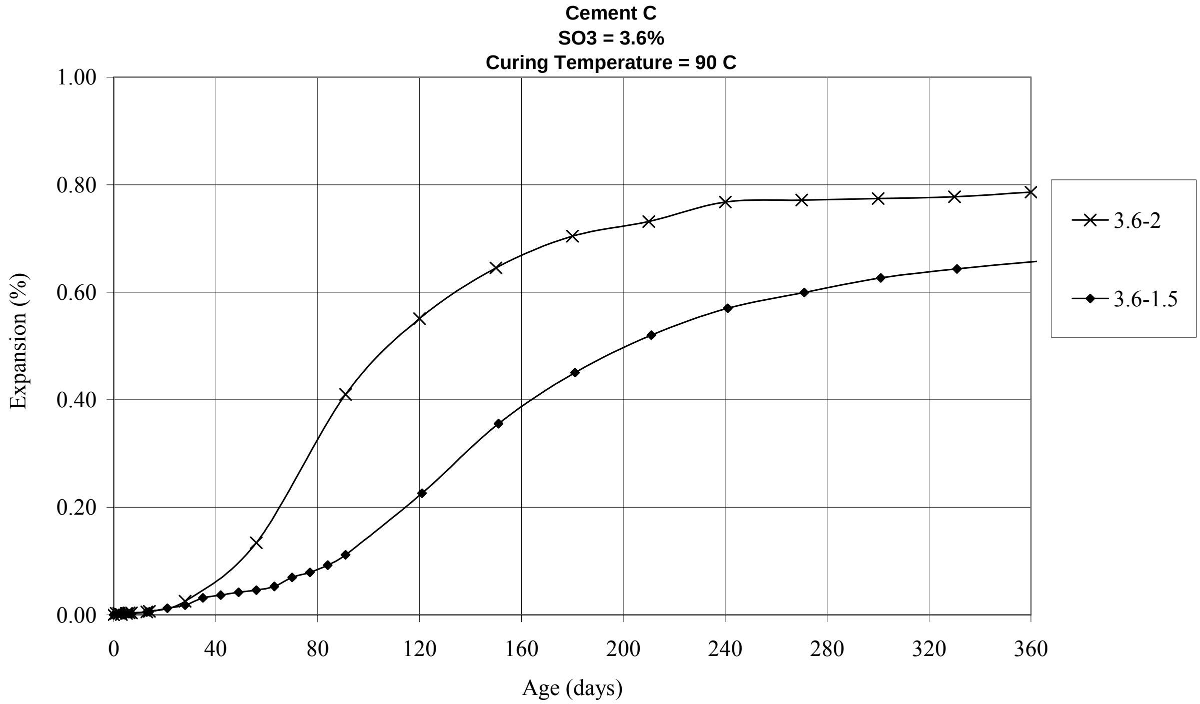


Figure 86: Expansion for Cement C

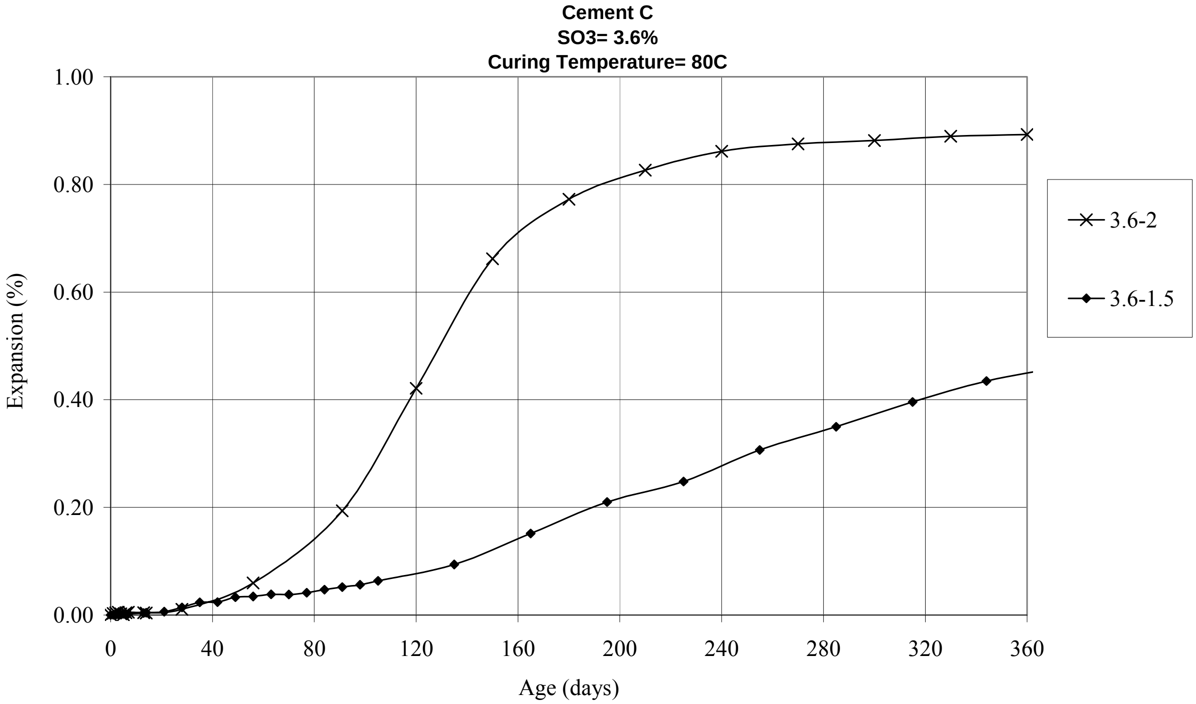


Figure 87: Expansion for Cement C

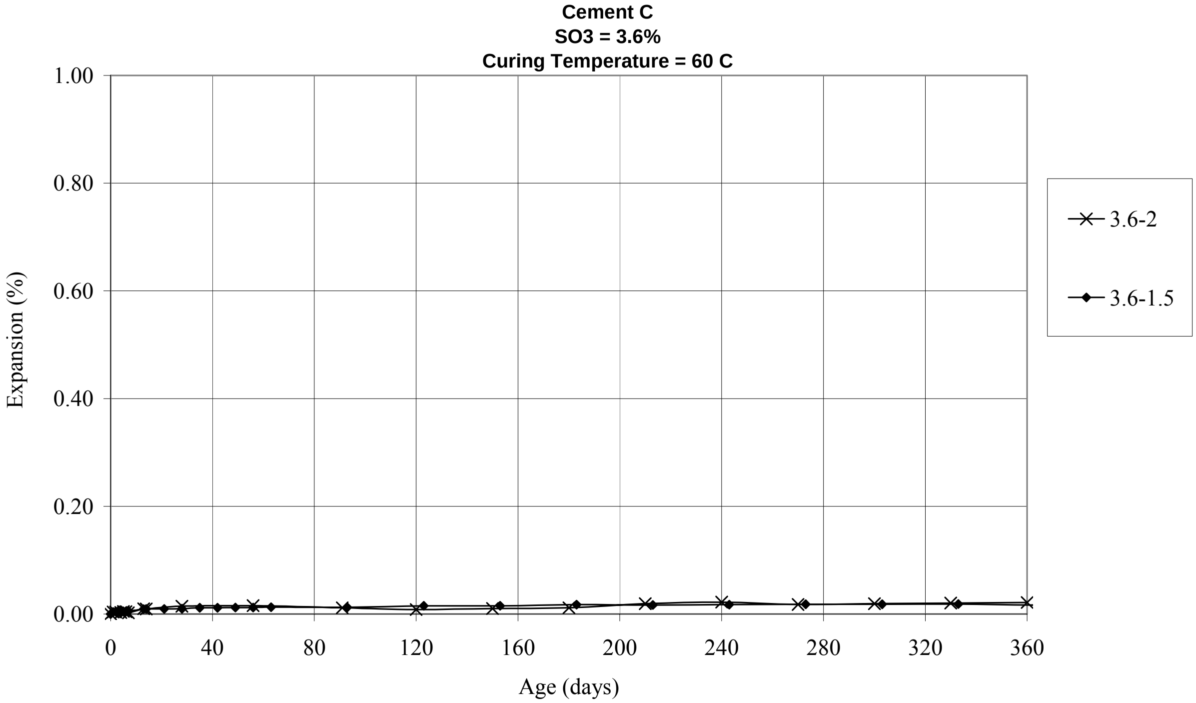


Figure 88: Expansion Cement C

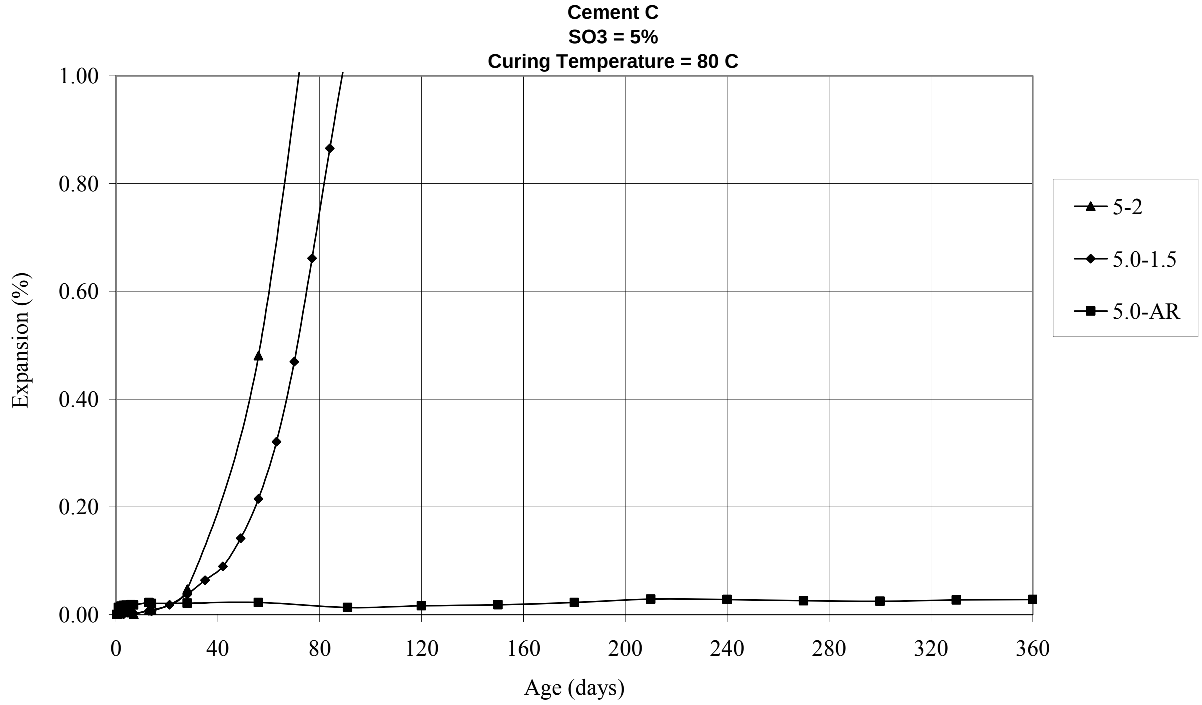


Figure 89: Expansion behavior for Cement C

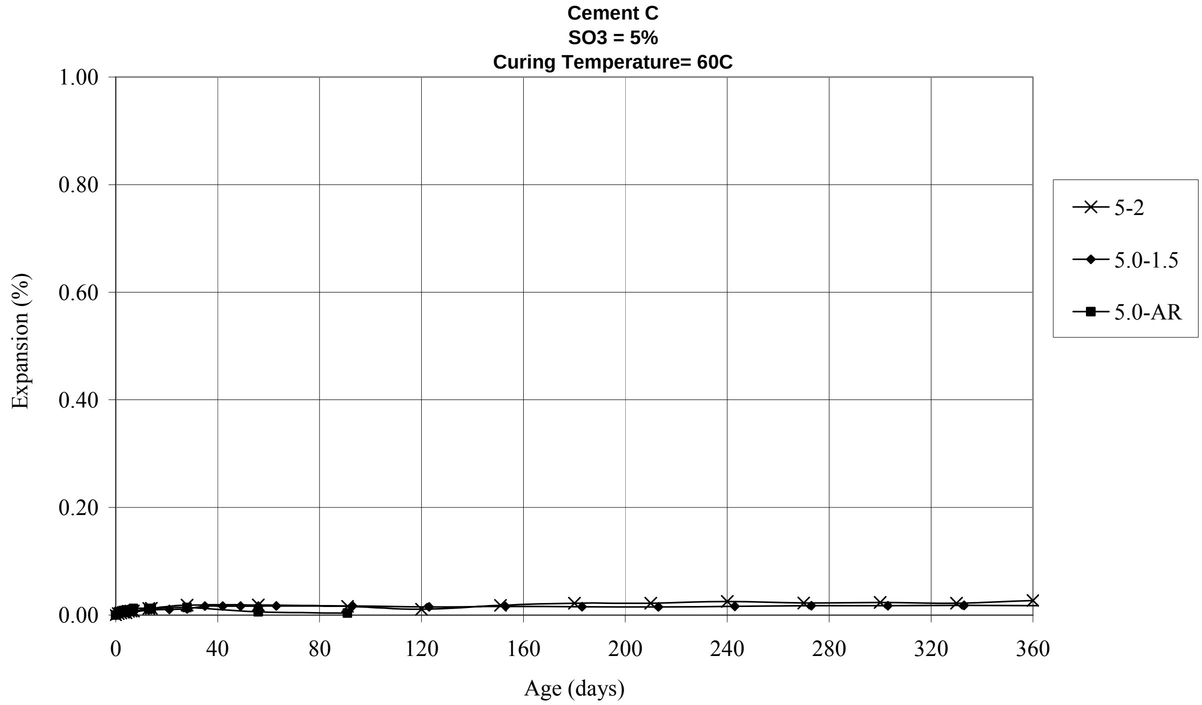


Figure 90: Expansion for Cement C

Increasing the curing temperature up to 90° C did not result in any significant deterioration for cement E irrespective of the sulfate and alkali content. Expansion measurements for cement E were reported for a period of one year with an alkali content of as-received, 1.5% and 2% and a sulfate content of as-received, 3.6 and 5% for heat curing temperatures of 60°, 80° and 90°C. Cement E is characterized by moderate fineness, C_3S of 54% and C_3A of 4%. However, cement C showed significant expansion for curing temperatures of 80° and 90° C at SO_3=3.6%, 5% with alkali= 1.5% mixes and SO_3= 3.6, 5%, with alkali=2% mixes. Cement C and E share similar tricalcium aluminate content with the main difference being tricalcium silicate content. Cement E has C_3S of 54% while cement C has 67%. The findings are indicative of the significance of C3S on durability of structural elements if concrete is exposed to elevated temperatures. In assessing this observed trend, MH3 cement was also examined under the same conditions. MH3 cement has C_3S and C_3A content of 72% and 2%. Its fineness is 395 which is similar to cements E and C fineness. The results are shown in Figures 91 to 93.

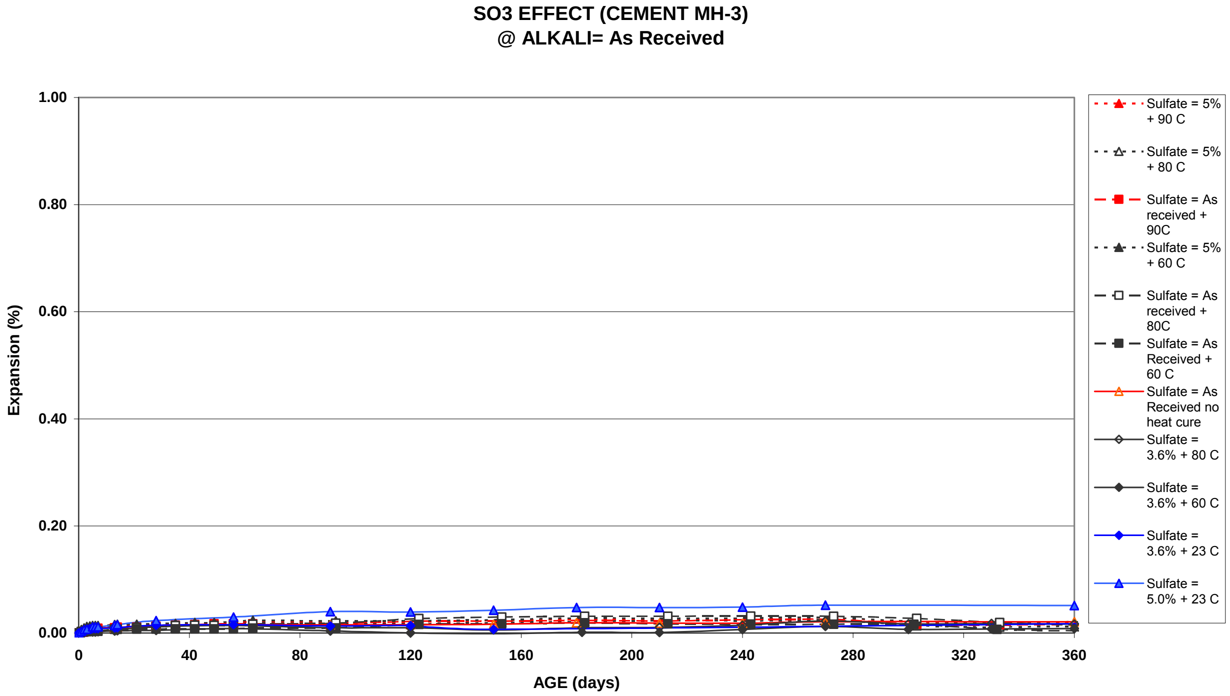


Figure 91: Expansion for Cement MH3

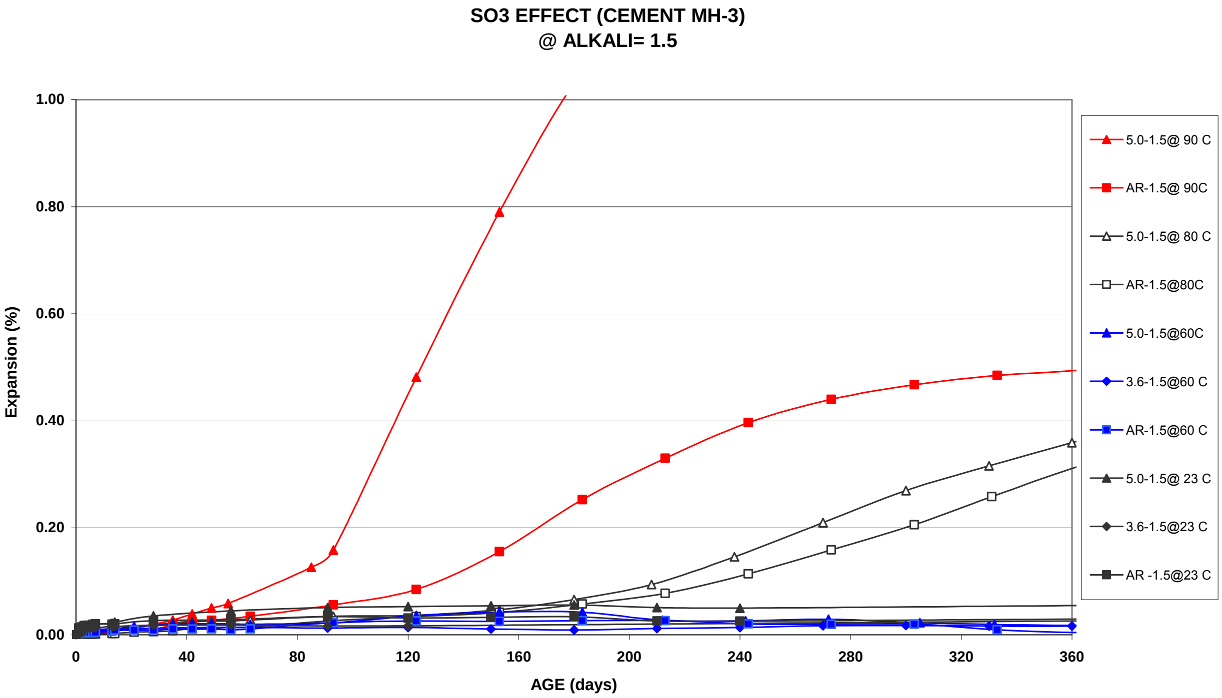


Figure 92: Expansion for Cement MH3

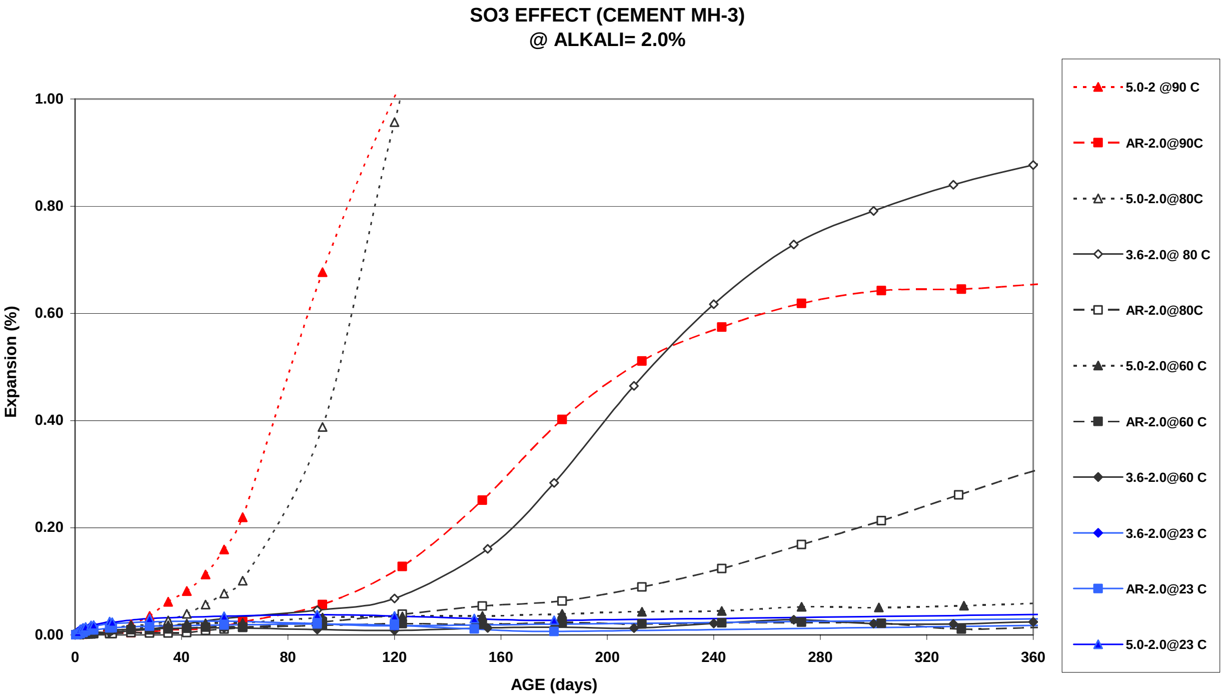


Figure 93: Expansion for Cement MH3

The results indicate similar deterioration profiles for cement MH3 to what has been observed for Cement C. It appears that increasing curing temperatures to 80°C has resulted in deterioration when SO_3 content was 3.07, and 5% at an alkali content of 1.5% or 2%. The findings also indicate that for the conditions studied here, a temperature of 60°C did not result in deterioration.

The effect of increasing tricalcium aluminate content of cement on durability of mixes at elevated temperatures was also studied through using cement MH4. MH4 has C_3S and C_3A content of 65% and 10% respectively. The results are depicted in Figures 94 through 96. It can be seen that increasing the temperature to 80°C for mixes containing cements that have high tricalcium silicate and aluminate content, and a sulfate and alkali content of 5% and 1.5%, is detrimental to its durability. Increasing tricalcium aluminate appears to have increased the level of sulfate, at a given alkali content, that can be tolerated by cement without generating deterioration at 80°C. The same conclusion can be drawn through considering the results for ERD07 depicted in Figures 97 and 98.

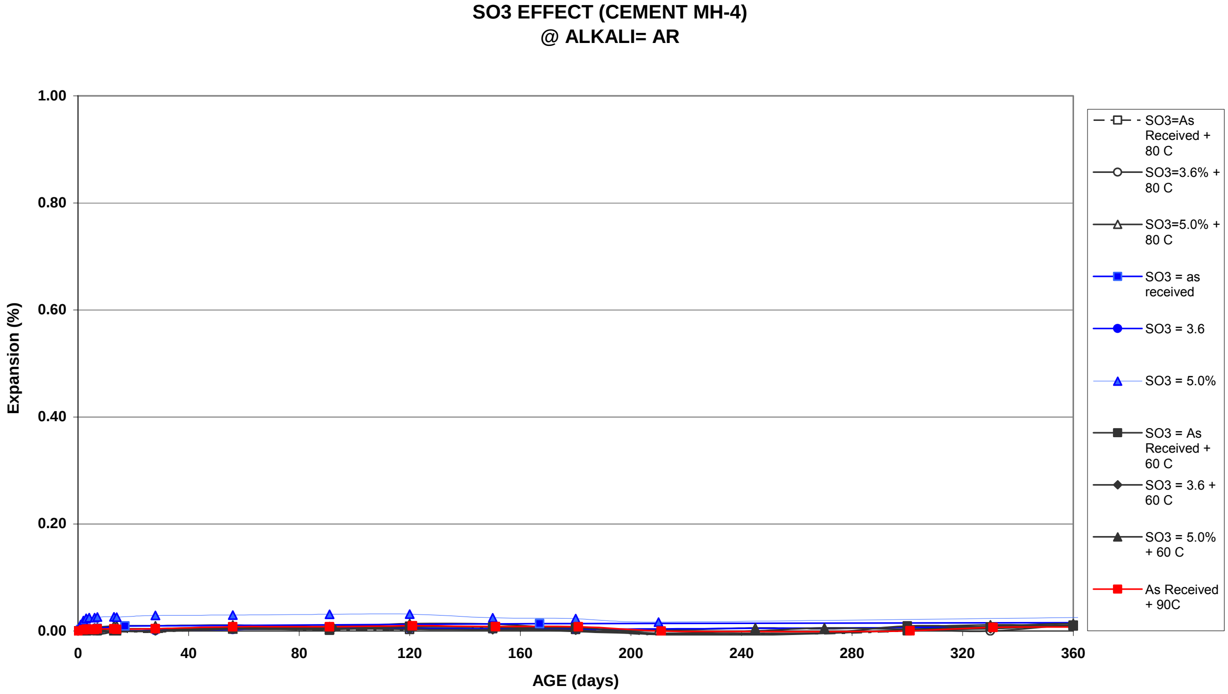


Figure 94: Expansion for Cement MH4

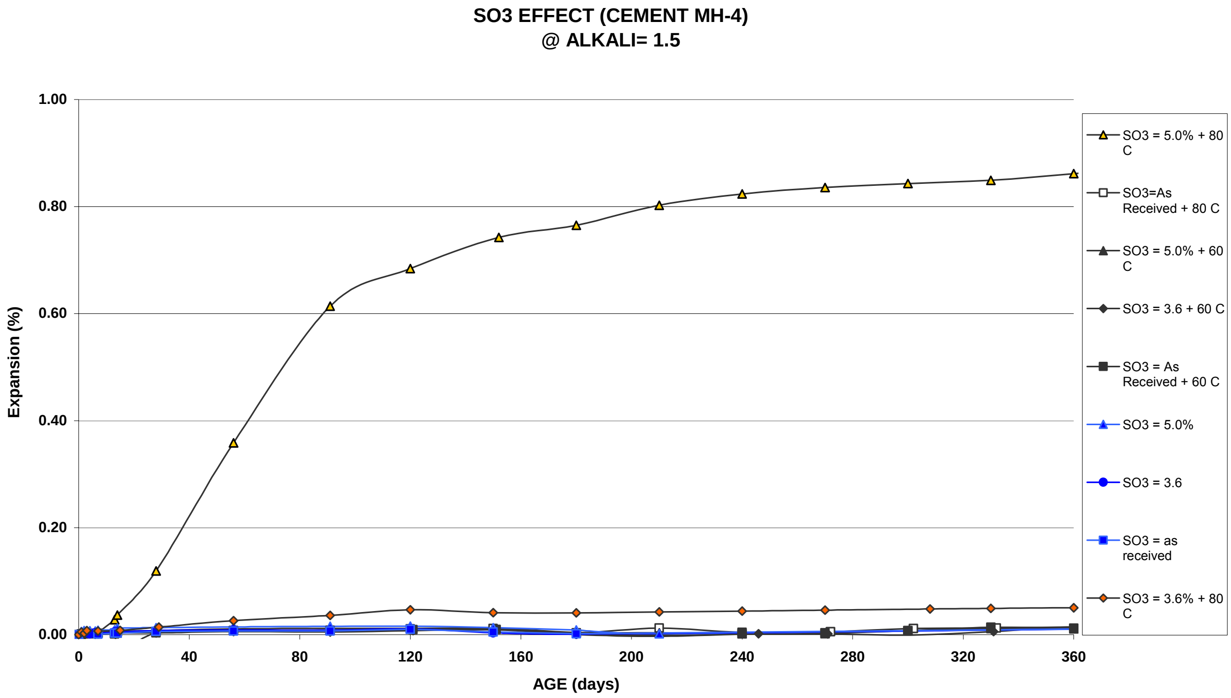


Figure 95: Expansion for Cement MH4

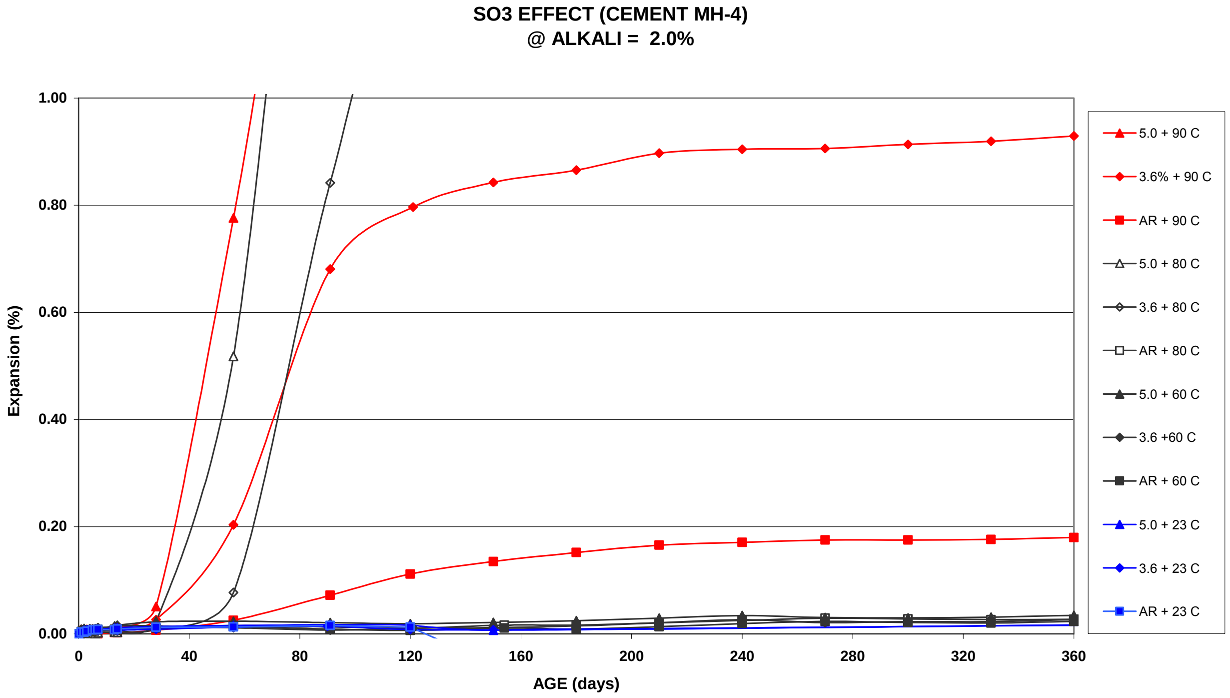


Figure 96: Expansion for Cement MH4

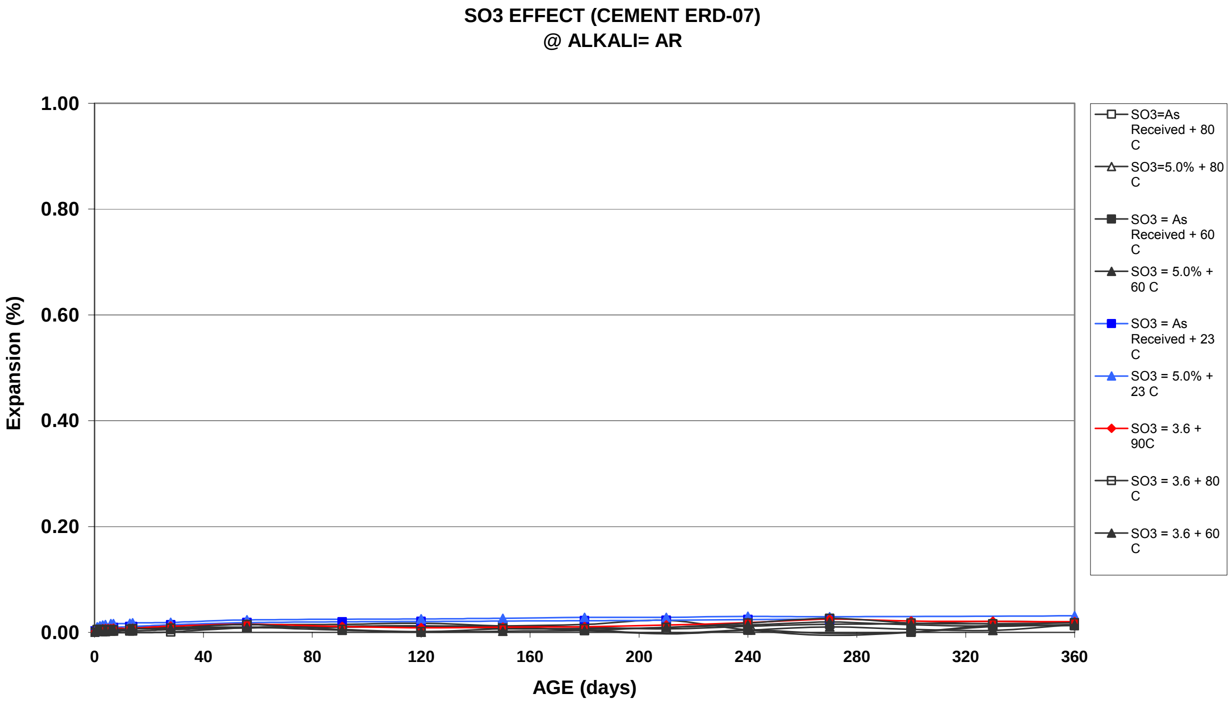


Figure 97: Expansion for Cement ERD07

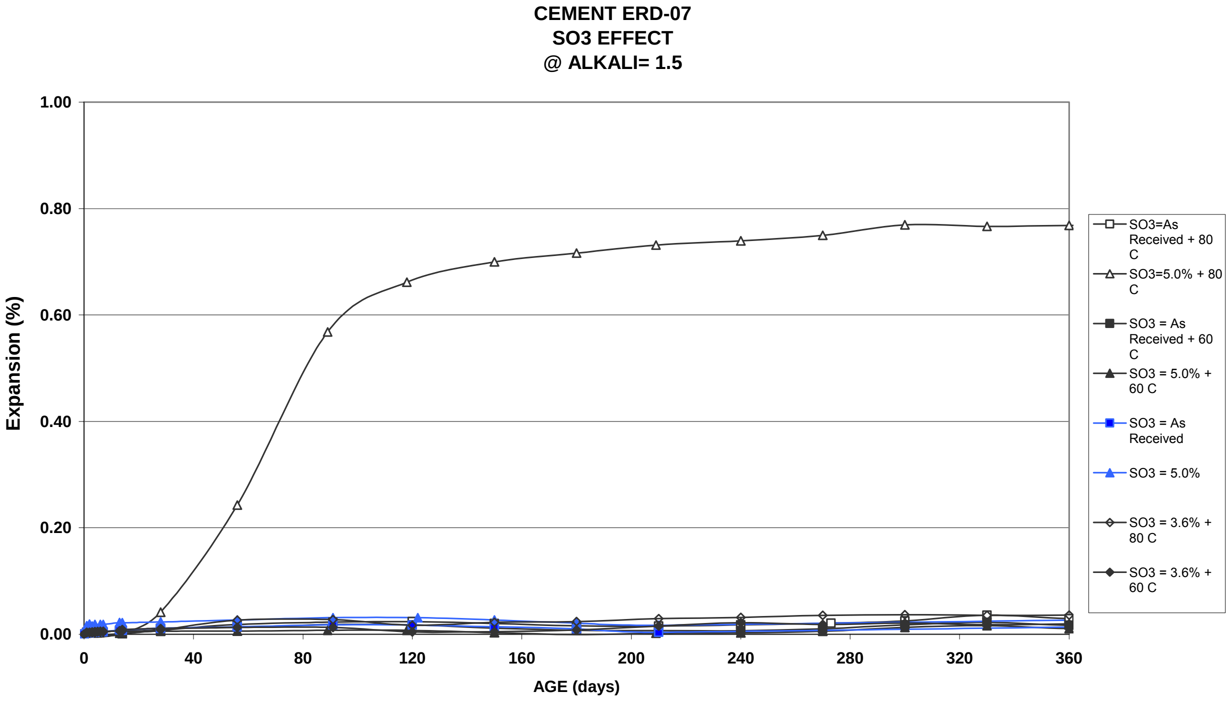


Figure 98: Expansion for Cement ERD07

Temperature effects on structural durability are primarily due to its influence on ettringite stability and the microstructure quality of C-S-H gel [5, 47, and 74]. The results indicate that increasing temperature has significance depending on the alkali, sulfate and mineralogical composition of cements. The results also indicate that while increasing tricalcium silicate content at lower tricalcium aluminate content can trigger deterioration at sulfate content as low as 3.07 and an alkali content of 1.5%, increasing tricalcium aluminate appears to increase cement tolerance to higher sulfate content.

In addressing the role of service conditions such as those existing in marine conditions for structural elements subjected to cycles of wet and dry exposures as well as continuous salt exposure, several mixes were prepared and the results are depicted in Figures 99 and 100. Durability of structural elements on exposure to marine conditions depends on the nature of exposure; that is, continuous or cyclic. Mixes continuously submerged in marine solution appear to experience higher degree of expansion than those subjected to cyclic exposure. Additionally, the amount of expansion appears to depend on cement mineralogy. Cements high in tricalcium silicate and aluminate appear to be affected the most. However, incorporation of mineral admixture, as a replacement for cement, appears to diminish the adverse effects of high tricalcium aluminates and silicates content in cements.

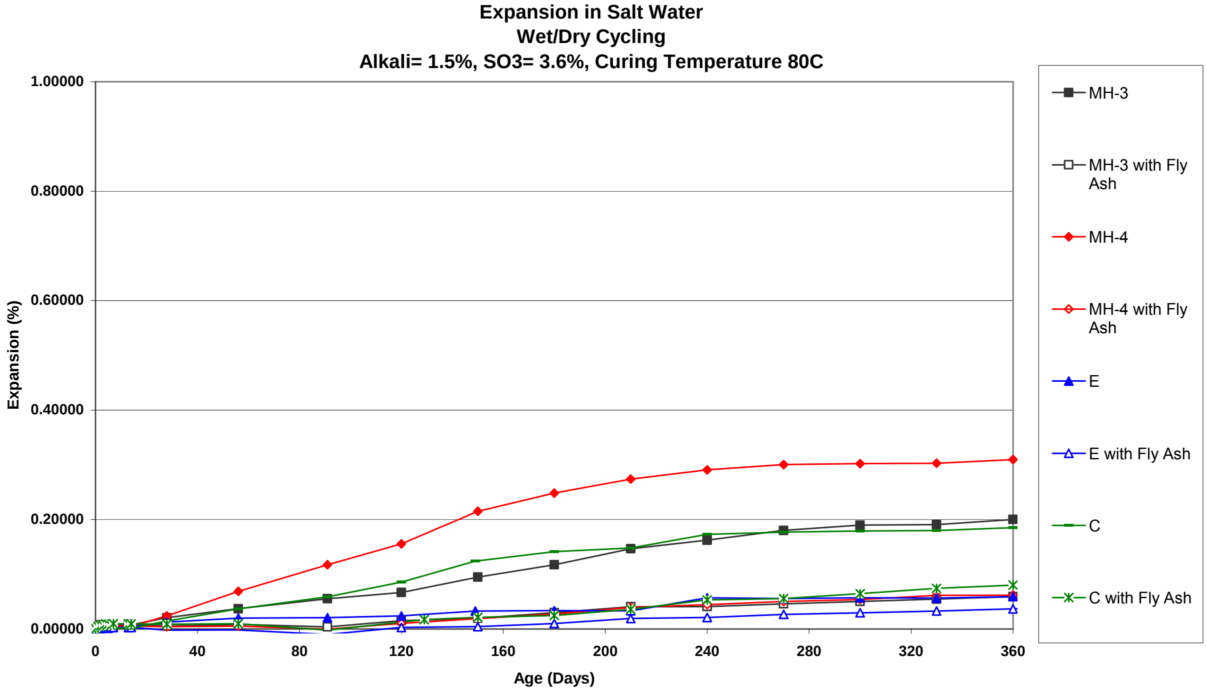


Figure 99: Expansion in Salt Solution

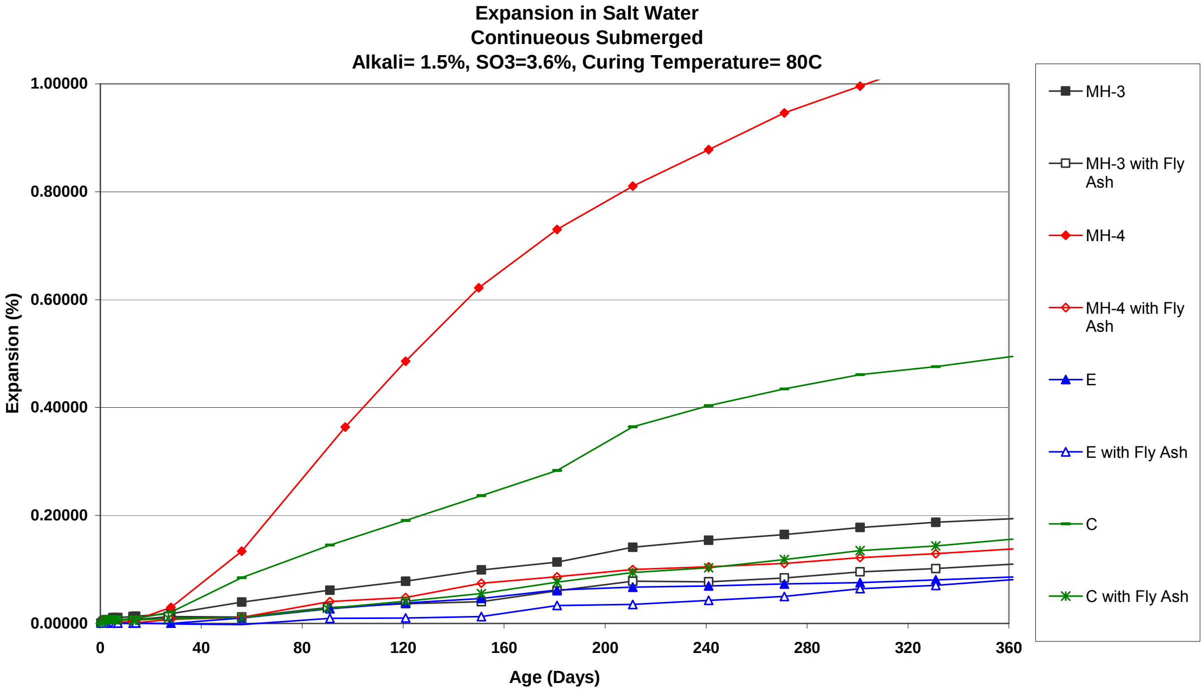


Figure 100: Expansion in Salt Solution

CHAPTER III
DISCUSSION AND CONCLUSION

The findings of this study indicate that for all the cements studied here, increasing sulfur trioxide content increases expansion. The increase was accompanied by an increase in the amount of ettringite determined by x-ray diffraction. This can be seen from Figures 101 and 102 for Cements E and C.

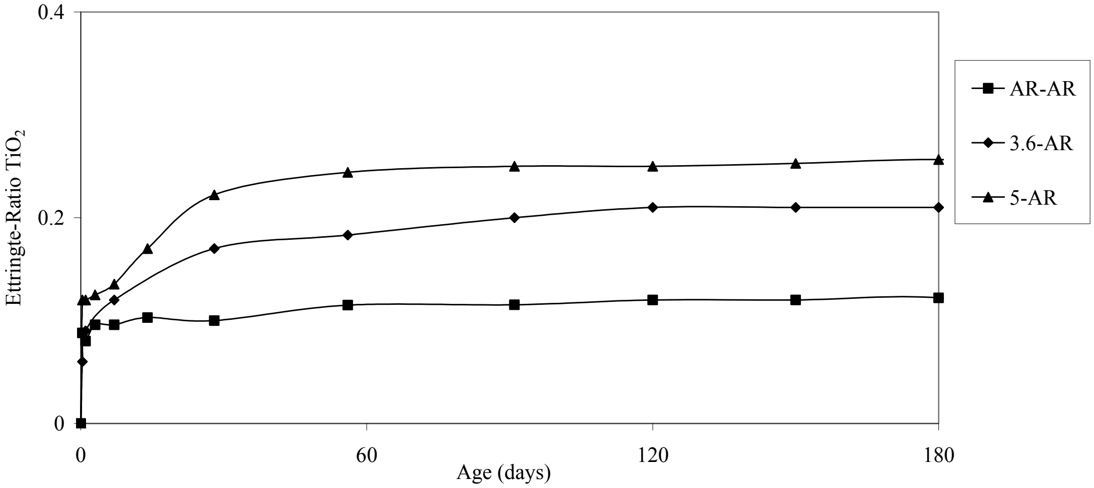


Figure 101: Effect of Sulfate Content on Ettringite Formation in Cement E

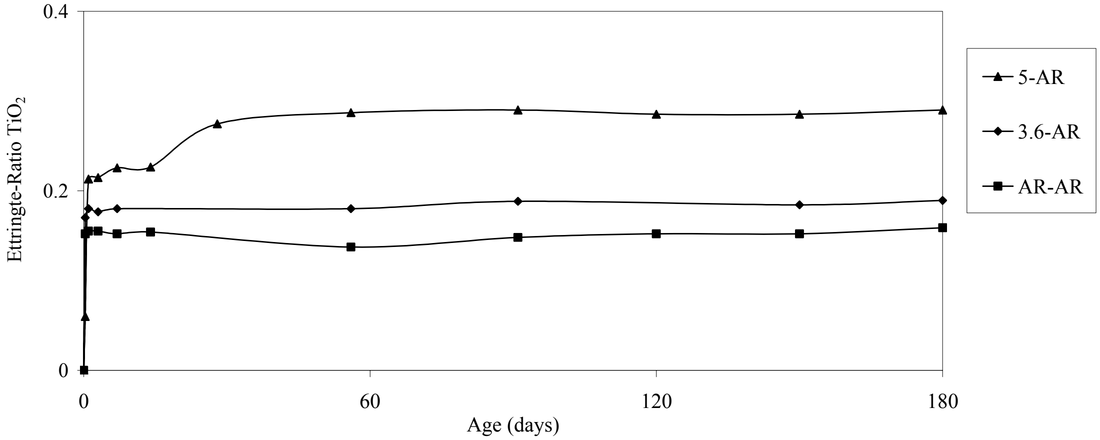


Figure 102: Effect of Sulfate Content on Ettringite Formation in Cement C

The degree of expansion was found to depend on cement mineralogy. Cements with higher tricalcium silicates but lower aluminates experienced higher expansion than cements with higher silicates and aluminates. Also, high silicate/low aluminate cements experienced a decrease in their early strength on increasing sulfur trioxide content. This could be explained from XRD analysis on the quantification of unreacted tricalcium silicate during the first days of hydration. Figures 14 and 15 indicate that the amount of unhydrated tricalcium silicate increases with increasing the sulfate content. The effect was insignificant after 7 days of hydration. This could render a weaker matrix due to slower hydration of tricalcium silicate. Increasing the SO_3 content also affected the hydration process. This is evident from the delay of the appearance of the first peak in heat of hydration curves (Figures 103 and 104). While the addition of sulfates delayed the peak position, it is also clear that the effect of the delay was more significant in Cement C with higher tricalcium silicate content than cement E.

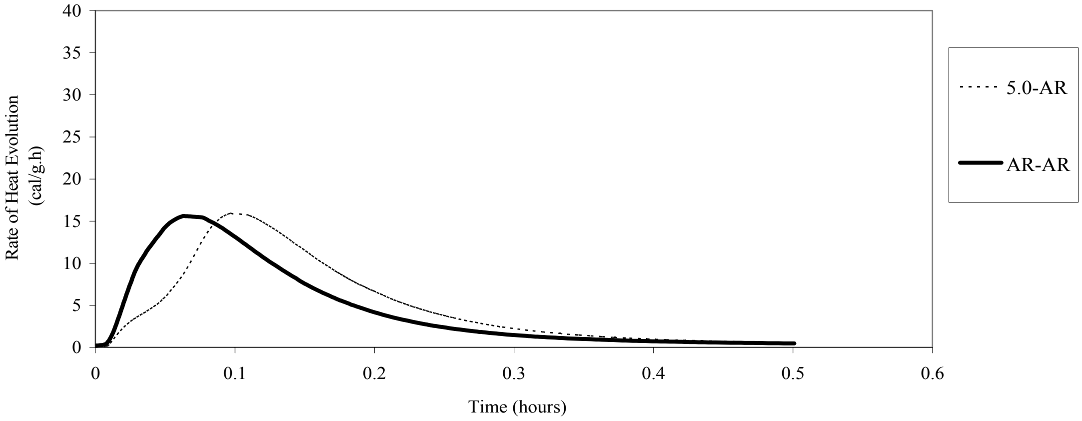


Figure 103: Effect of Sulfate Content on Heat of Hydration for Cement E

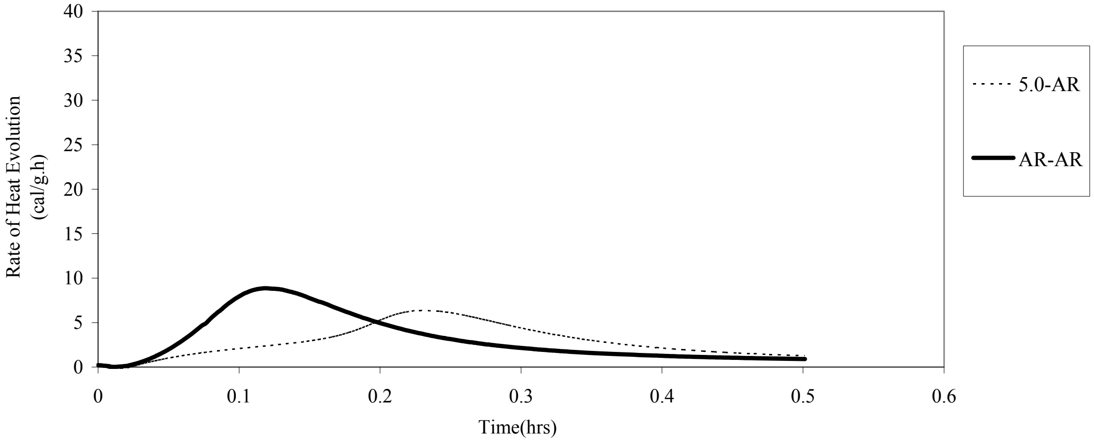


Figure 104: Effect of Sulfate Content on Heat of Hydration for Cement C

Cements that are high in their aluminate and silicate content showed less expansion at the same sulfate level in comparison to high silicate/low aluminate cements. MH4 has high C_3S content, yet it did not experience high expansion on increasing its sulfate content to 5% as that experienced by cements C and MH3. With low C_3A content, more sulfates are available in pore solution and possibly for adsorption by C-S-H gel. They may later be released to form ettringite at numerous sites throughout the matrix. In cements with high C_3A, even with high C_3S, the primary reaction for sulfates is their reaction with the aluminate phase to form ettringite or other aluminosulfate phases. This means less sulfates are available for C-S-H adsorption and later release for delayed ettringite formation.

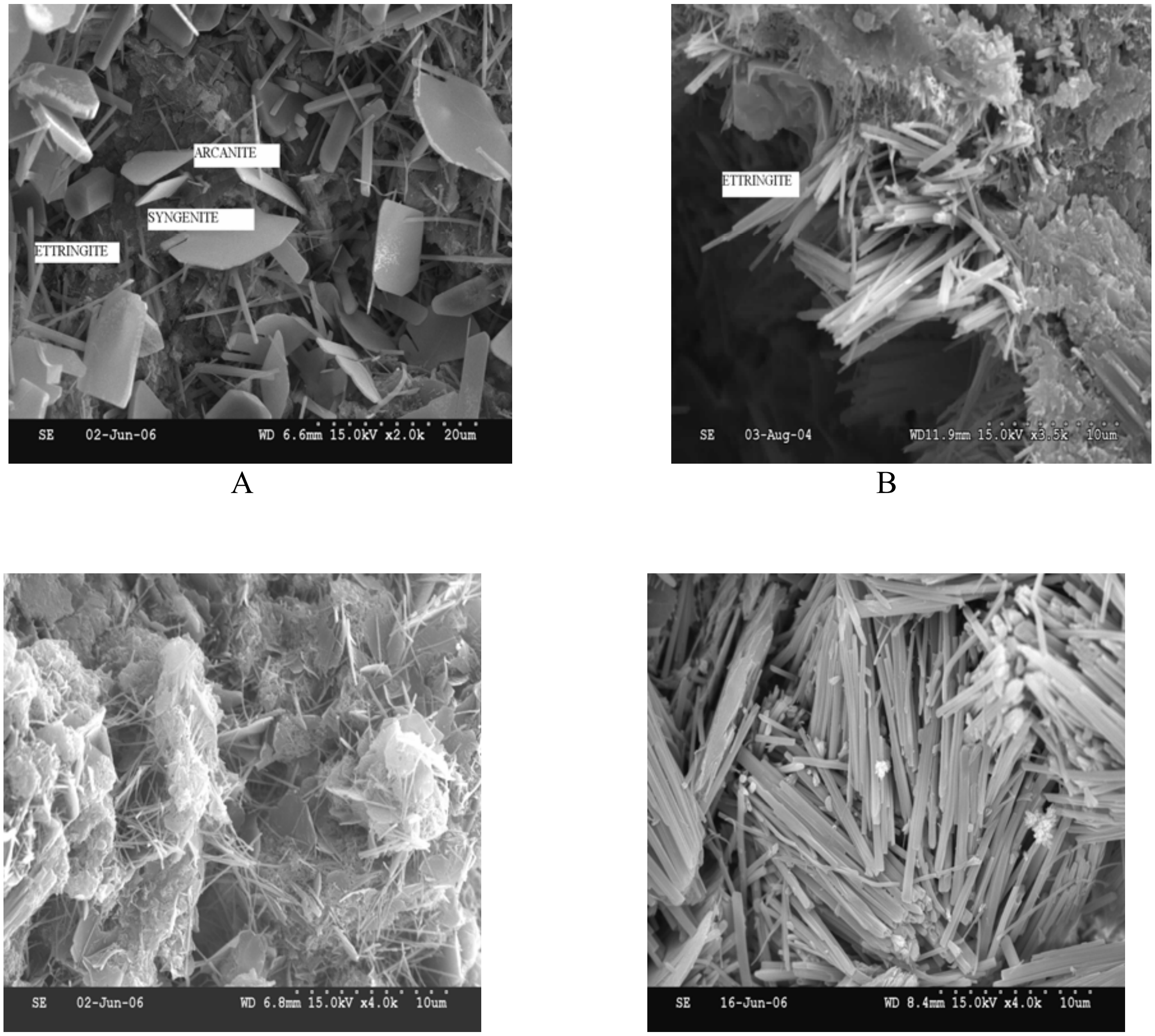
It has been reported in the literature (8) that C-S-H gel has affinity to adsorb sulfate ions. These ions can be released at a later time and become available for ettringite formation and potential expansion. Sulfur trioxide content and its substitution in the hydration gel is also known to affect gel quality. The formation of C-S-H gel requires an optimum amount of sulfate for well-refined uniform gel. While the effects of sulfur trioxide and sulfate/aluminate molar ratio on durability have been identified in the literature, the role of tricalcium silicate content is believed to be of significance. It is also believed to affect specific tolerable limits on sulfur trioxide and sulfate/aluminate molar ratio. As an example, cements MH3 and E both had the same sulfate/aluminate molar ratio (approximately 1.0) yet cement MH3 expanded higher than E. Consequently, it is important not to consider molar ratio in isolation, since other factors such as C_3S could affect expansion behavior as indicated in this study.

In conclusion, as to the effects of increasing the sulfate content on cements durability, the findings indicate that sulfate content has its significance on the hydration process, hydration products, matrix morphology/microstructure, strength and expansion of mortar.

Increasing the alkali content to 1.5% and 2%, under ambient curing and lime exposure, did not result in a major impact on expansion behavior for all cements, and for all sulfate levels. The expansion behavior was dramatically altered when the alkali level increased to 3.8% for all sulfate levels.

A correlation between the expansion behavior and the ettringite formation was established earlier, the expansion increased as the amounts of ettringite formed increased. This relationship holds entirely true for low alkali contents, and was dependent on sulfate content of cement. Increasing the alkali content did not affect the total amount of ettringite formed ultimately. The addition of the alkali, however, and depending on the sulfate content, results in delay of the appearance of the ettringite as detected by XRD. This implies ettringite instability at higher alkalinity, a finding that is consistent with what has been reported previously in the literature (1). This phenomenon depends on the sulfate content; at 5% SO_3 ettringite appeared as early as 8 hours in cases 5-3.8 while for AR-3.8 it was delayed for days.

Expansion behavior can not be totally explained by the amount of ettringite formed and detected by XRD. For example, the amount of ettringite was almost the same in the 5% sulfate cases, yet, only the 5-3.8 case showed excessive expansion and the eventual damage. Again, for the 3.6% sulfate cases, at all tested alkali contents, showed the same amount of ettringite, yet the 3.6-3.8 case is the only case that showed excessive expansion. In order to understand the role of alkalis in expansion, SEM was used to assess the morphology of ettringite. Figure 105 shows ettringite images for cases E-5-3.8 and C-5-3.8. At 3 days, ettringite had a fine needle morphology and dispersion throughout the gel. At 91 days the needles appeared well crystallized and much thicker. The change in ettringite morphology and the accompanying excessive expansion could be explained through crystal growth theory proposed by Mehta (4) and Charlotte (5).



A B

C D

Figure 105: SEM Images on Paste samples for Cements C and E-Case 5-3.8

A. E-5-3.8@ 3 days B. E-5-3.8 @ 91 days

C. C-5-3.8@ 3 days D. C-5-3.8 @ 360 days

It seems however, that a key parameter, besides the ettringite formation is mortar strength and the gel quality. Considering strength curves, it could be seen that the initial strength of 3.8% alkali cases was almost the same at all sulfate levels. However, the damage occurred in the 5% case, then 3.6% case, and did not occur in the AR case for cement E, though it did in cement C. Noting from the collected data on cases AR-3.8 that expansion was highest in the first 28 days, yet ettringite was not detected up to that age. This could indicate a possible interaction between alkalis and hydrated C-S-H gel or tricalcium silicate hydration products. The higher expansion could be due to the moisture absorption by the porous structure that formed due to high alkali content.

In order to examine this hypothesis, the total porosity and surface area were measured for cases C-AR-AR and C-AR-3.8 at a degree of hydration of 98%. Porosity is an indication of the gel quality. The hydration of C_3S and, hence, the formation of C-S-H gel goes through different stages. Each part of the formed gel has a typical pore size associated with its formation. The normal hydration process of C_3S is described as follows: 1. hydrolysis stage, 2. induction stage during which the first layer of gel forms around the unhydrated C_3S grain, 3. acceleration stage, 4. deceleration stage and 5. steady state. During the acceleration stage the gel begins to break down allowing further hydration of inner grain and more layers of gel form resulting in its thickening. This gel layer forms a barrier through which water must diffuse to allow further hydration of the most inner grains. The gel formed as a result of the last stages of hydration is typically denser than the gel formed on the outer layers, and has pore sizes in the range of 1-4 nm in diameter (20). The results of the pore size distribution are presented in Figure 106. It can be seen that the pore volume (or total surface area) for pore diameters classified as “small pores” was higher for the AR-AR case. This indicates that AR-AR case has more complete hydration of the inner grains than AR-3.8. This is consistent with the results reported by Juenger et al (20) and indicates the poor quality of the inner gel as a direct effect of increasing alkali content of cement.

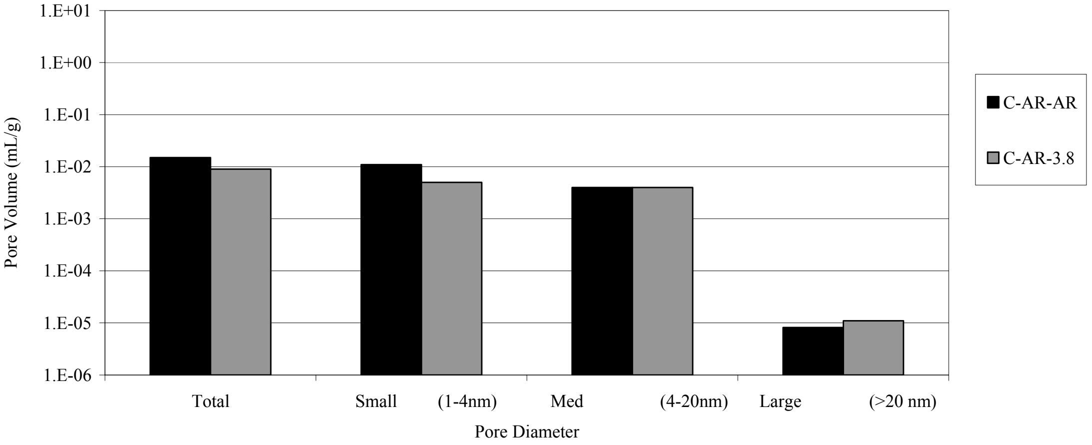


Figure 106: Pore Size Distribution for Cement C

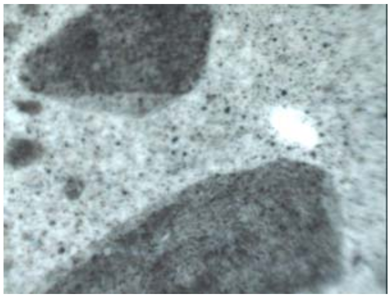


Figure 107: Microstructure of Cement C-5-3.8

The presented results in this study showed that increasing alkali content results in strength reduction, at all levels. It was also shown through porosity studies that inner gel quality was affected by the alkali content of the cement. Additional examination of the microstructure was conducted in order to better understand the alkali effect on the morphology and nature of the hydrated gel. Using light microscopy, the microstructure of cement C-5-3.8 and C-5-AR was examined. The images showed clear differences between alkali-doped cements and the cases of as-received alkali content. Figure107 shows the microstructure of the high alkali cement. It can be observed that there are distinctively dark and white regions. These spots were removed from the paste and further examined using XRD and SEM.

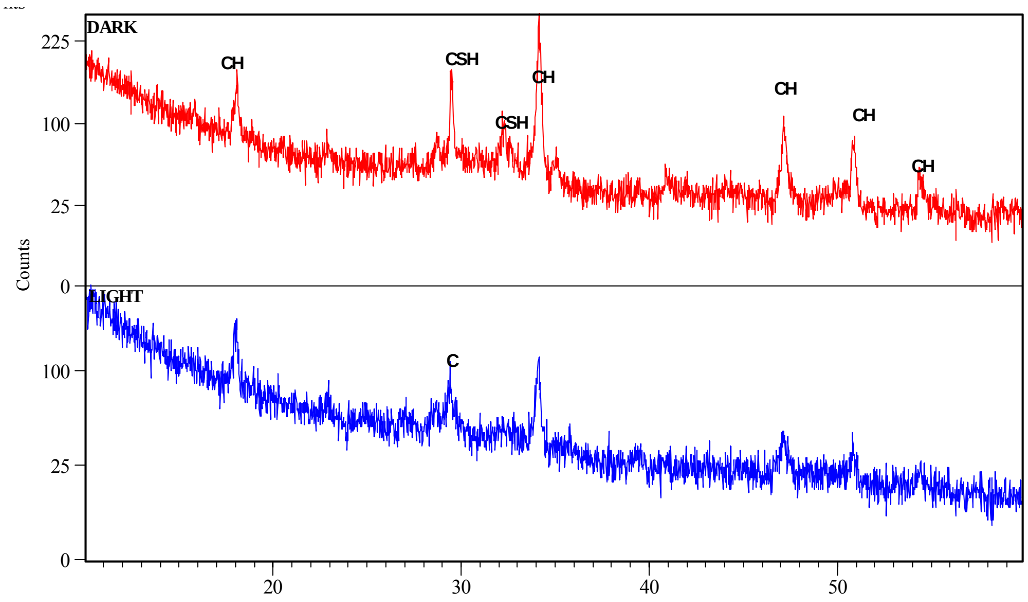


Figure 108: XRD Pattern for Cement C-5-3.8, Case A in Figure 105
CH= Calcium Hydroxide, CSH= Calcium Silicate Hydrate Gel, C=Calcite

Examination using XRD showed that the dark regions contained crystalline C-S-H gel. The crystalline nature of the gel formed in higher alkali content was reported by other researchers (50) where it was indicated that a higher degree of crystallinity results in preferentially weaker planes and a lower compressive strength.

The white spots were identified as CH using XRD. Earlier data collected on high alkali specimens using Rietveld analysis on the hydrated paste revealed these differences, especially in the first 24 hours (Figures 55 through 57). This also was confirmed by chemical analysis on the liquid phase, where calcium ions concentration was lowest in the higher alkali cases (Figures 68 through 73). The conclusion was that in high alkali cases, CH precipitated faster. CH deposits early on (within the first few hours) would interfere with further gel nucleation and results in a less continuous gel structure. Also, it is believed that the alkali accelerates the stiffening of the cement paste. This is evident from the shortening of the dormant period. The presence of the alkalis is believed to accelerate the nucleation around the cement grains prior to the dormant period thus preventing the diffusion and further hydration of the inner cement particles later on. This will result in a less refined, less continuous microstructure of poor quality.

It has been reported in the literature that higher alkalinity results in a lower Ca/Si ratio (19, 26, 27, and 35). This could not be verified in the current investigation using polished sections under SEM/EDS. However, calcium ion concentration in the liquid phase was always lower as the alkali content increased; this may result in a lower Ca/Si gel, but it could not be verified in this study.

Inclusion of other ions within the gel seems to impact the Ca/Si ratio. Other ions (S, Fe, Mg, and Al) were always present in the gel with some variations; however, a trend could not be established. The effect of ion inclusion, in minor quantities, on the quality of the gel is not quite clear. It was mentioned in the literature (10) that hydrated gel has affinity to adsorb sulfate ions, and this affinity increases at higher alkalinity. It was also mentioned elsewhere (75) that sulfate ions could substitute up to 1/6 of the Si in the gel. This may result in a weaker structure. Again, this could not be verified in the current investigation. Other researchers (37) have mentioned that in cases where the mixes were doped with alkalis (NaOH), the sodium ions substituted for the Si ions in the C-S-H gel, a similar notion was reported by K. Suzuki et al (35) which resulted in a lower Ca/Si ratio. In the current investigation, the potassium was not detected in any of the cases.

SEM work on fractured surfaces for certain cases of cements C and E indicated difference between cases C-AR-3.8 and C-AR-AR. In the former, the gel appeared disintegrated and less continuous. For E-AR-AR case the bars did not experience the degradation that was experienced by cement C. This is believed to be due to the higher C_3S content of cement C. The effect of the C_3S lies in the production of higher amounts of C-S-H gel early on, and higher amounts of calcium hydroxide. The effect of C_3S is evident from the expansion results for cement MH3 and C. The expansion results were higher for that cement.

Cements C, MH3 and E, all have very low C_3A content. The difference in behavior between cements MH3 and C as compared to cement E was explained by the C_3S content. But, cement MH4 has a high C_3S content, yet the expansion values were lower compared to cement MH3. This is believed to be due to the difference in the C_3A content. The C_3A content is about 10% (Rietveld) for cement MH4 as compared to 2% for cement MH3.

Increasing the alkali content seems to increase the rate of hydration early on, especially the rate of hydration of C_3A. This was evident at 3.8% alkali content from the heat of hydration curves. This effect was not as clear at 1.5% and 2% alkali levels. As shown earlier, increasing the sulfate content delayed the appearance of the first peak. This implies that sulfates delay the hydration of the C_3A. Increasing the sulfate level (at higher alkali content) results in slowing down the reaction. This did not delay the appearance of the first peak but generated less heat (cases 5-3.8).

The effect of increasing the curing temperature is predominantly on lowering the alkali and sulfate content that triggers excessive expansion. In most cements, an alkali content of 1.5% and a sulfate content of 5% generated excessive expansion when mixes were cured at temperatures of 80°C. Salt exposure appears to be more damaging if the mortar is continuously submerged. The damage was most pronounced in high tricalcium aluminate cement. This is due to the presence of an external source of sulfate provided through the salt solution.

The presence of high alkali concentration seems to interrupt the growth of the C-S-H gel fibers as these crystals grow on the surface of the C_3S grains. This will prevent the bridging action and the interlocking of these fibers. This will result in a weaker microstructure. High alkali concentration would also result in early precipitation of calcium hydroxide which may interfere with the growth of the C-S-H gel fibers.

Without proper retardation, alkalis seem to impact the first layer formed around the C_3S grains. Typically this layer will breakdown and become more permeable at the end of the dormant period, allowing diffusion and more water to help the hydration of the inner unhydrated grains. The presence of alkalis results in early stiffening of this layer and this hinders further diffusion and further hydration of the inner particles. This may explain the lower portion of the gel pores (1-4 nm) in the higher alkali cases. These pores are typical of the denser phenograins and have positive strength contribution. Also, ettringite formed in the presence of high OH^- is expansive in nature. The combination of the porous microstructure and expansive ettringite results in high expansion, reduction in compressive strength and eventual failure.

CHAPTER IV
CONCLUSIONS AND RECOMMENDATIONS

The following is a list of conclusions on the role of alkalis and sulfates on durability of structural elements:

1. Increasing sulfate content of cements increased expansion over a period of 360 days when mortar mixes were exposed to a saturated lime solution. The degree of expansion was found to be dependent on mineralogical composition of cement with cements low in tricalcium aluminate but high in tricalcium silicate experiencing the highest expansion.
2. Increasing the sulfate content of cement increased the amount of ettringite.
3. Compressive strength did not show significant change on increasing sulfate content of cements. However, increasing sulfate content appears to lower early compressive strength. The effect does not seem prominent beyond 180 days.
4. Increasing sulfate content was found to increase the time for gypsum dissolution.
5. Increasing alkali content, under ambient curing conditions, was found to affect the compressive strength of mortar at all sulfate content. The results indicate that a strength loss of 2,000 psi occurs on increasing the alkali content from the as-received condition (0.27, 0.4, and 0.83%, 0.93) to 1.5% through the addition of Terra Alba gypsum. The effect appears to be independent of the sulfate content of the cement. This trend was shared independent of tricalcium silicate content of the cement.
6. For cement with high initial alkali (1.03%), and cubic tricalcium aluminate content (9%), increasing alkalis to 1.5% results in strength drop of 1,000 psi from the as-received strength values. It is to be noted that the decrease in strength is relative to the as-received mix values. This implies that a decrease of 1,000 psi is no less damaging than 2000 psi due to the fact that it corresponds to a lower alkali doping dosage from the as-received alkali value.
7. Increasing the alkali content, in general, was found to have negative effects on the compressive strength of mortar. The effect appears to be more negative for high tricalcium aluminate cements.
8. Though increasing alkali content of cements showed strong effect on compressive strength of mortar, expansion measurements, in accordance with ASTM C1038,

did not reveal a dependence of expansion on alkali content of cement. The only exception was for mixes where alkali content was increased to 3.8%.

9. Alkali effect on durability appears to be evident in delaying ettringite formation.
10. Alkali content was found to affect the nature of the hydration gel with implications on porosity and calcium hydroxide rate of formation.
11. Increasing alkali content to 2% and sulfate content to 5% did not adversely affect the expansion behavior of all mixes studied here under ambient curing conditions.
12. Increasing alkali content to 1.5%, at all sulfate contents, had a negative effect on the compressive strength of mortar, under ambient conditions.
13. Increasing the curing temperature to 80°C for mixes with alkali content of 1.5% generated high expansion than values reported for ambient curing. The degree of expansion was found to depend on cement mineralogy and sulfate content. For cements high in their tricalcium silicate content, excessive expansion occurred at sulfate levels of 3.6 and 5%. However, if cements are high in tricalcium silicates and aluminates, the amount of sulfate that generated rapid expansion at an alkali content of 1.5% was found to increase to 5%.
14. Exposure of heat cured mixes, doped to sulfate content of 3.6% and alkali content of 1.5%, to a salt solution, generated expansion. The degree of expansion experienced by different cements appeared to depend on tricalcium silicate and aluminate contents. The highest expansion was recorded for the cement that is high in its tricalcium aluminate and silicate content. The least expansion was experienced by cement E which has tricalcium aluminate of 4% and tricalcium silicate of 54%.
15. Continuous submersion in salt solution was found to result in higher expansion than wet/dry cycles. Incorporation of mineral admixture, replacement basis, reduced the observed expansion for all mixes.

Based on the findings of this investigation, it is recommended that:

1. In order to maintain durability of structural concrete elements exposed to elevated temperatures and salt environment, it is recommended that current limits on SO_3 content be maintained. It is also recommended that alkali content has to be maintained below 0.60%. This is especially critical for cements that have tricalcium silicate above 58% (XRD) and tricalcium aluminate above 4% (XRD).

2. Initiate a study to address the effects of incorporating mineral admixtures on improving durability of cements that have high alkali and sulfate content.

REFERENCES

1. Jochen Stark, Katrin Bollmann, “Delayed Ettringite Formation in Concrete”, Bauhaus-University Weimar/Germany.

2. H.Y. Ghorab, D. Heinz, U. Ludwig, T. Meskendahl and A. Wolter, “On the Stability of Calcium Aluminate Sulfate Hydrates in Pure Systems and in Cements”, 7th International Congress on Chemistry of Cement, Paris (1980), pp.496-503.

3. M. Collepardi, “A State-of-the art Review on Delayed Ettringite Attack on Concrete”, Cement and Concrete Composites 25 (2003), pp 401-407.

4. P. K. Mehta, “Mechanism of Expansion Associated with Ettringite Formation”, Cement and Concrete Research Vol. 3 (1973), pp.1-6.

5. C. Famy, Expansion of Heat-Cured Mortars, PhD Thesis, Imperial College of Science, Technology and Medicine (University of London) (1999).

6. Deng Min and Tang Mingshu, “Formation and Expansion of Ettringite Crystals”, Cement and Concrete Research, Vol. 24 (1994), pp. 119-126,.

7. I. Odler, “Interaction Between Gypsum and C-S-H Phase Formed in C3S Hydration”, 7th international Congress on Chemistry of Cement, Vol. 4 (1980), pp. 439-495.

8. Yan Fu, Ping Gu, Ping Xie, J.J Beadoin, “A kinetic Study of Delayed Ettringite Formation in Hydrated Portland Cement Paste”, Cement and Concrete Research, Vol. 25, No. 1 (1995), pp. 63-70.

9. L. Divet and R. Randriambololona, “Delayed Ettringite Formation: The Effect of Temperature and Basicity on the Interaction of Sulfate and C-S-H phase”, Cement and Concrete Research, Vol. 28, No. 3 (1998), pp. 357-363.

10. D. Heinz and U. Ludwig, “Mechanism of Secondary Ettringite Formation in Mortars and Concretes”, ACI SP100-105, pp. 2059-2071.

11. William Lerch, “The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes”, Presented at the Forty Ninth Annual Meeting of the Society (ASTM), June 24-28, 1946.

12. Ivan Odler and Michael Gasser, “Mechanism of Sulfate Expansion in Hydrated Portland Cement”, J. American Ceram. Soc. 71,11(1998), pp.1015-1021.

13. Cheng Sheng Ouyang, Antonio Nanni and Wen F. Chang, “Internal and External Sources of Sulfate Ions in Portland Cement Mortar: Two Types of Chemical Attack”, Cement and Concrete Research, Vol. 18 (1988), pp. 699-709.

14. D. L. Kantro, “Sulfate Specifications as a Constraint to Gypsum Addition to Cement and Possible Repalcement of Gypsum as an additive”, PCA, 1979.

15. H.F.W. Taylor, "Ettringite in Cement Paste and Concrete", Concrete; From Material to Structure; Arles, France, September 11-12, 1996; Proceedings of the RILEM International Conference.

16. S. Sprung and W. Rechenberg, "Influence of Alkalis on the Hydration of Cement", Effects of Alkalis on Properties of Concrete, Proceedings of a Symposium held in London, 1976.

17. B. Osbaeck, "Alkalis and Cement Strength", Proceedings of the 6th International Conference on Alkalis in Concrete; Research and Practice, Copenhagen, Denmark, 1983, pp.93-100.

18. I. Odler and R. Wonnemann, "Effects of Alkalis on Portalnd Cement Hydration, I. Akalai Oxides Incorporated into the Crystalline Lattice of Clinker Minerals", Cement and Concrete Research, Vol. 13 (1983), pp. 477-482.

19. S. J. Way and A. Shayan, "Early Hydration of a Portland Cement in Water and Sodium Hydroxide Solutions: Compositions of Solutions and Nature of Solid Phases", Cement and Concrete Research, Vol. 19 (1989), pp. 759-769.

20. Maria C. Garci Juenger and Hamlini M. Jennings' "Effects of High Alkalinity Cement on Pastes", ACI Materials Journal, V. 98, No. 3 May-June 2001, pp. 251-255.

21. Dale P. Bentz, "Influence of Alkalis on Porosity Percolation in Hydrating Cement Pastes", Submitted for CCR 2005.

22. Inam Jawed and Jan Skalny, "Alkalis in Cement: A Review, II. Effects of Alkalis on Hydration and Performance of Portland Cement", Cement and Concrete Research, Vol. 8 (1978), pp. 37-52.

23. I. Odler and R. Wonnemann, "Effects of Alkalis on Portalnd Cement Hydration, II. Akalis Present in Form of Sulfates", Cement and Concrete Research, Vol. 13 (1983), pp. 771-777.

24. Vagn Johansen, "Influence of Alkalis on the Strength Development of Cements", Proceedings of the Symposium on the Effects of Alkalis on Properties of Concrete, London, Sept. 1976, p 81.

25. H. Y. Ghorab and S.H. Abu El Fetouh, "Factors Affecting the Solubility the Solubility of Gypsum, Part II, the Effect of Sodium Hydroxide under Various Conditions", Journal of Chemical Technology and Biotechnology, 35A, (1985), pp. 36-40.

26. Sujin Song, Hamlin M. Jennings, "Pore Solution Chemistry of Alkali-Activated Ground Granulated Blast-Furnace Slag", Cement and Concrete Research 29 (1999), pp. 159-170.

27. S. Song, D. Sohn, H. M. Jennings, T. O. Mason, "Hydration of Alkali-Activated Ground Granulated Blast Furnace Slag", Journal of Materials Science 35 (2000) pp. 249-257.

28. B. Osbaeck, “On the Influence of Alkalis on Strength Development of Blended Cements”, pp. 375-383.

29. K. M. Alexander and C.E.S. Davis, “Effect of Alkali on the Strength of Portland Cement”, Australian Journal of Applied Sciences, V. 11, No. 1, 1960, pp. 146-156.

30. Walter J. McCoy and Ottomar L. Eshenour, “Significance of Total and Water-Soluble Alkali Content of Cement” Proceedings of the 5th International Symposium on the Chemistryu of Cement, Vol II, (1968), pp.437-443, Tokyo.

31. B. Osbaeck and E. S. Jons, “The influence of the content and Distribution of Alkalis on the Hydration Properties of Portland Cement”, 7th International Congress on the Chemistry of Cement, Volume 2 (1980), pp. 135-140.

32. M. S. Y. Bhatty and N. R. Greening, “Interaction of Alkalis with Hydrating and Hydrated Calcium Silicates”, Portland Cement Association, pp. 87-111.

33. A.I. Jelenic, A. Panovic, R.Halle and T. Gacesa, “Effect of Gypsum on the Hydration and Strength of Commercial Portland Cements Containing Alkali Sulfates”, Cement and Concrete Research, Vol. 7 (1977), pp. 239-246.

34. J. Gebauer and M. Kristman, “The Influence of the Composition of Industrial Clinker on Cement and Concrete Properties”, World Cement Technology, Match 1979, pp. 46-51.

35. K. Suzuki, T. Nishikawa, H. Ikenaga and S. Ito, “Effect of NaCl or NaOH on the Formation of C-S-H”, Cement and Concrete Research, Vol. 16, pp. 333-340.

36. N. Smaoui, M. A. Berube, B. Fournier, B. Bissonnette, B. Durand, “Effecets of Alkali addition on the Mechanical Properties and Durability of Concrete”, Cement and Concrete Research (Articles in Press) 2004.

37. A. Shayan and I. Ivanusec, “Influence of NaOH on Mechanical Properties of Cement Paste and Mortar with and without Reactive Aggregate”, Proceedings of 8th International Conference on Alkali-Aggregate Reaction, 1989, pp. 715-720.

38. M.P. Luxan, M. Frias and F. Dorrego, “Potential Expansion of Cement Mortars in the Presence of K_2SO_4 and Pozzolan”, Cement and Concrete Research, Vol. 24, No. 4 (1994), pp. 728-734.

39. H. E. Vivian, “The Effect of Added Sodium Hydroxide on the Tensile Strength of Mortar”, CSIRO (Australia), Bulletin No. 299,256, 1950, pp. 48-52.

40. W. G. Hime and S.L. Marusin, “Delayed Ettringite Formation: Many Questions and Some Answers”, ACI SP177-13, pp. 199-206.

41. J. Stark and K. Bollmann, “Laboratory and Field Examinations of Ettringite Formation in Pavement Concrete”, ACI SP177-12, pp. 183-198.

42. Charlotte Famy and Hal F. W. Taylor, "Ettringite in Hydration of Portland Cement Concrete and its Occurrence in Mature Concretes", ACI Materials Journal July-August 2001, pp 350-356.

43. M.D.A Thomas, "Ambient Temperature DEF: Weighing the Evidence", Fifth Canmet/ACI International Conference on Durability of Concrete, Barcelona, Spain 2000, pp 43-56.

44. H.F.W. Taylor, C. Famy and K.L Scrivener, "Review: Delayed Ettringite Formation", Cement and Concrete Research 31 (2001), pp 683-693.

45. Paul D. Tennis, Sankar Bhattacharja, Waldemar A. Klemm, and F. MacGregor Miller, "Assessing the Distribution of Sulfate in Portland Cement and Clinker and its Influence on Expansion in Mortar", The Symposium on Internal Sulfate Attack on Cementitious Systems, Dec. 7-12, 1997, pp 212-216.

46. F.M. Miller and F.J. Tang, "The Distribution of Sulfur in Present-Day clinkers of Variable Sulfur Content", Cement and Concrete Research, Vol. 26, no. 12 (1996), pp 1821-1829.

47. Hewlett, Peter C, Lea's Chemistry of Cement and Concrete, 4th ed. John Wiley and Sons, Inc., New York, NY (1989).

48. R. Barbarulo, H. Peycelon, S. Prene, J. Marchand, "Delayed Ettringite Formation Symptoms on Mortars Induced By High Temperature due to Cement Heat of Hydration or Late Thermal Cycle", Cement and Concrete Research, 35 (2005) pp. 125-131.

49. H. Y. Ghorab, E. A. Kishar, and S.H. Abou Elfetouh, "Studies on the Stability of Calciumsulfoaluminate Hydrates.Part II: Effect of Alite, Lime, and Monocarboaluminate Hydrate", Cement and Concrete Research, Vol. 28, No. 1 (1998) pp. 53-61.

50. Yan Fu, Ping Xie, Ping Gu, J.J. Beaudoin, "Effect of Temperature on Sulfate Adsorption/Desorption by Tricalcium Silicate Hydrates", Cement and Concrete Research, Vol. 24, No. 8 (1994), pp. 1428-1432.

51. C. D. Lawrence, "Long-Term Expansion of Mortars and Concrete", Ettringite-The Sometimes Host of Destruction, ACI SP177, pp 106-123.

52. Yan Fu and James J. Beaudoin, "Mechanisms of Delayed Ettringite Formation in Portland Cement Systems", ACI Materials Journal July-August 1996, pp 327-333.

53. Zhaozhou Zhang, Jan Olek, Sidney Diamond, "Studies on Delayed Ettringite Formation in Early-age, Heat-Cured Mortars. I. Expansion Measurements, Changes in Dynamic Modulus of Elasticity, and Weight Gains", Cement and Concrete Research 32 (2002), pp 1729-1736.

54. Zhaozhou Zhang, Jan Olek, Sidney Diamond, "Studies on Delayed Ettringite Formation in Early-age, Heat-Cured Mortars. II. Expansion Characteristics of Cements that may be Susceptible to DEF", Cement and Concrete Research 32 (2002), pp 1737-1742.

55. S. Diamond, "Delayed Ettringite Formation-Processes and Problems", Cement and Concrete Composites 18 (1996), pp 205-215.

56. F.P Glasser, "The Role of Sulfate Mineralogy and Cure Temperature in Delayed Ettringite Formation", Cement and Concrete Composites 18 (1996) 187-196.

57. H.F.W. Taylor, C. Famy and K.L. Scrivener, "Review: Delayed Ettringite Formation", Cement and Concrete Research, 31 (2001), pp 683-693.

58. C.D. Lawrence, "Mortar Expansion Due to Delayed Ettringite Formation. Effect of Curing Period and Temperature", Cement and Concrete Research 25 (1995), pp 903-914.

59. Yan Fu, Jian Ding, and J.J Beaudoin, "Expansion of Portland Cement Mortar Due to Internal Sulfate Attack", Cement and Concrete Research, Vol. 27, No. 9 (1997), pp 1299-1306.

60. Yan Fu and J.J. Beaudoin, "Microcracks as a Precursor to Delayed Ettringite Formation in Cement Systems", Cement and Concrete Research, Vol. 26, No. 10 (1996) pp 1493-1498.

61. Oscar R. Batic, Carlos A. Milanesi, Pedro J. Maiza, Silvina A. Marfil, "Secondary Ettringite Formation in Concrete Subjected to Different Curing Conditions" Cement and Concrete Research 30 (2000) 1407-1412.

62. D.W. Hobbs, "Expansion and Cracking in Concrete Associated with Delayed Ettringite Formation", ACI Sp177-11, pp.159-181.

63. W.G. Hime, "Clinker Sulfate: A Cause for Distress and a Need for Specification", Concrete for Environment Enhancement and Protection, 1996.

64. J. Stark and K. Seyfarth, "Ettringite Formation in Hardened Concrete and Resulting Destruction", ACI SP177-9, pp. 125-140.

65. C. D. Lawrence, J. A. Dalziel , and D. W. Hobbs, "Sulfate Attack Arising from Delayed Ettringite Formation", BCA Interim Technical Note, May 1990.

66. Waldemar A. Klemm and F. MacGregor Miller, "Internal Sulfate Attack: A Distress Mechanism at Ambient and Elevated Temperatures?", PCA R&D Serial No. 2125. Prsented at the 1997 Spring Convention, ACI, Seattle.

67. Sharon L. Tracy, Stephen R. Boyd , and James D. Connolly, "Effect of Curing Temperature and Cement Chemistry on the Potential for Concrete Expansion Due to DEF", PCI Journal Vol. 49, No. 1, January-February 2004, pp. 46-57.

68. S. Kelham, “The Effect of Cement Composition and Fineness on Expansion Associated with Delayed Ettringite Formation”, Cement and Concrete Composites 18 (1996), pp-171-179.

69. David McDonald, “Technical Note: Delayed Ettringite Formation and the Heat Curing-Implication of the Work of Kelham”, Cement and Concrete Research, Vol. 28, No. 12 (1998), pp 1827-1830.

70. Wieslaw Kurdowski, “Role of Delayed Release of Sulfates from Clinker in DEF”, Cement and Concrete Research 32 (2002), pp 404-407.

71. Renhe Yang, Christopher D. Lawrence, Cyril J. Lynsdale, John H. Sharp, “Delayed Ettringite Formation in Heat-cured Portland Cement Mortars”, Cement and Concrete Research 29 (1999), pp. 17-25.

72. Nikola Petrov and Arezki Tagnit-Hamou, “Is Microcracking Really a Precursor to Delayed Ettringite Formation and Consequent Expansion?”, ACI Materials Journal, V. 101, No. 6, Nov/Dec. (2004), pp. 442-447.

73. Inam Jawed and Jan Skalny, “Alkalis in Cement: A Review, I. Forms of Alkalis and Their Effect on Clinker Formation”, Cement and Concrete Research, Vol. 7 (1977), pp. 719-730.

74. Stutzman, Paul, “Chemistry and Structure of Hydration Products”, Cement Research Progress. Chapter 2, American Ceramic Society (1999), pp 37-69.

75. Howard M. Kanare and Ellis M. Gartner, “Optimum Sulfate in Portland Cement”, Cement Research Progress 1984, pp. 214-250.