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Effect of Tricalcium Silicate Content on Expansion in Internal Sulfate Attack

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Effect of Tricalcium Silicate Content on
Expansion in Internal Sulfate Attack

by

Troy T. Whitfield

A thesis submitted in partial fulfillment
of the requirements for the degree of
Masters of Science in Civil Engineering
Department of Civil and Environmental Engineering
College of Engineering
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LIST OF SYMBOLS AND ABBREVIATIONS

AASHTO	American Association of State Highway and Transportation Officials
ASTM	American Society of Testing and Materials
ISA	Internal Sulfate Attack
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction

Cement Chemistry Abbreviations

A	Alumina, Al_2O_3
C	Calcium Oxide CaO
F	Ferric Oxide, Fe_2O_3
H	Water, H_2O
S	Silica, SiO_2
Š	Sulfur Trioxide, SO_3
C_3A	Tricalcium Aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$
C_4AF	Tetracalcium Aluminoferrite, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$
C_2S	Dicalcium Silicate, $2\text{CaO}\cdot\text{SiO}_2$
C_3S	Tricalcium Silicate, $3\text{CaO}\cdot\text{SiO}_2$
CH	Calcium Hydroxide, $\text{Ca}(\text{OH})_2$
C Š H_2	Gypsum, $\text{Ca}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$
C-S-H	Calcium Silicate Hydrate, $n\text{CaO}\cdot\text{SiO}_2\cdot m\text{H}_2\text{O}$

C₆A Š H₃₂ Ettringite, 3CaO•Al₂O₃•3CaSO₄•32H₂O

C₄A Š H₁₂ Monosulfoaluminate, 3CaO•Al₂O₃•CaSO₄•12H₂O

EFFECT OF TRICALCIUM SILICATE CONTENT ON EXPANSION IN INTERNAL SULFATE ATTACK

Troy T. Whitfield

ABSTRACT

The purpose of this study was to determine the cementitious parameters and placement temperature that impact internal sulfate attack in concrete. Concrete structures make up a large percentage of the infrastructure and multifamily housing. Durability is very important. Cements can be formulated to reduce the impact of external environmental exposure such as high salinity from marine environments or high sulfate levels from soils or surface waters. Concrete is also subject to internal attack such as alkali aggregate reaction, (AAR), and delayed ettringite formation, (DEF). This study focused on some of the cement chemistry issues that determine susceptibility of cement to DEF. Expansion due to DEF can weaken the concrete matrix resulting in microcracks that in some cases may progress to severe matrix cracking. The end result is loss of load carrying capacity and costly repairs.

In this study, mortar bars were made with the as received cement chemistry and using additions of sulfate, and alkalis. The bars were then heat cured at various temperatures and stored in a saturated lime solution at room temperature. Measurements were made at predetermined time intervals. The series of mixes were made to determine the effect of varying sulfate levels, heat curing temperature, and alkali content in order to

isolate the effect of these constituents. The cements were selected on the basis of tricalcium aluminate, alkali content, sulfate levels, C₃S levels and fineness. The results indicate that a relationship exists between the rate and level of expansion experienced by the mortar bars and cementitious parameters, namely, alkali content, sulfate content, C₃S levels and heat curing temperature.

CHAPTER 1

INTRODUCTION

1.1 Objective

There are a large number of concrete structures built every year for infrastructure, industry, and multi-family housing. Durability is a very important factor to consider in the design process. Environmental exposure can lead to durability issues. Most mix designs take this into account. Other durability issues come from within the concrete members themselves. Examples of these include delayed ettringite formation, (DEF), and alkali aggregate reaction, (AAR). DEF or ISA, (internal sulfate attack), refers to ettringite formed in the cement after its initial set and hardening. It was originally considered a problem for heat cured precast cement members such as railway sleepers. Initial research focused on determining a maximum temperature that the members could be exposed to without durability issues. The research then expanded to cement chemistry. The earliest research focused upon SO_3 and C_3A content. Present research has expanded the scope to include alkali content in the form of Na_2O_{equiv} and C_3S . It is common knowledge that C_3A , C_3S , Alkali content, heat curing temperature, and internally generated heat from thick cross-sections work both separately and together to provide a mechanism for DEF. There is much research linking alkali levels, sulfate levels and heat curing temperatures to the expansion due to delayed ettringite formation that is experienced by laboratory concretes. The ettringite formed in the cement after its

initial set and hardening causes internal stresses that lead to durability issues. Many researchers have explored the link between C_3S levels and expansion due to ettringite formation. A common problem in these studies is that the cement chemistry is not closely controlled enough to definitively state a correlation exists between the C_3S level of a cement and its propensity to experience expansion due to ettringite formation over time. This is because the C_3A levels, fineness, sulfate content, and alkali content also have a large effect. In this study, there was an attempt to eliminate these variables to isolate the effect of higher levels of C_3S on expansion.

1.2 History of the Manufacture of Portland Cement

Portland cement was invented in England in 1824. It differs from lime based cements by the manufacturing method and the chemical reactions that take place. In the 1870's Portland cement began to be manufactured in the United States. The process by which it is produced has changed little in concept since that time. What has changed is the equipment used to manufacture the cement, better control of the chemistry of the raw material, and the ability to monitor and control the temperature.

The process to manufacture Portland cement requires the burning of a finely ground mixture of about 75% limestone for the calcium oxide, along with shale or clay to provide the needed silica, alumina, and iron oxides. The burning of this material takes place at around 3000°F in a kiln. The product that is produced is called clinker and consists of C_3S , C_2S , C_4AF , C_3A and various other minor constituents such as MgO, and alkali containing compounds. This clinker then finely ground and combined with calcium sulfate to produce Portland cement. Although the process seems simple, it

requires constant attention to detail since the constituent proportions, grinding size, thoroughness of mixing, and kiln temperatures must be monitored closely as they have large effects on the end product.

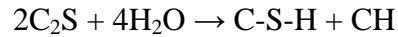
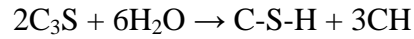
A typical kiln is located near the source of the bulk raw material used in manufacturing. In Florida, the material excavated consists of sand, silt, and clay along with limestone. This is finely ground and thoroughly mixed before sampling. Any deficiencies are corrected by adding the needed iron, silica and calcium to the finely ground mixture. These are added by using limestone, sand, or iron pellets. The batch is then run through a rotary kiln and the temperature is closely maintained throughout the process. The clinker that is produced is cooled at a fixed rate and ground in a ball mill to a fine powder. This powder is then mixed with a predetermined proportion of calcium sulfate to produce cement. The calcium sulfate can take the form of Anhydrite, Hemihydrate, or Gypsum.

1.3 Chemistry of Portland Cement

Clinker is chiefly composed of four compounds. These are tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), and tetra-calcium aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$). In this paper they will be abbreviated using shorthand notation as C_3S , C_2S , C_3A , and C_4AF . Also present in clinker are small amounts of free lime, alkali sulfates, alkali oxides, and magnesium oxides.

Most of the strength of the cement is due to the reaction of water with C_3S and C_2S . This reaction with water results in the formation of calcium silicate hydrate (average composition $3\text{CaO}\cdot 2\text{SiO}_2\cdot 3\text{H}_2\text{O}$) and calcium hydroxide ($\text{Ca}[\text{OH}]_2$) the

shorthand notations for these two products are C-S-H and CH respectively. The chemical reaction that results in the formation of these products is written below.



It is evident from the above reactions that although the products are the same, they vary in proportion. C-S-H is an amorphous gel that actually has a large variation in chemistry. An example of this would be the Ca/Si ratio which can vary between unity and 2:1. CH has a defined structure as compared to the amorphous structure of C-S-H.

Although most of the strength of cement is from CH and C-S-H, the aluminates compounds have the largest effect on durability. Internally or externally generated sulfates combine with the aluminates and lead to the formation of sulfoaluminates. Because the formation of some of the sulfoaluminates is expansive, the reaction can lead to tensile stresses that result in expansion and finally the deterioration of concrete due to cracking.

Portland cement is subdivided into five types by the American Society of Testing and Materials depending upon both chemistry and fineness. These cement types meet the chemical and physical requirements needed for specific purposes.

Table 1: ASTM Portland cement types and uses taken from FHWA website

Cement Type	Use
I	General purpose cement
II	Use for moderate sulfate attack resistance
III	Use when high early strength is required
IV	Use when low heat of hydration is required for massive structures
V	Use when high sulfate resistance is required

Generally the C_3A content is limited to 15% for type III, 8% for type II, 7% for type IV and 5% for type V. The C_3A levels are used by ASTM to determine sulfate resistance. In addition type IV also has a limit of 40% C_2S and 35% C_3S to help control the hydration temperature. Type I and III have the same chemistry requirements but differ in how fine they are ground. Type III achieves higher early strength by the greater rate of hydration due to its smaller particle size.

ASTM also limits the maximum sulfate content to 2.3% for type IV and V. Type I is limited to 3.0% if C_3A is less than 8% and 3.5% when the C_3A content is greater than 8%. Type II is limited to 3% maximum sulfate content. Type III is similar to type I with the sulfate content limited to 3.5% if C_3A is less than 8% and 4.5% when the C_3A content is greater than 8%. The largest source of sulfate is from the added calcium sulfate, but sulfur can also be present in alkali sulfates as well as a trace element in all four of the basic constituents of Portland cement clinker.

1.4 Hydration of the Major Components of Cement

The hydration of cement changes the major components such as calcium silicates and calcium aluminates/ferrites into a series of calcium silicate hydrates, calcium hydroxides, and calcium aluminate/ferrite hydrates. One of the minor components is calcium sulfate. This reacts with the calcium aluminates to form ettringite. The early formed ettringite helps control the hydration process by forming a coating on the calcium silicates thereby restricting access to water and slowing their hydration. As long as there is not too much calcium sulfate, and the early formed ettringite is stable, the hardened cement is not susceptible to cracking caused by delayed ettringite formation. Unfortunately this early ettringite is partially destroyed during the heat curing process. This destruction allows the bound sulfates to be temporarily adsorbed by the C-S-H gel and also to concentrate in the pore water.

Calcium silicates react with water to form calcium hydroxide and calcium silicate hydrate gel. The latter is an amorphous solid that can have varying chemistry. It is usually written as C_xSH_n with the x falling between 0.8 and 2.5.

The hydration of calcium aluminates yields C_3AH_6 which then reacts with the sulfate present to form monosulfate or ettringite depending upon the sulfate content of the cement. The sulfate also is adsorbed to a lesser extent by the C-S-H gel. The stability of ettringite depends upon the temperature at which the cement is exposed, the pH of the pore solution, and the sulfate concentration of the pore water.

Calcium alumino-ferrites react with water to form a solid solution series with a chemistry that falls between C_3AH_6 and C_3FH_6 . These also react with sulfate to form a more iron rich monosulfate and ettringite. The literature refers to these compounds as

mono-sulfo-ferrite and tri-sulfo-ferrite respectively. These behave similarly to their aluminum rich counterparts with the exception of the iron rich monosulfate being slightly less stable.

L.O. Hoglund ran a series of experiments to find out the regions of stability for ettringite in regards to temperature and sulfate concentration of the pore water. Ettringite begins to decompose at temperatures above 25°C if the sulfate level in the pore waters falls below 0.25mg/l. This fact directly influences the result of the experiments used in this paper. It would be expected that in the low sulfate mortars the early formed ettringite would have fully decomposed during heat cure. The mixes with five percent sulfate would not share a similar fate. Some of the early formed ettringite would have survived in these mixes, this would account for the higher levels of expansion experienced by these mixes at early ages.

1.5 Recent Developments

In recent years there has been a shake-up of the industry due to both fuels used in the kiln, and making the process more efficient by re-circulating the exhaust gasses to pre-heat the raw materials. In earlier times the fuel used was locally produced natural gas, coal or oil. This has changed in recent years because of higher energy costs. Much of the domestic industry has been purchased by a growing Mexican company. This company generated much of the money needed to expand by making the process more efficient and using petroleum coke, a waste product of oil refining, as a fuel. The 1970's saw the use of hazardous wastes as both a fuel and to increase profitability by the revenue generated by its high temperature destruction. Re-circulating the exhaust gasses has lead

to higher alkali contents. As in all processes, changing any of the inputs results in a product that is also changed.

In the 1970's durability became an issue. A series of failures of precast cement elements were initially attributed to alkali aggregate reaction. Upon further inspection, expansion due to internal sulfate attack was blamed. Internal sulfate attack is the result of the destruction of ettringite that was formed during initial hydration. The sulfates that were then released are adsorbed into the C-S-H gel or held in the pore water. The formation of Ettringite after initial hydration can be expansive and lead to damage in concrete. The initial studies showed a strong association with the rate of internal sulfate attack to the levels of C_3A , alkalis, sulfates and high heat curing temperatures. In response both AASHTO and ASTM set limits on cement chemistry. Several states and countries have set limits on the maximum temperature that the concrete member experiences. Texas through MNM 116 and 117 allows up to $150^{\circ}F$ ($66^{\circ}C$), or $82^{\circ}C$ for truly dry service conditions. Germany and Canada limit the temperature to $60^{\circ}C$. In the United States the NPCA recommends a maximum of $65^{\circ}C$ unless safeguards are taken to prevent DEF. Even with the safeguards, the NPCA sets the temperature limit to $70^{\circ}C$.

1.6 Review of Previous Investigations

Several studies have noticed a correlation between the occurrence of internal sulfate attack and high C_3S content. The effect of high C_3S levels is chiefly in its effect on the hydration products and the heat of hydration.

Rasheeduzzafar in his 1992 paper states the many reasons why the C_3S/C_2S ratio affects the resistance of a paste to sulfate attack. Since C_3S produces 2.2 times as much CH as an equivalent amount of C_2S the largest effect of high levels of the former lies

chiefly in its hydration product. Calcium hydroxide acts as a buffer and is more easily dissolved from the paste than C-S-H. This dissolution can provide the calcium needed for other products, and can lead to higher porosity. Higher levels of calcium hydroxide result in increased gypsum formation. This leads to a corresponding decrease in the strength of the paste, allowing the tensile stresses due to ettringite formation to overcome the tensile strength of concrete leading to cracking and spalling. In addition, the solubility of expansive hydrated calcium aluminates is significantly lowered in a saturated lime environment, the sulfate reaction becomes topochemical and expansive by nature.

Mehta hypothesized that the form that the ettringite crystals take is related to the levels of calcium hydroxide present. In rich environments, the ettringite formed is colloidal. The ability of ettringite to absorb water is greater than it would be if lath-like crystals were formed. The adsorption of water leads to expansion and ultimately destruction of the paste.

Divet and Randriambololona found in their 1998 paper that a high C_3S/C_2S ratio results in a two fold effect on the formation of the C-S-H gel. First, high levels of CH increase the lime/silica ratio (>1.5) resulting in a weaker C-S-H gel. This weaker paste will be damaged at lower stress levels. The stress can be caused by the reaction of sulfates with C_4AF , or monosulfate. The second effect is due to the higher pH in pore solutions in hydrating cement. At higher pH levels more sulfur tends to be adsorbed by the C-S-H gel. The result of less sulfate being available is lower amounts of primary ettringite being formed. The formation of primary ettringite helps slow the hydration rate. The solution used in the field to this problem is to increase the level of calcium sulfate.

Thus, more gypsum is needed in the unhydrated cement to achieve the same level of deceleration. This greater level of sulfates contributes to a greater level of internal sulfate attack. The sulfates that are adsorbed by the C-S-H gel are desorbed at a later time into the pore solutions providing a source of sulfate. Divet and Randriambololona found the rate of both adsorption and desorption are determined by both the temperature and pH of the pore solutions. The pH influences both the maximum quantity absorbed and the rate of absorption.

In their 1998 paper, Divet and Randriambololona also found that high levels of C_3S result in higher heats of hydration. The occurrence of delayed ettringite formation is linked to the maximum temperature a cement experiences. The heat can come from external sources such as a heat curing or from the internally generated heat from hydration in thick structures. In addition, the adsorption of sulfate by C-S-H gel is also temperature dependant. Both the solubility and amount of sulfates adsorbed are influenced by temperature. As the solubility decreases and the amount of adsorbed sulfate increases, so does the likelihood of internally generated sulfate attack. The substitution of aluminate ions in C-S-H gel is also increased at higher temperatures. Both sulfate and aluminate are essential for ettringite formation. Higher temperatures also help limit the amount of primary ettringite formed. The sulfate not consumed in the formation of ettringite is held in the C-S-H gel where it can leach out over time providing a source of sulfate and aluminates for delayed ettringite formation.

The alkali content of the cement also has a bearing on the amount of ettringite formed at a later date. F.P. Glasser in his 1996 paper proved that the higher the alkali content, the higher the level of sulfate ion that can be present in the pore solutions. This

is due to the increase in solubility of the sulfate ion and instability of ettringite at high alkali levels. At temperatures above 50°C the solubility of the sulfate ion increases rapidly leading to the destruction of previously formed primary ettringite in the cement matrix. Much of this sulfate tends to be adsorbed by C-S-H gel due to its ability to adsorb a greater amount of sulfate as the temperature increases. This previously adsorbed sulfate becomes available over time for the formation of ettringite as it is slowly desorbed. The adsorption capacity of the C-S-H gel is quite high and was measured in experiments by Diver and Randriambololona. They found the level of adsorption was dependant on pH, alkali content and temperature of exposure. Increases in any or all of these allow much greater levels of adsorption. The rate of desorption was also studied in the above paper. It was proven that all of the adsorbed sulfate ion will be desorbed over time as the capacity of the C-S-H gel to hold the sulfate decreases due to lower temperatures and pH. The rate of desorption is much slower than the rate of initial adsorption. This desorption allows for the slow formation of ettringite over time.

Early age thermal cracking is also increased at higher temperatures. The cracking is caused by the differential between the surface and core temperatures. These cracks provide a place for the ettringite crystals to deposit. Researchers are varied in their opinion whether these crystals can cause damage.

The first study to isolate the effect of C_3S upon expansion was done by Rasheeduzzafar in 1974. He noticed a correlation between the C_2S/C_3S ratio and expansion for external sulfate attack. Since that time many other studies have confirmed that this is true for both internal and external sulfate attack. In doing a review of these studies, it is evident that other factors could be causing the expansion that was credited to

the C_2S/C_3S ratio. This study was conducted to eliminate most of the other variables by careful cement selection and equalizing cement chemistry.

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 Composition Determination

The compositions of the cements in this study were determined chemically or by mineralogy. Chemical composition or as it is better known as oxide chemical composition determines the percentage of each oxide present. In this method the cement sample is fused at 1000°C with $\text{Li}_2\text{B}_4\text{O}_7$ and analyzed by x-ray fluorescence spectrometry. The results of this method are listed in table 3.

The calculation of phases using the Bogue method follows a procedure outlined in ASTM C-150. Each compound has a different formula in which the oxide composition is entered. The results are dependant upon ratios the oxides to each other and give only a fairly accurate analysis of the compounds present. The results of this method are presented in table 2.

The internal standard method is better known as the curves method. In a study done by Natalya Shanahan calibration curves were prepared for C_3S and cubic and orthorhombic C_3A according to ASTM C-1365-98. She collected a series of X-ray scans on the Phillips X'Pert PW3040 located in our lab. The samples had fixed compositions and curves that related the percentage of C_3S to the results were prepared. Table 4 shows the results using this method. Because of the use of internal standards, this method was probably the most accurate.

The final method used to determine composition was through the use of X-ray powder diffractometry. In this method Reitveld analysis is used to determine the composition. An internal standard of titanium oxide is added and constitutes 10% of the sample by weight. Each compound emits a certain wavelength under x-ray diffraction. The peaks formed are compared to the peak emitted by the titanium oxide. Since the percentage of titanium oxide is known, the composition of the cement sample can be inferred by comparing the peak heights.

2.2 Materials

This study was done using three cements. In addition, graded sand, distilled water, KOH and Terra Alba gypsum were also used. The cement chemistry was modified by the use of Terra Alba Gypsum and KOH. The cement was mixed in the following conditions: As received alkali and sulfate, as received sulfate with alkali adjusted to 1.5% (and 2% for cement MH-3), sulfate levels of 3.6% or 5% with alkali levels remaining as received, or sulfate levels adjusted to 3.6% or 5% with alkali levels adjusted to 1.5%. Potassium hydroxide was used to adjust the alkali level. Cement MH-3 had as received sulfate levels of 3.1% and was tested at this level rather than 3.6%.

Table 2: Bogue calculations, fineness and C_3S/C_2S ratio

Compound	Cement E (%)	Cement MH-3 (%)	Cement C (%)
C_3S	57	67	66
C_2S	18	7	14
C_3A	6	6	7
C_4AF	11	8	11
C_3S/C_2S	3.17	9.57	4.29
Blaine fineness (square meters per kilogram)	380	395	384

Table 3: Chemical analysis of the two cements used in the study

Cement	E	MH-3	C
Compound	Wt %	WT%	Wt %
SiO ₂	21.15	20.20	20.52
Al ₂ O ₃	4.78	4.02	4.92
Fe ₂ O ₃	3.76	2.78	3.70
CaO	64.41	64.02	64.31
MgO	0.95	2.47	1.71
SO ₃	2.58	3.09	2.81
Na ₂ O	0.18	0.21	<0.01
K ₂ O	0.34	1.10	0.41
TiO ₂	0.33	0.22	0.27
P ₂ O ₅	0.07	0.15	0.03
Mn ₂ O ₃	0.03	0.06	0.04
SrO	0.12	0.04	0.04
Cr ₂ O ₃	<0.01	<0.01	<0.01
ZnO	0.02	0.04	<0.01
Na ₂ O _{eq}	0.40	0.93	0.27

Table 4: Analysis of cements using the internal standard method and Reitveld analysis

Compound	Cement E (%)	Cement MH-3 (%)	Cement C (%)
C ₃ S	58	67	70
C ₃ A	4.0	3.3	3.0

2.3 Procedure

2.3.1 Mix Design

Mix proportioning was done by weight using the spreadsheet shown in Table 5.

The oxide chemistry of the cement in the as received condition was entered in the spreadsheet. The target SO₃ level as well as the KOH weight in grams is entered as variables. The spreadsheet calculates the gypsum needed as well as the Na₂O_{eq} in the spreadsheet itself. Under the spreadsheet the weight of Terra Alba Gypsum, KOH, and cement are automatically calculated from the data in the spreadsheet. These weights are

used along with 243 ml of distilled water and 1375 g of oven dried sand to make the mortar mix. The sand was oven dried at 100 plus or minus five degrees centigrade.

Table 5: Spreadsheet used in mix design

Increase Cement MH-3 to 5.0% Using Gypsum, Keep the Alkali Level in the As Received Condition									
	Wt(g)						Amounts		
MH-3	100	After KOH	Target	Gypsum Needed	Gypsum (g)	KOH (g)	Remaining	Added	Net
	As is								
SO ₃ %	3.09	3.09	5	0.044	4.40	0			
Al ₂ O ₃	4.02						3.84		
Na ₂ O %	0.21						0.201		0.201
K ₂ O %	1.1						1.052	0.000	1.052
Na ₂ O _{eq}	0.93		0.89					Na ₂ O _e =	0.89
Cement		478.00							
KOH		0.00							
Gypsum		22.0							

2.3.2 Procedure for Mixing Mortars

The mortar was mixed in compliance with ASTM C-305-99 “Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars”. Before mixing, the cement, sand, water, and needed KOH and/or Terra Alba Gypsum were weighed out. When KOH was needed this was premixed with the water using a magnetic stirrer. The gypsum if needed was also premixed with the water after this point using the mixer for fifteen seconds. Cement was then added to the mixing water and mixed at slow speed for thirty seconds. The sand was then added to the mixture over the next thirty seconds. The mixer was then turned off to allow the change of speed to medium speed. This mixture was then mixed at medium speed for a period of thirty seconds. The mixer was then again stopped and the sides of the bowl and paddle scraped for fifteen seconds. The bowl was then covered for an additional minute with plastic to prevent the escape of moisture.

After this period the mixer was again turned on at medium speed for a period of one minute.

2.3.3 Slump Test

The slump or workability test was performed on all mixes. The procedure followed a modified form of ASTM C-143 “Standard Test Method for Slump of Hydraulic-Cement Concrete”. After mixing the mortar was put into the metal slump mold in two layers. The first layer was about one inch high and was tamped using the appropriate rod twenty times working from the outside inward in a circular pattern. This was followed by a second layer of mortar that was tamped twenty times also. The same procedure was followed except the level of tamping was done just to under the level of the first layer. After the final layer was tamped, the mold was struck off by rolling the tamping rod horizontally. The table was then mechanically lifted and dropped a total of twenty-five times and the resulting spread of the mortar measured.

2.4 Casting of Bars

The molding of bars followed ASTM C-157 “Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete”. Four bars were cast from each batch. The bars were stored in their molds for one hour at 100% relative humidity. After this time, the bars while still in their molds were subjected to the heat curing cycle specified.

2.5 Heat Curing Cycle

Four different cycles were used in this study. Each is discussed separately giving the time allowed for each part of the cycle since they vary with the temperature. The room temperature cured bars were left in the humid cabinet for a total of twenty-four

hours. They were then demolded, marked and measured using the comparator. The bars were then stored for a period of one hour in distilled water and again measured. The second set of measurements was used as the zero point in the study.

The initial steps in high temperature heat curing are the same for the 60°C, 80°C, and 90°C heat cures. The bars were put in the humid cabinet for a period of one hour after molding. They were then placed in sealed plastic bags and put into a furnace that was at room temperature. The furnace was turned on and the set point adjusted to the heat curing temperature of 60°C, 80°C or 90°C. The bars were allowed one hour and fifteen minutes to come to temperature; this is shown in Figure 1. The heat cure cycle was verified by thermocouples imbedded within a single bar along with thermocouples placed in the furnace at various locations. A twelve hour cycle was run at temperature and then the bars cooled over a period of four hours in the furnace. Upon removal from the furnace, the bars were demolded and appropriately marked for identity. At this time the process differs depending upon temperature of heat curing. The bars done at 90°C were allowed an additional forty-five minutes to cool to room temperature before measurement. The bars done at 80°C were allowed thirty-five minutes, and the bars done at 60°C were allowed thirty minutes. After the initial measurement the bars were soaked in distilled water for one hour and re-measured. This measurement is considered the zero point in the study. The bars were then soaked in a saturated lime water solution and measured at proscribed intervals.

The one hour pre-curing cycle was based upon the 1997 paper by Fu, Ding and Beaudoin that measured the expansion rate as a function of pre-curing time. The short pre-cure was done to enhance the expansion rate of the mortar bars.

The storage of the bars in a saturated lime water solution was done to reduce the leaching of CH and alkalis. Several studies focused on the stability of ettringite. The average range of stability was between a pH of 10.6 to 12.5. The use of a lime water bath was also to keep the pH within this range. A saturated lime solution has a pH of 12.4 according to the Handbook of Chemistry and Physics.

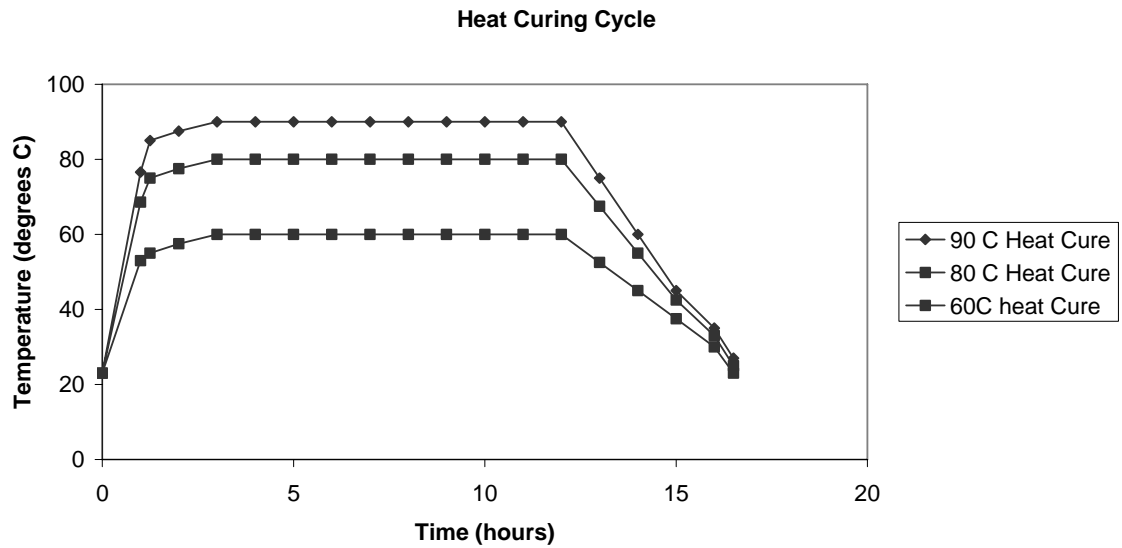


Figure 1: Heat curing cycle adopted in this study

2.6 Length Change on Mortar Bars

2.6.1 Measurement Cycle

Measurements were taken daily every twenty-four hours plus or minus one half hour for the first seven days after being put in the saturated lime water solution. They were again measured at thirteen and fourteen days. After this time the cycle was increased to weekly until sixty-three days had elapsed since putting the bars into the lime water solution. Thirty day cycles plus or minus one day were followed after this time, and continued until the end of the test.

2.6.2 Measurement Procedure

The length change measurements followed ASTM C-490 “Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete”. The device used was a Humbolt H 3250. This device measured to 0.0001 inches. The measurement of a reference bar that allowed the machine to be set to a zero point preceded each set of measurements. The bars were placed in the comparator with the arrow pointing upward. This arrow was drawn on the bars when they were identified prior to their first water exposure. The bars were then spun in a clockwise direction and the minimum gauge reading was recorded. Figure 2 shows a typical mortar bar. The bar pictured shows the typical bending seen on bars with expansion levels greater than 1%.



Figure 2: Mortar bar showing bending

CHAPTER 3

RESULTS AND DISCUSSION

Assessment of the effects of tricalcium silicate, sulfate, alkali content, and temperature on the ISA phenomenon in this study was done primarily using length measurements. Phase transformation accompanying expansion was studied using X-ray diffraction techniques. Semi-quantification and identification of phase transformation was done using Reitveld analysis. In the following pages, the findings of this study are presented and discussed.

3.1 Length Measurement Results

The experimental procedure was designed to speed up the process of secondary ettringite formation in the following ways; the one hour room temperature cure before high temperature curing helped to limit the amount of primary ettringite formed, the high temperature heat cure cycle destroyed this primary ettringite, and storage in limewater assured the constant pH required to keep the secondary ettringite stable. The short time allowed for pre-curing was based upon work by Fu and Beaudoin in 1996.

Brown and Bothe findings in 1993 indicate high curing temperatures and increased alkali content provide a mechanism by which high levels of sulfate and aluminate were incorporated in the C-S-H gel. It was suggested that this adsorption and later desorption provide the chemical basis for secondary ettringite formation. The heat

cure temperatures used here were selected to determine a critical temperature for internal sulfate attack in the cements used in the study.

The dominant factors in the expansive behavior of cement due to ISA can be summarized as the sulfate level, alkali level, C_3A level, C_3S level, C_3S/C_2S ratio and cement fineness. It is relevant that C_3A and cement fineness were relatively constant and can be eliminated as a variable. The as received alkali and C_3S content show some variation in the three cements. Table 3 shows the oxide composition and Table 4 shows the composition from XRD work and internal standard method. The sulfate content varies from 2.58 weight percent in cement E to 3.09 weight percent in cement MH-3. Alkali content as measured in Na_2O equivalent ranges from 0.27% in cement C to 0.93% in cement MH-3. The C_3S/C_2S ratio shows the same trend with cement E having a ratio of 2.32 to 5.36 for cement MH-3. The rate of expansion also mirrors the chemistry as shown in the figures below.

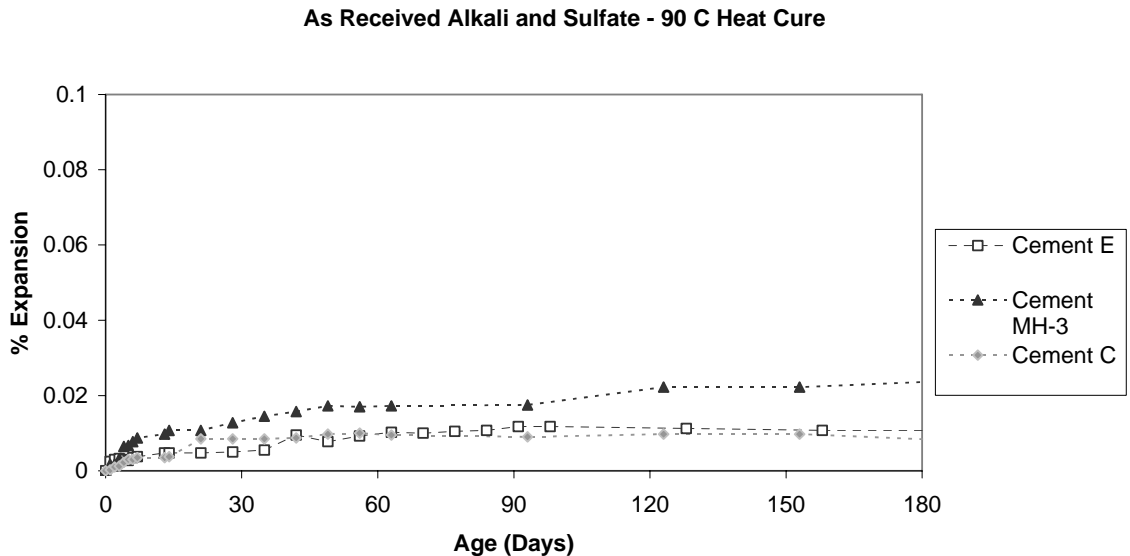


Figure 3: All three cements as received and heat cured at 90°C

As Received Alkali and Sulfate - 80 C Heat Cure

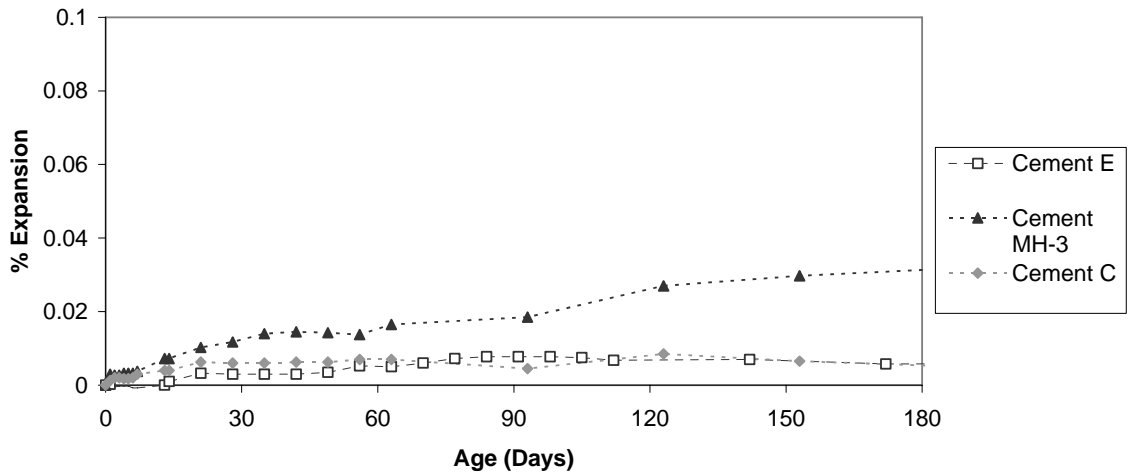


Figure 4: All three cements as received and heat cured at 80°C

As Received Alkali and Sulfate - 60 C Heat Cure

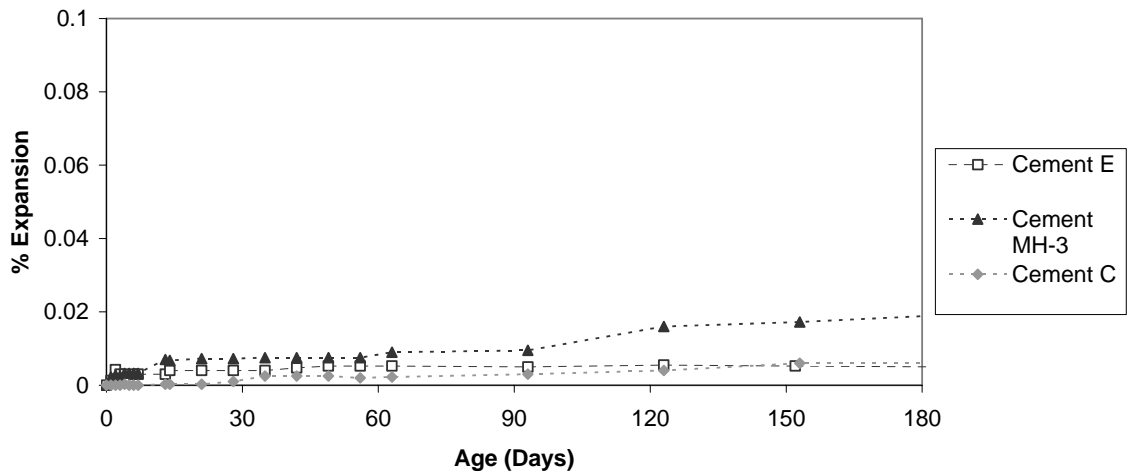


Figure 5: All three cements as received and heat cured at 60°C

As Received Alkali and Sulfate - 23 C Heat Cure

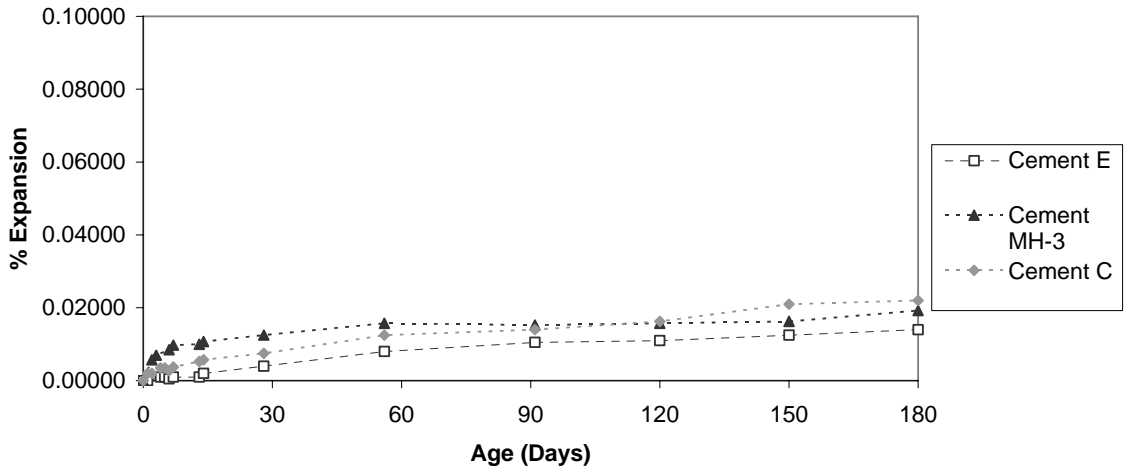


Figure 6: All three cements as received and heat cured at 23°C

The effect of temperature can also be read from these graphs by comparing the expansion exhibited by the cements (Figures 7 thru 9). In all three heat cures, MH-3 expanded the most followed by cement C then cement E. This behavior when compared to the as received chemistry shows the dominant factors in expansion to be the sulfate level and C_3S/C_2S ratio.

E As Received Chemistry - Temperature Effect

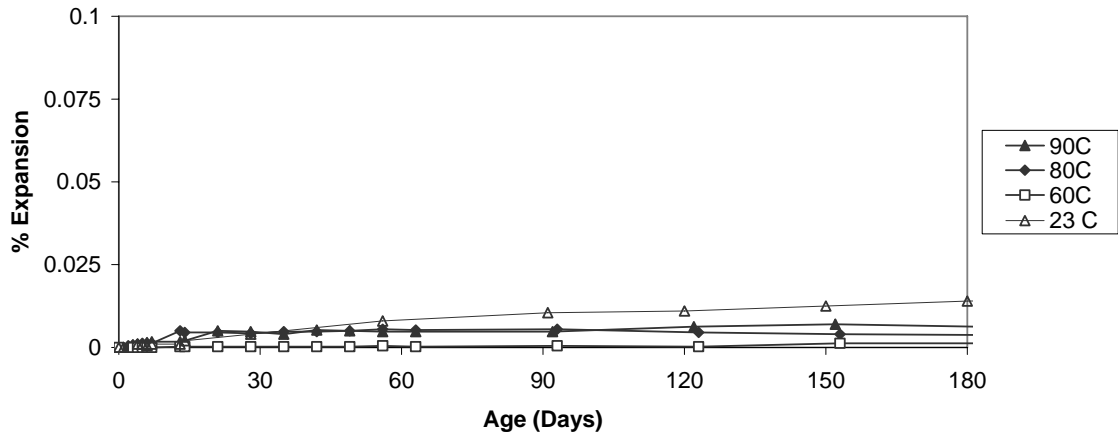


Figure 7: Cement E showing the effect of temperature on as received chemistry

MH-3 As Received Chemistry - Temperature Effect

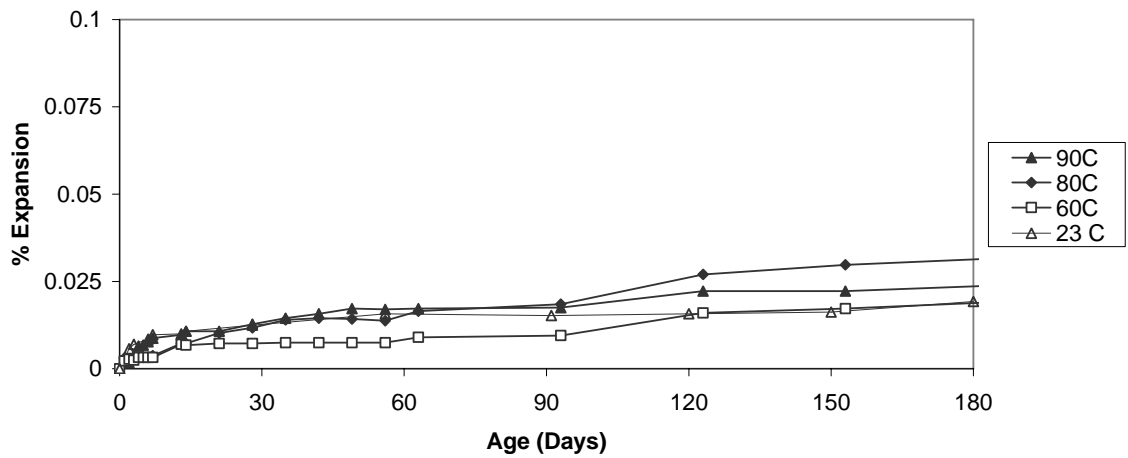


Figure 8: Cement MH-3 showing the effect of temperature on as received chemistry

C As Received Chemistry - Temperature Effect

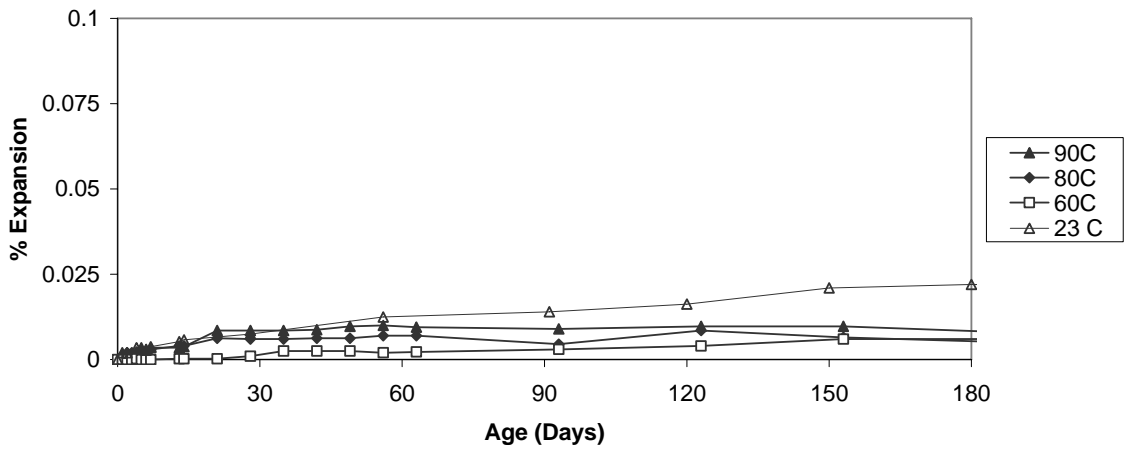


Figure 9: Cement C showing the effect of temperature on as received chemistry

The next logical step is to isolate each of the three variables to determine the impact of each on the rate of expansion. Cement E shows little expansion at either alkali level. The as received sulfate content is 2.58% for this cement. Figures 10 thru 12 show the effect of alkali content on this cement.

E: As Received SO₃, Variable Alkali - 90C Heat Cure

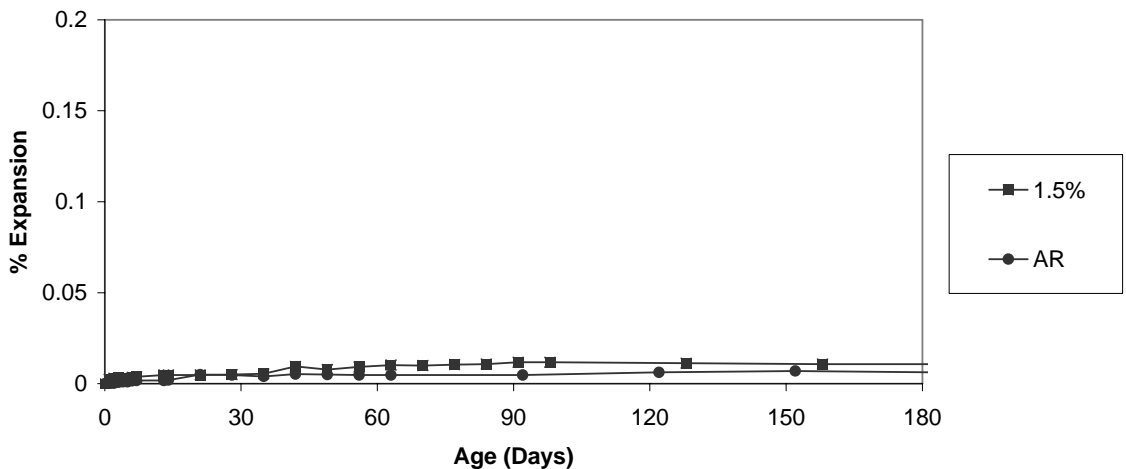


Figure 10: The effect of alkali content after 90°C heat cure cycle for cement E

E: As Received SO3, Variable Alkali - 80C Heat Cure

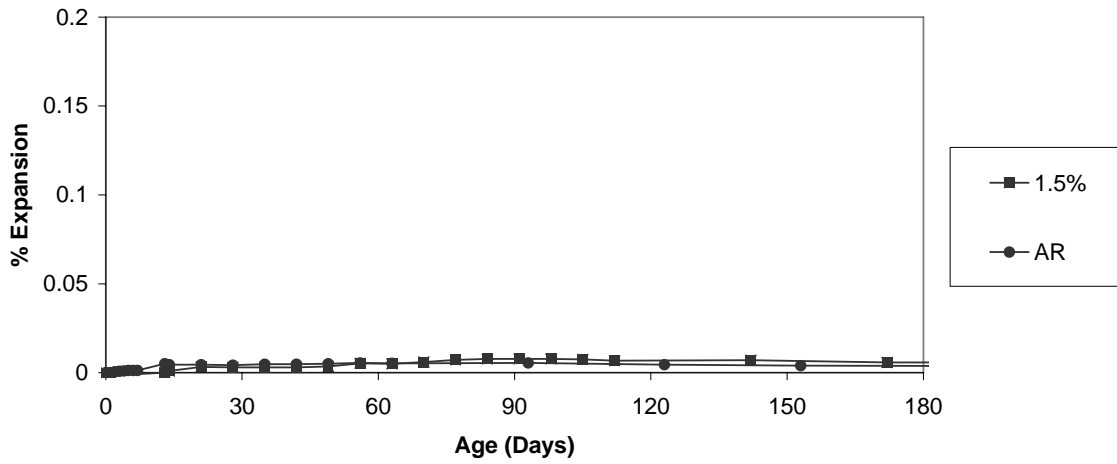


Figure 11: The effect of alkali content after 80°C heat cure cycle for cement E

E: As Received SO3, Variable Alkali - 60C Heat Cure

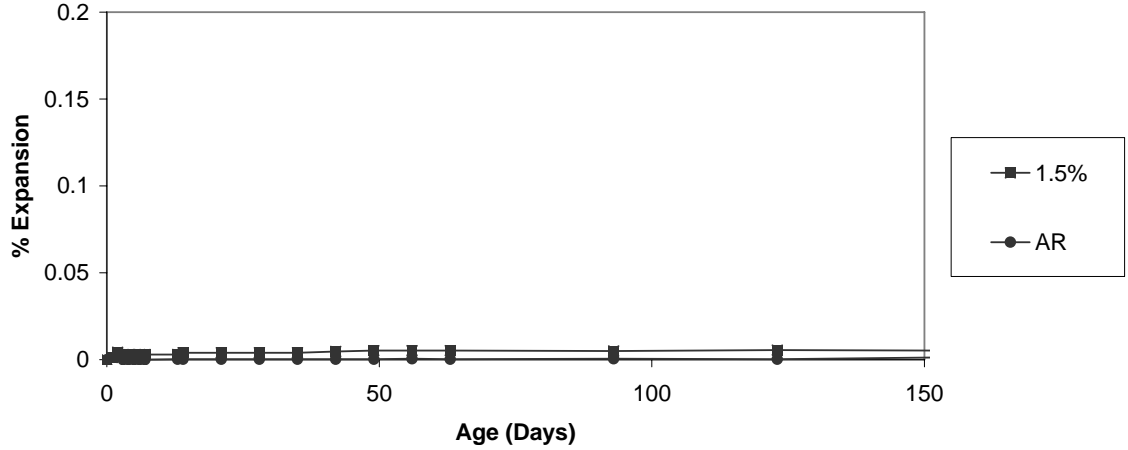


Figure 12: The effect of alkali content after 60°C heat cure cycle for cement E

E: As Received SO₃, Variable Alkali - 23C Heat Cure

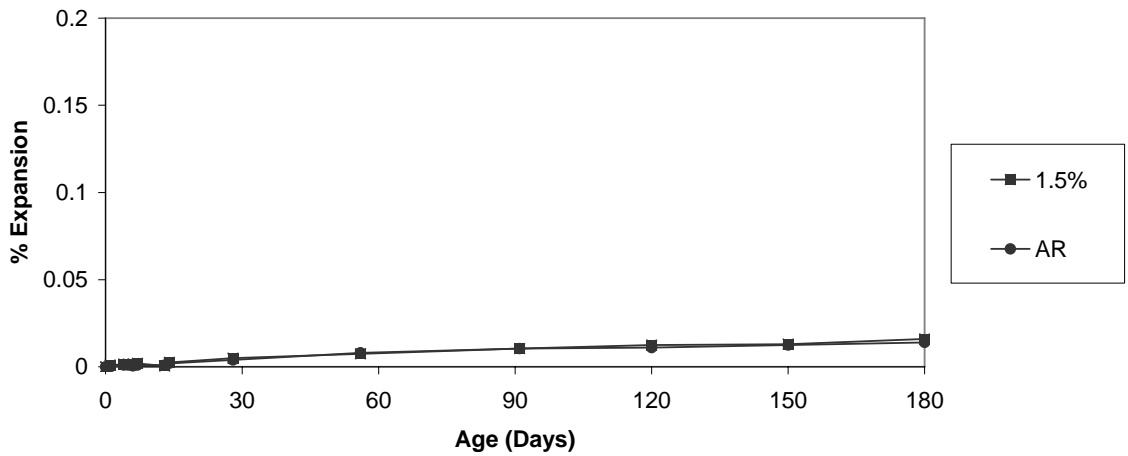


Figure 13: The effect of alkali content after 23°C heat cure cycle for cement E

To study the effect of increasing the alkali level, three different alkali levels were selected for cement MH-3. The alkali levels used were as received, 1.5% and 2.0%. Figures 14-17 show both the effect of alkali levels and curing temperatures for cement MH-3. At both 80° and 90°C, higher alkali levels are associated with increased levels of expansion. This is due to the destruction of the primary ettringite during the high heat curing temperature and the ability of pore waters in to keep more sulfates in solution as the alkalinity increases. As the pore water alkalinity decreases due to leaching, the sulfates become available for incorporation into ettringite. At 60°C and 23°C, the primary ettringite is not destroyed to the same degree and the effect of high alkali content was lessened.

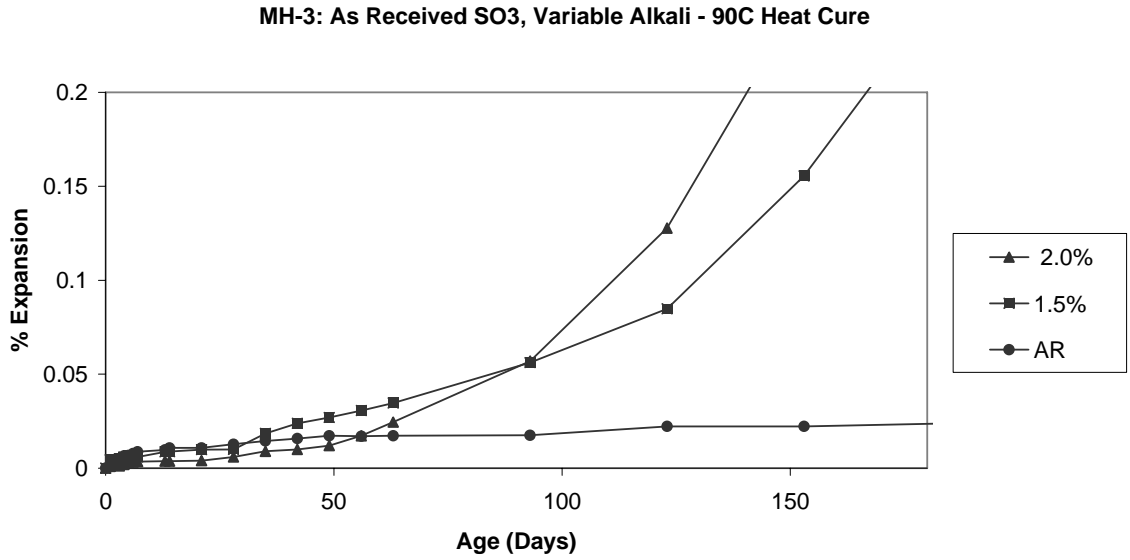


Figure 14: The effect of alkali content after 90°C heat cure cycle for cement MH-3

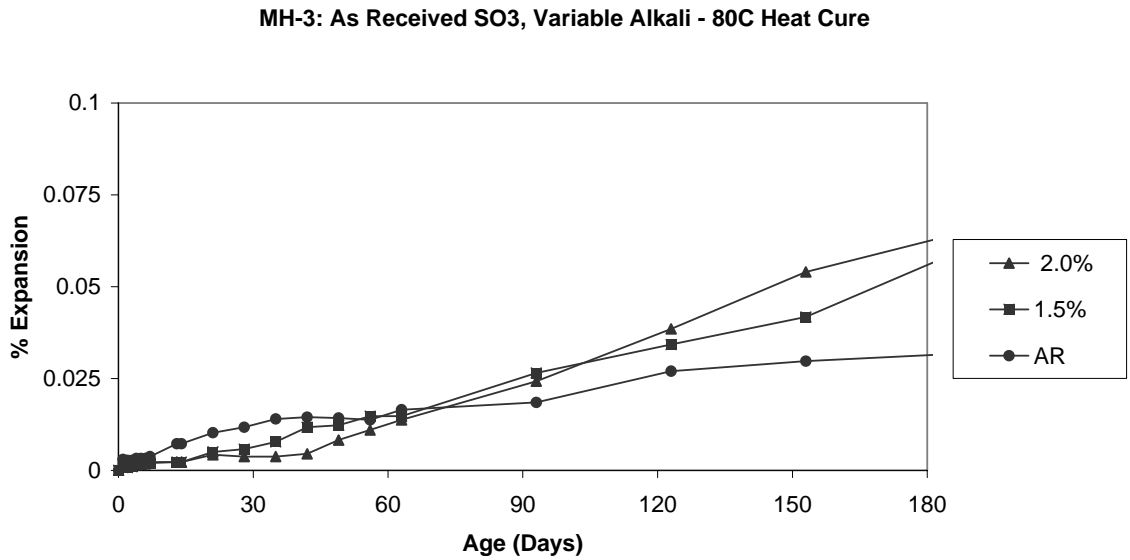


Figure 15: The effect of alkali content after 80°C heat cure cycle for cement MH-3

MH-3: As Received SO₃, Variable Alkali - 60C Heat Cure

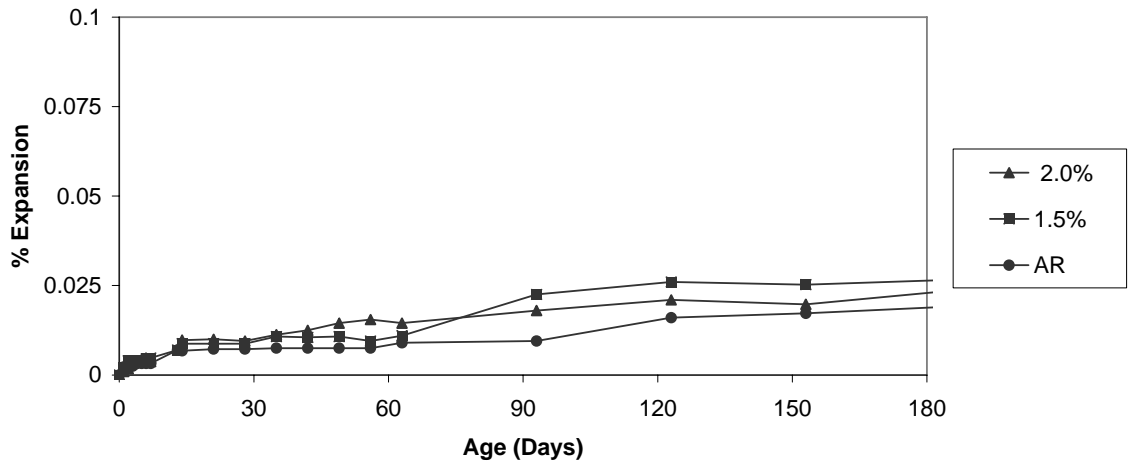


Figure 16: The effect of alkali content after 60°C heat cure cycle for cement MH-3

MH-3: As Received SO₃, Variable Alkali - 23C Heat Cure

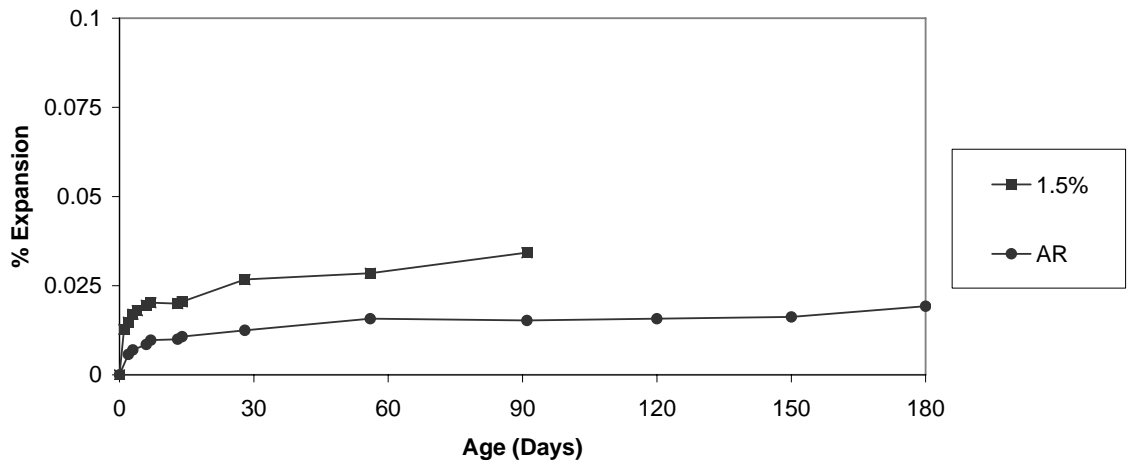


Figure 17: The effect of alkali content after 23°C heat cure cycle for cement MH-3

The same four charts were made for cement C. Unlike MH-3, there is only slightly more expansion at an alkali level of 1.5% than the as received alkali level when

the sulfate is maintained in the as received condition of 2.81. These four charts are shown in Figures 18 thru 21.

C: As Received SO₃, Variable Alkali - 90C Heat Cure

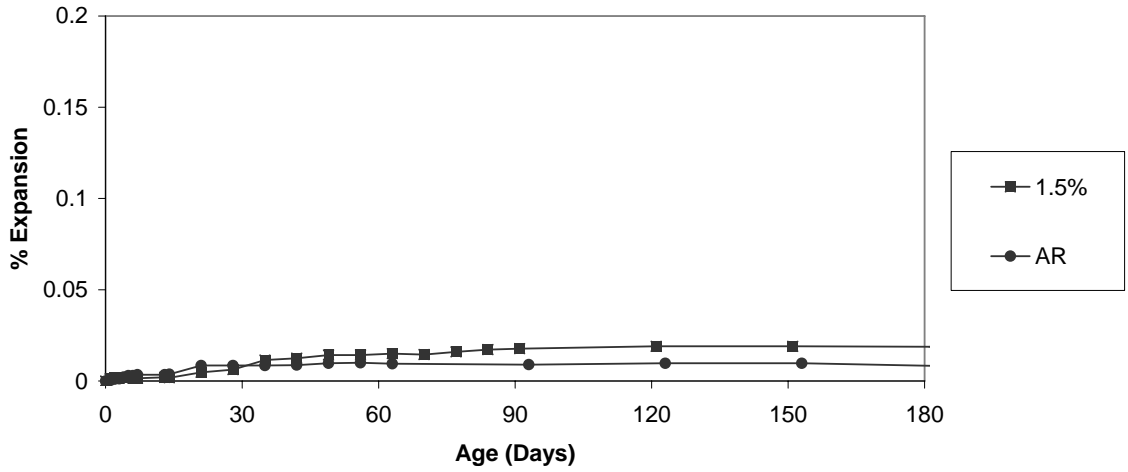


Figure 18: The effect of alkali content after 90°C heat cure cycle for cement C

C: As Received SO₃, Variable Alkali - 80C Heat Cure

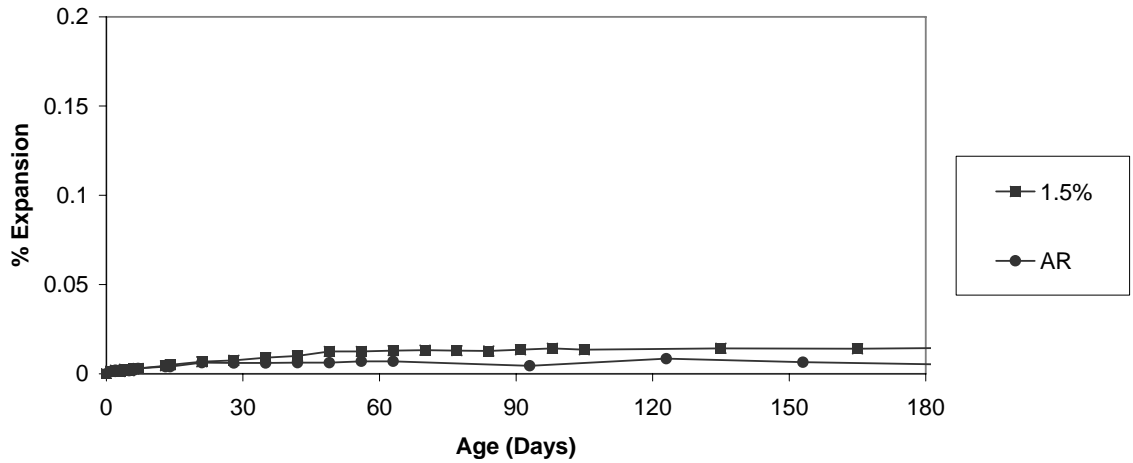


Figure 19: The effect of alkali content after 80°C heat cure cycle for cement C

C: As Received SO3, Variable Alkali - 60C Heat Cure

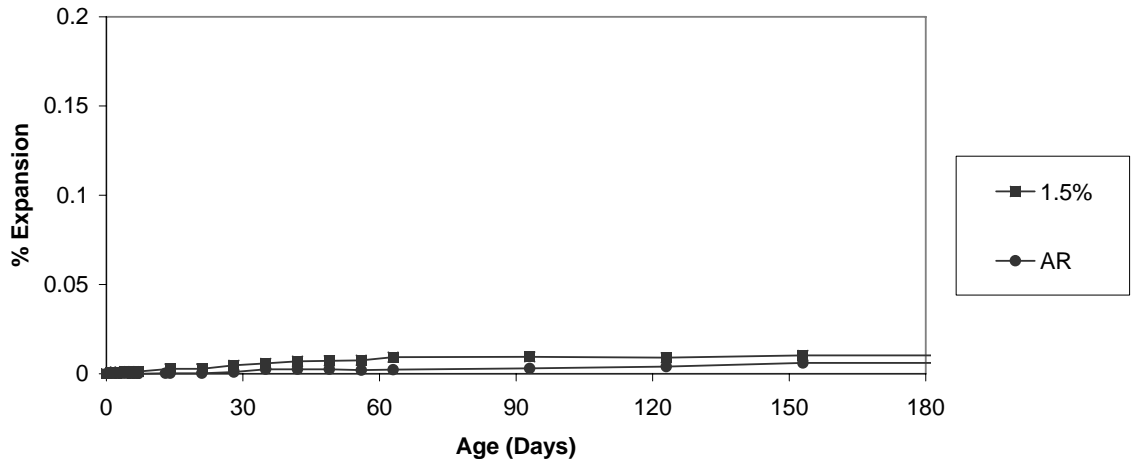


Figure 20: The effect of alkali content after 60°C heat cure cycle for cement C

C: As Received SO3, Variable Alkali - 23C Heat Cure

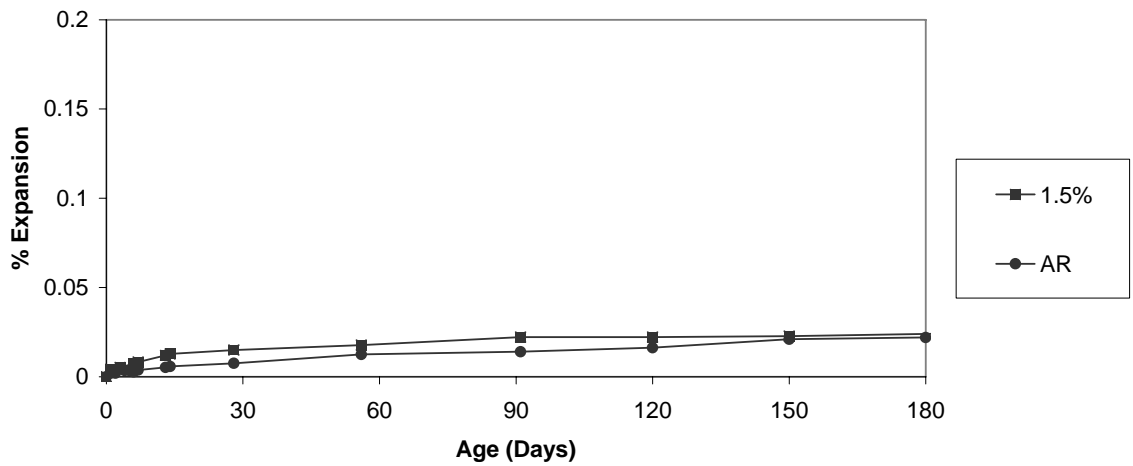


Figure 21: The effect of alkali content after 23°C heat cure cycle for cement C

The sulfate level present has a large effect on expansion. The experiment was set-up to generate results graphing sulfate levels against both alkali and temperature. At a given temperature, an increase in the sulfate level will generate increased rates of

expansion. In figures 22 thru 27 the effect of the sulfate level is graphed against an alkali level of 1.5% or 2.0% when heat cured at 90°, 80° and 60°C. Only cement MH-3 was mixed and measured at an alkali level of 2.0%. A comparison of the corresponding figures for each curing temperature show the difference that the additional alkali makes to the level of expansion experienced by the bars. The higher alkali level of 2.0% results in both earlier and increased levels of expansion for MH-3.

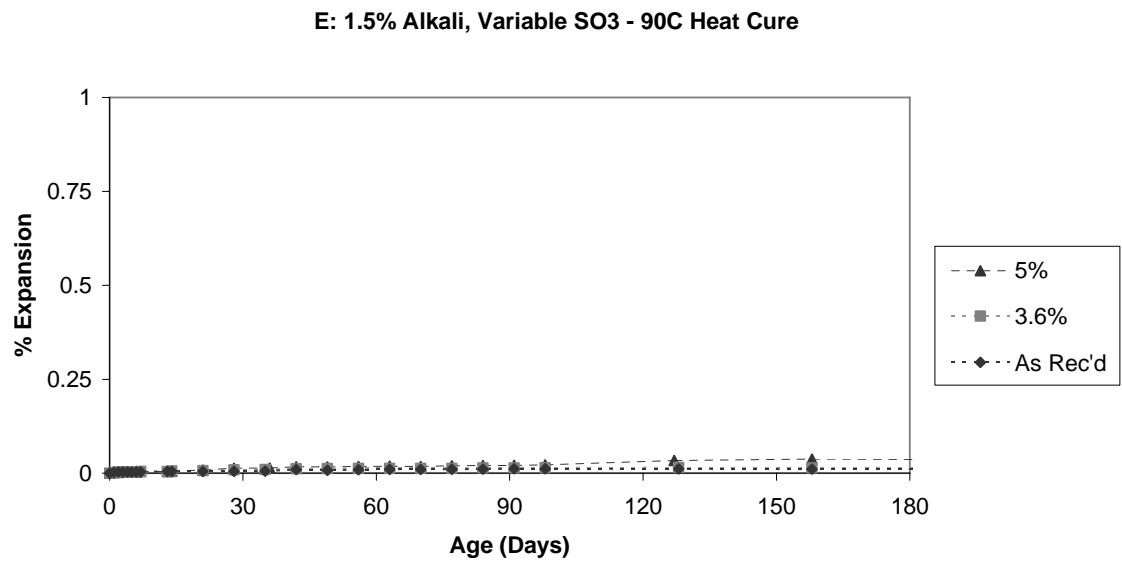


Figure 22: Expansion of cement E with 1.5% alkali content after 90°C heat cure

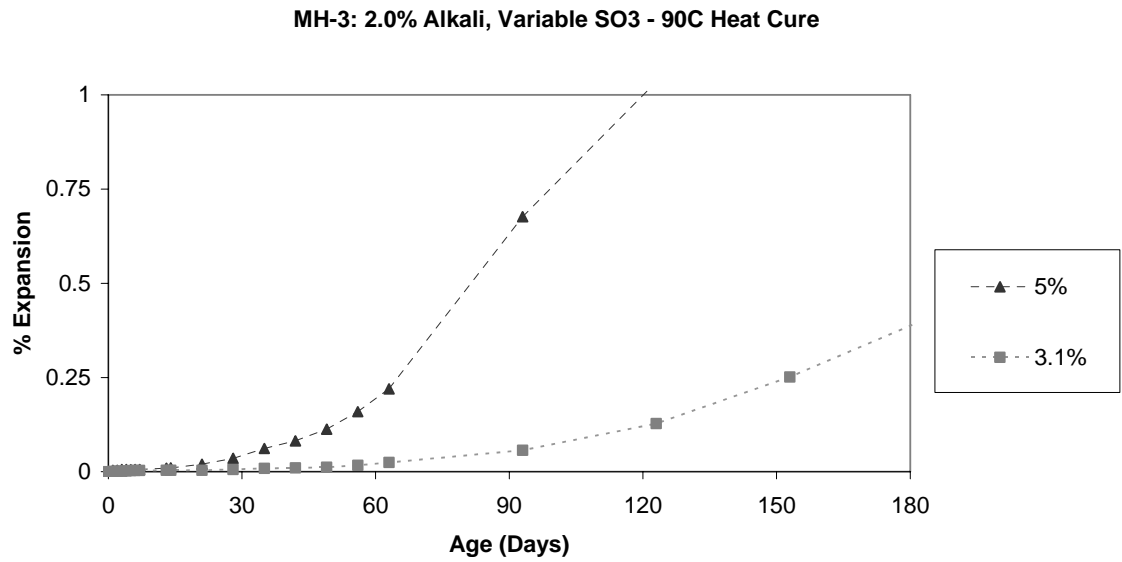


Figure 23: Expansion of cement MH-3 with 2.0 % alkali content after 90°C heat cure

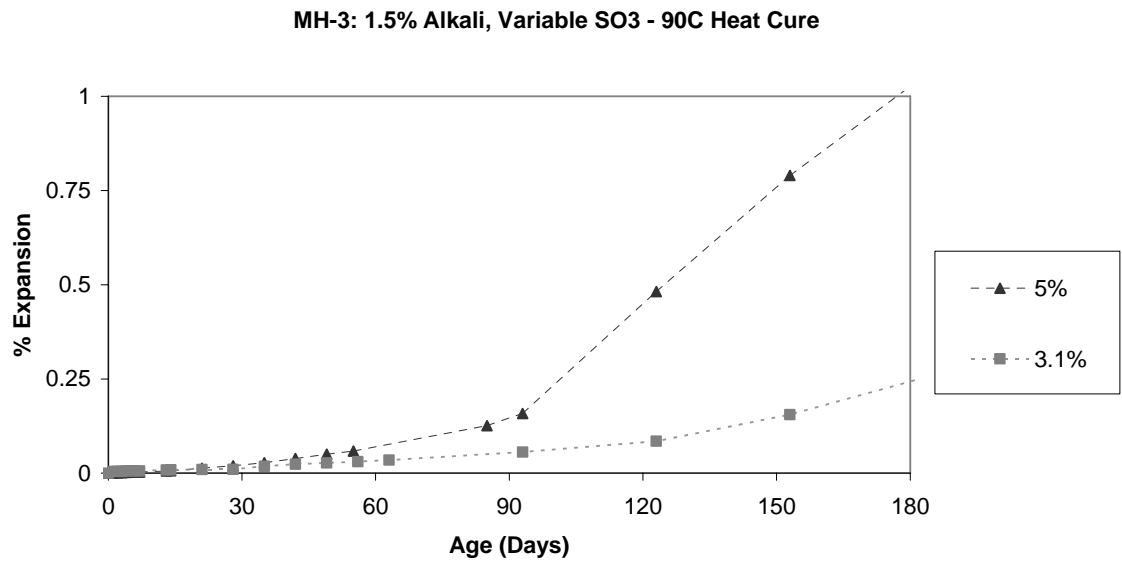


Figure 24: Expansion of cement MH-3 with 1.5% alkali content after 90°C heat cure

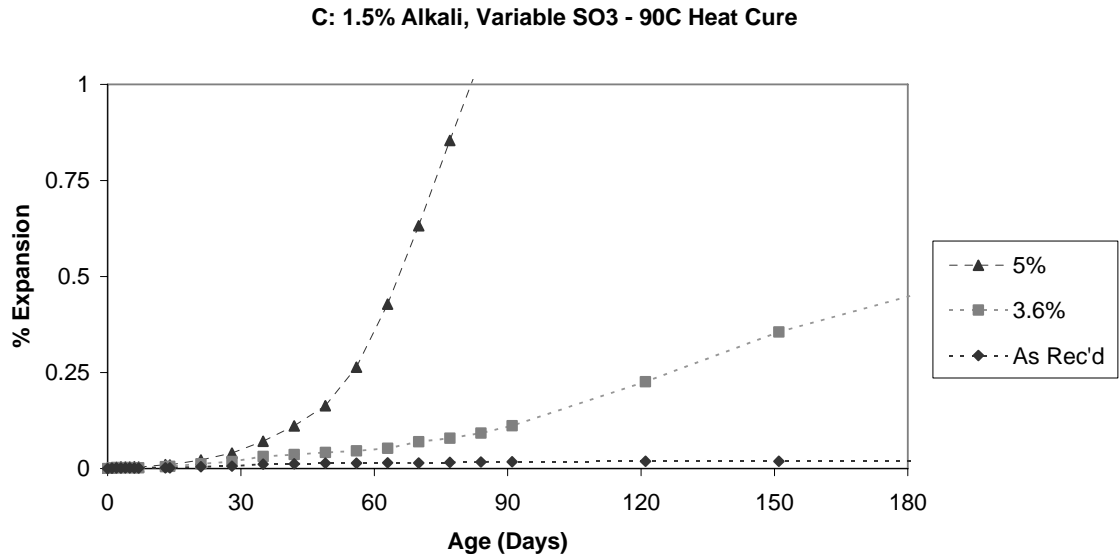


Figure 25: Expansion of cement C with 1.5% alkali content after 90°C heat cure

A comparison of expansion data from the previous four figures shows that cement C has the highest rates of expansion of all three cements at an alkali level of 1.5%. Cement MH-3 has an as received sulfate level of 3.09, this compares favorably with the other two cements at 3.6% sulfate.

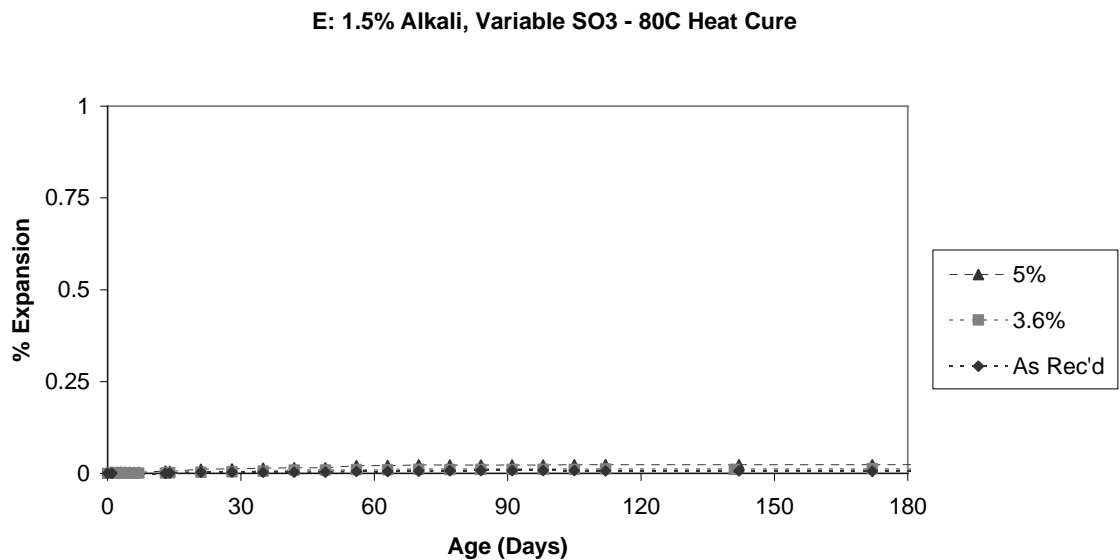


Figure 26: Expansion of cement E with 1.5% alkali content after 80°C heat cure

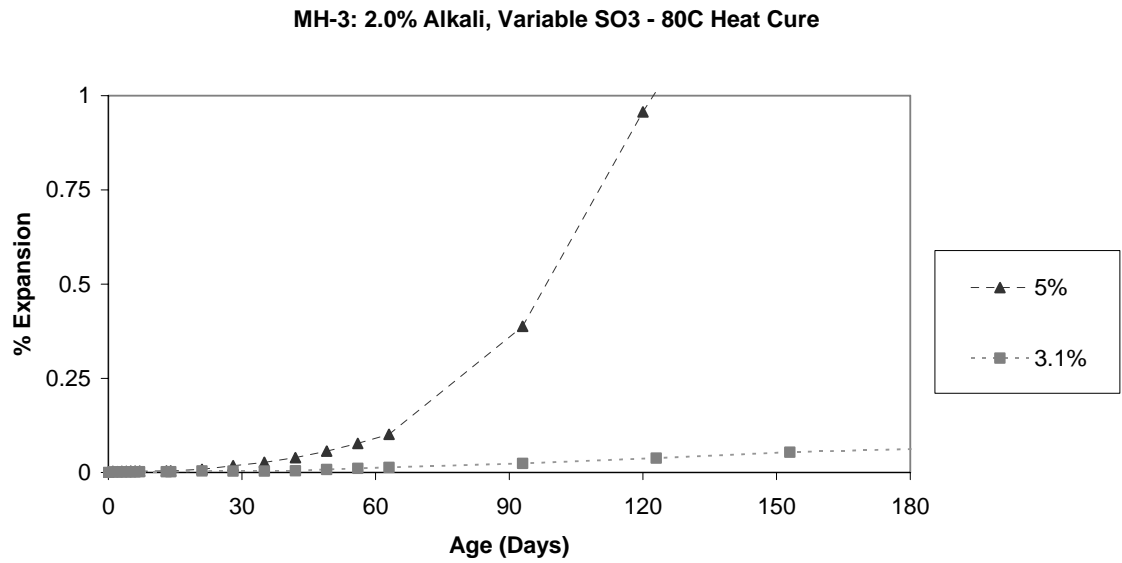


Figure 27: Expansion of cement MH-3 with 2.0% alkali content after 80°C heat cure

The additional alkali makes a large difference in the expansion levels of the 5.0% sulfate samples in MH-3. This is due to the alkali content and its effect on the capacity of the C-S-H gel and pore waters to hold higher levels of sulfate.

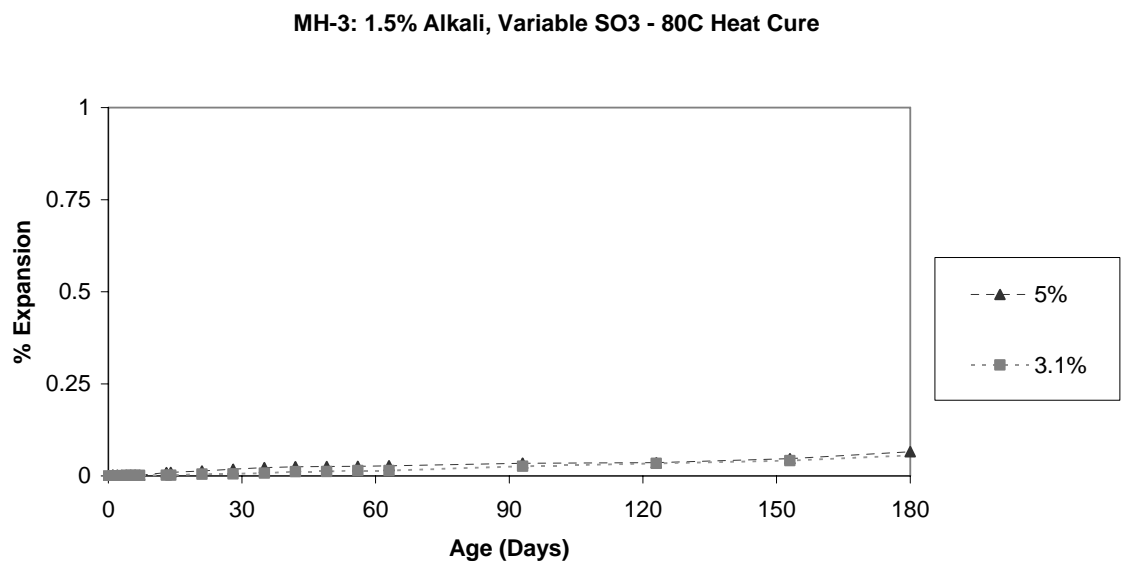


Figure 28: Expansion of cement MH-3 with 1.5% alkali content after 80°C heat cure

C: 1.5% Alkali, Variable SO3 - 80C Heat Cure

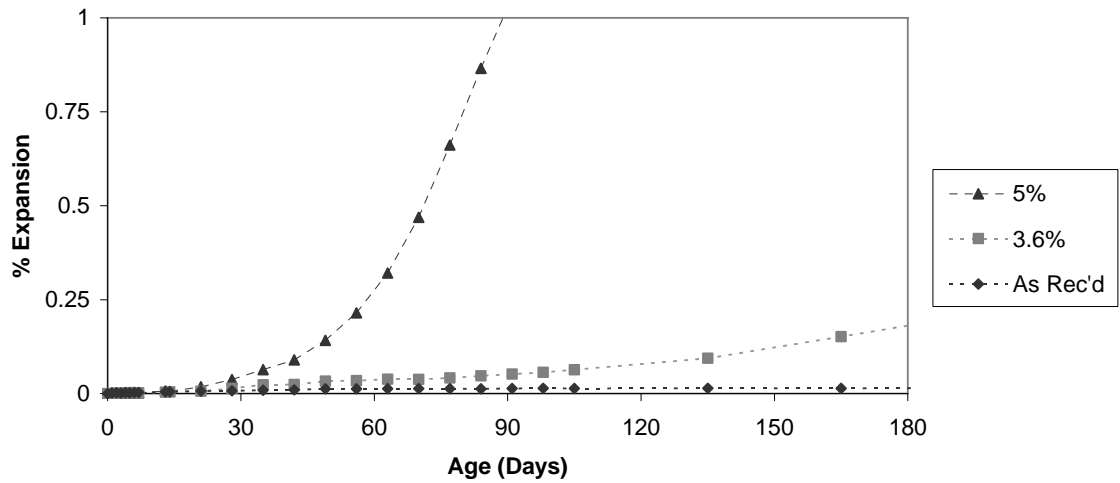


Figure 29: Expansion of cement C with 1.5% alkali content after 80°C heat cure

Figures 26 thru 29 show the expansion data for cements with 1.5% or 2.0% alkali and variable sulfate content after the 80°C heat curing cycle. As in the 90°C data the sulfate level determines the total expansion experienced by the mortar bar. The rate of expansion is lower for the bars heat cured at 80°C than for those done at 90°C.

E: 1.5% Alkali, Variable SO3 - 60C Heat Cure

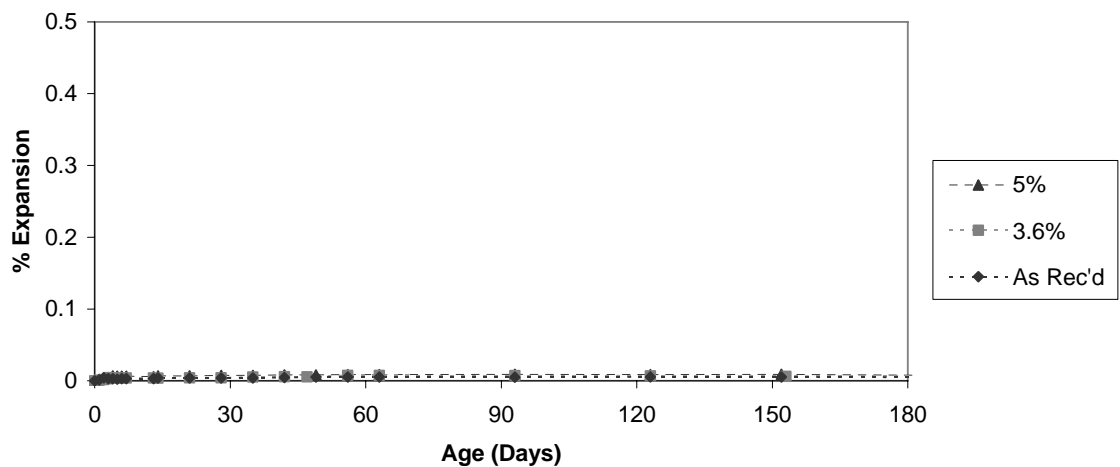


Figure 30: Expansion of cement E with 1.5% alkali content after 60°C heat cure

MH-3: 2.0% Alkali, Variable SO3 - 60C Heat Cure

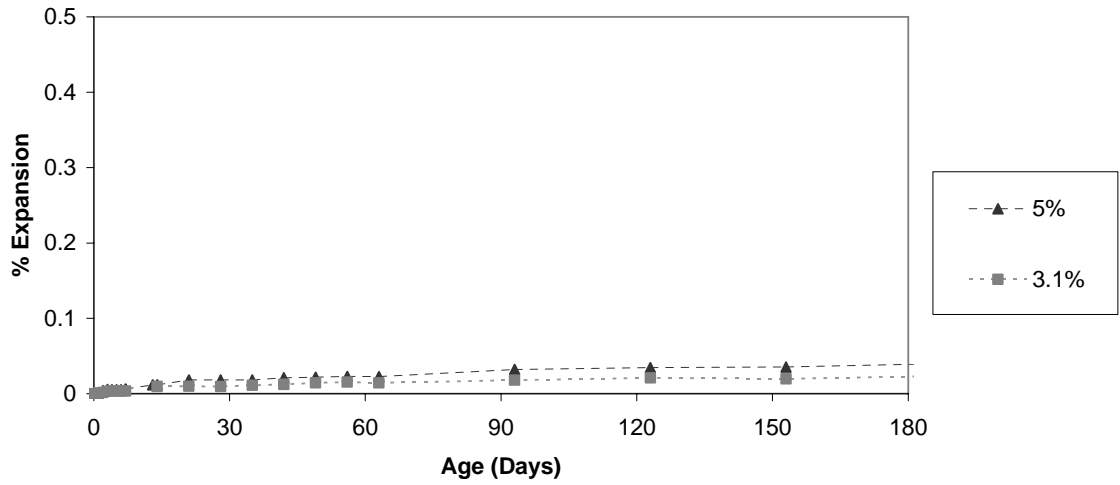


Figure 31: Expansion of cement MH-3 with 2.0% alkali content after 60°C heat cure

MH-3: 1.5% Alkali, Variable SO3 - 60C Heat Cure

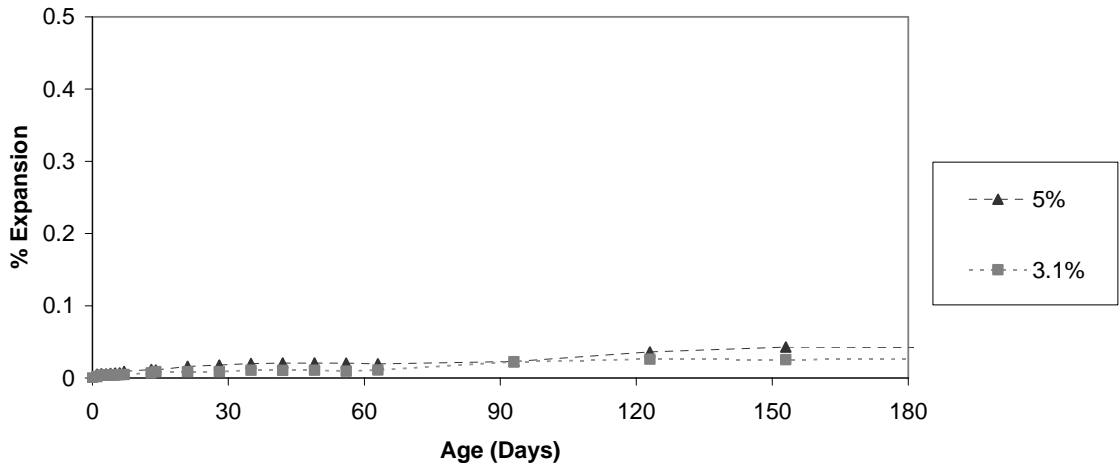


Figure 32: Expansion of cement MH-3 with 1.5% alkali content after 60°C heat cure

C: 1.5% Alkali, Variable SO3 - 60C Heat Cure

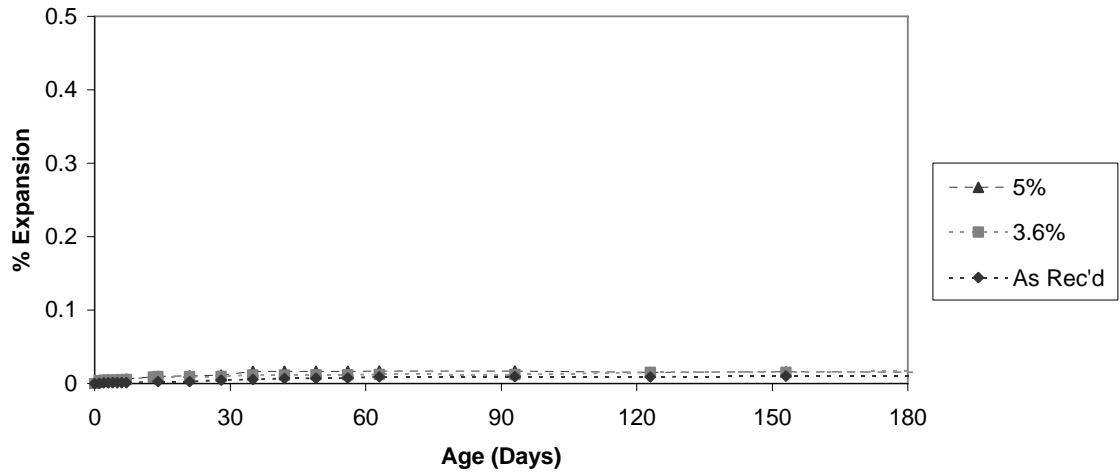


Figure 33: Expansion of cement C with 1.5% alkali content after 60°C heat cure

Figures 30 thru 33 show the same effects for the 60°C heat cure. The temperature has an effect on the amount of expansion experienced by the bar, but in all cases expansion increases with increasing sulfate and alkali content.

In all three cements the expansion is dependant upon the sulfate content. Equalizing the sulfate content, temperature, and alkali content between all three cements yields the data shown in figures 34 thru 37. In Figures 34 and 35 representing the 90° and 80°C heat cure, cement C exhibits the most expansion followed by MH-3 then lastly E. This is what was to be expected by the C₃S content using the calibration curve method. Cement C has the greatest value at 70% followed by MH-3 at 67% and Cement E at 58%. In figures 36 and 37, the 60°C and room temperature heat curing cycles, the expansion is greatest for cement MH-3. At these temperatures there is not much difference in expansion rates.

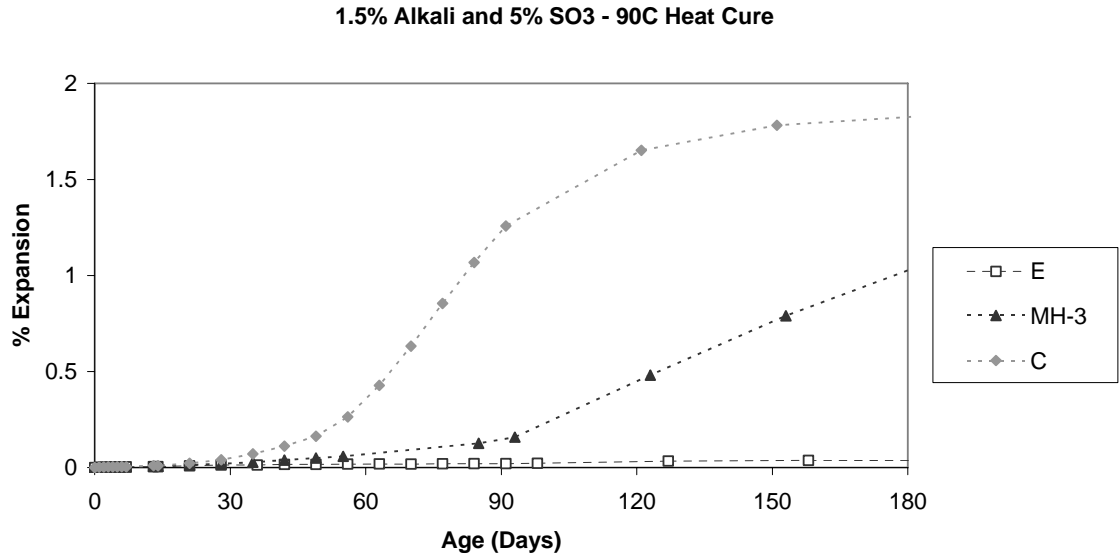


Figure 34: The effect of cement composition on expansion at constant alkali and sulfate Levels after 90°C heat cure

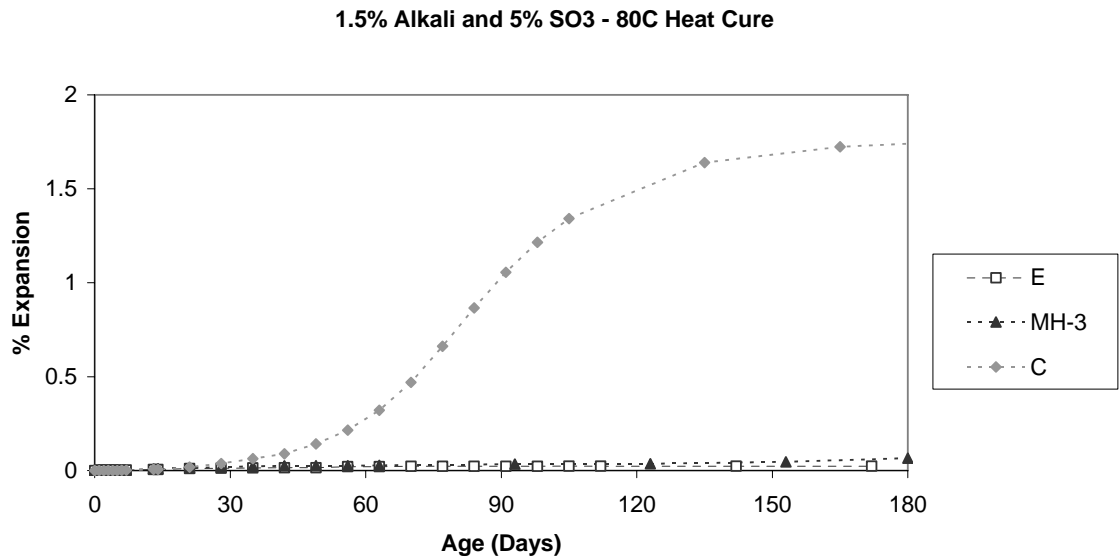


Figure 35: The effect of cement composition on expansion at constant alkali and sulfate Levels after 80°C heat cure

1.5% Alkali and 5% SO3 - 60C Heat Cure

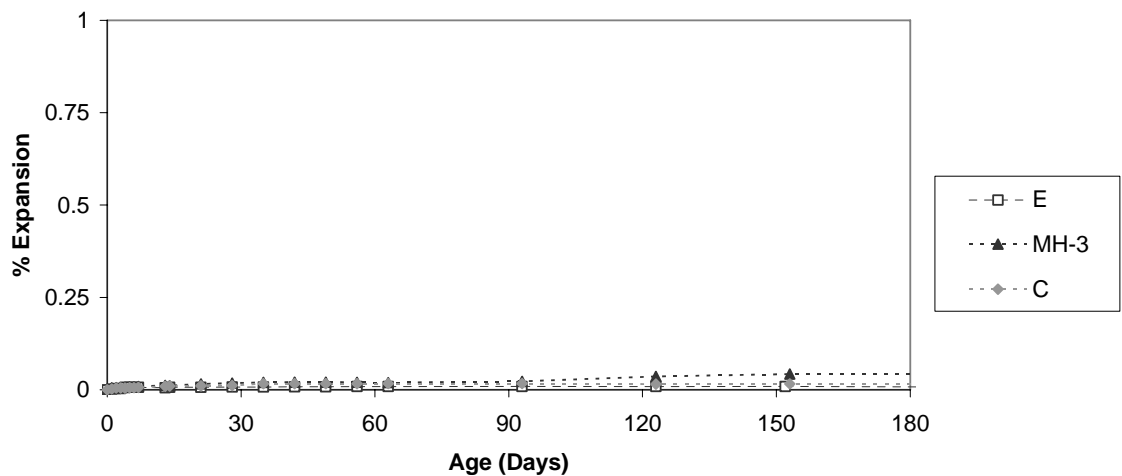


Figure 36: The effect of curing temperature on cement with 1.5% alkali and 5% sulfate after 60°C heat cure

1.5% Alkali and 5% SO3 - 23C Heat Cure

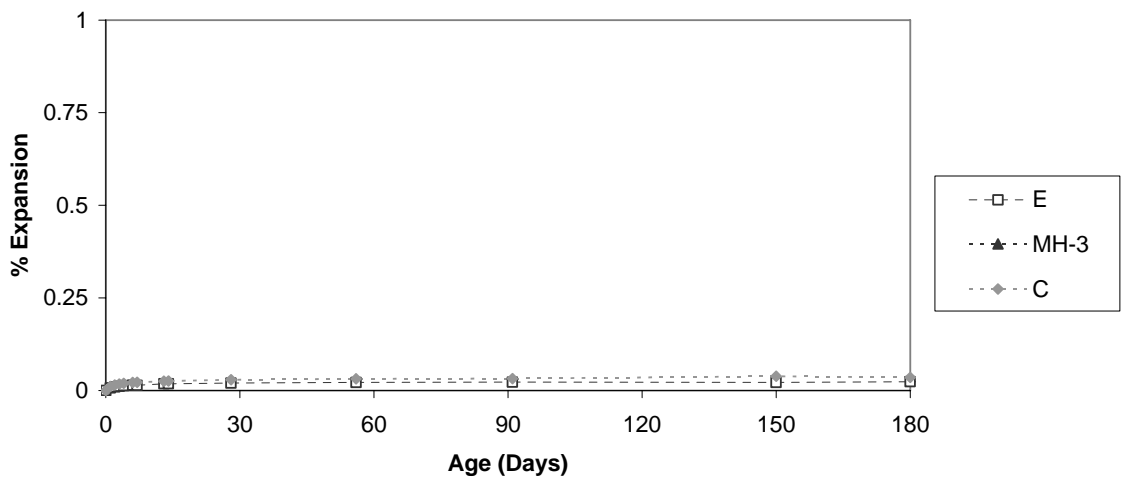


Figure 37: The effect of curing temperature on cement with 1.5% alkali and 5% sulfate after 23°C heat cure

The same comparisons are duplicated in charts 38 thru 41 with the sulfate content at 3.6%. As in the previous charts, cement C shows the greatest expansion after both the 90° and 80°C heat curing cycles.

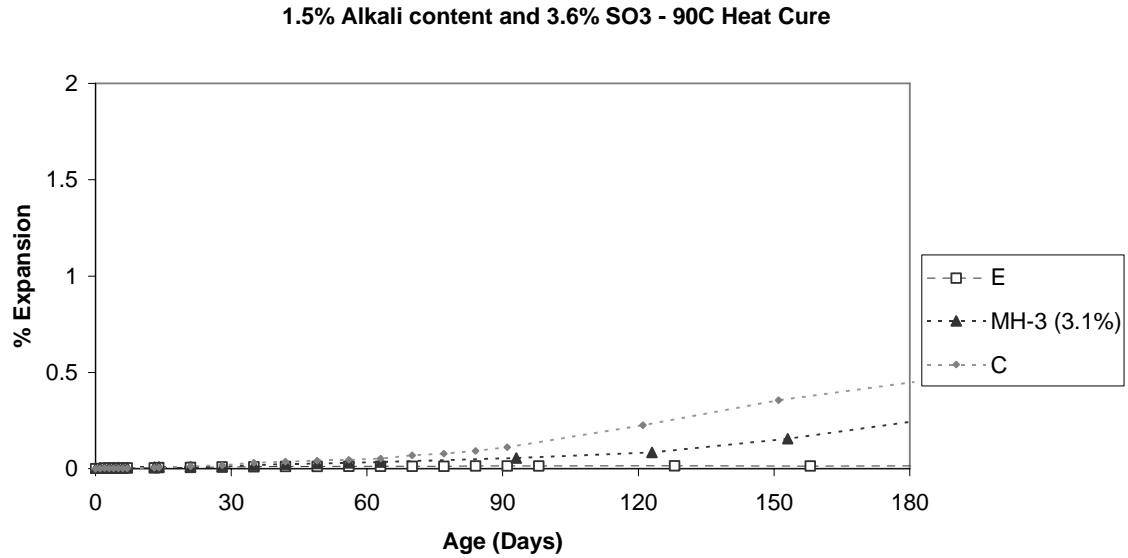


Figure 38: The effect of curing temperature on cement with 1.5% alkali and 3.6 % sulfate after 90°C heat cure

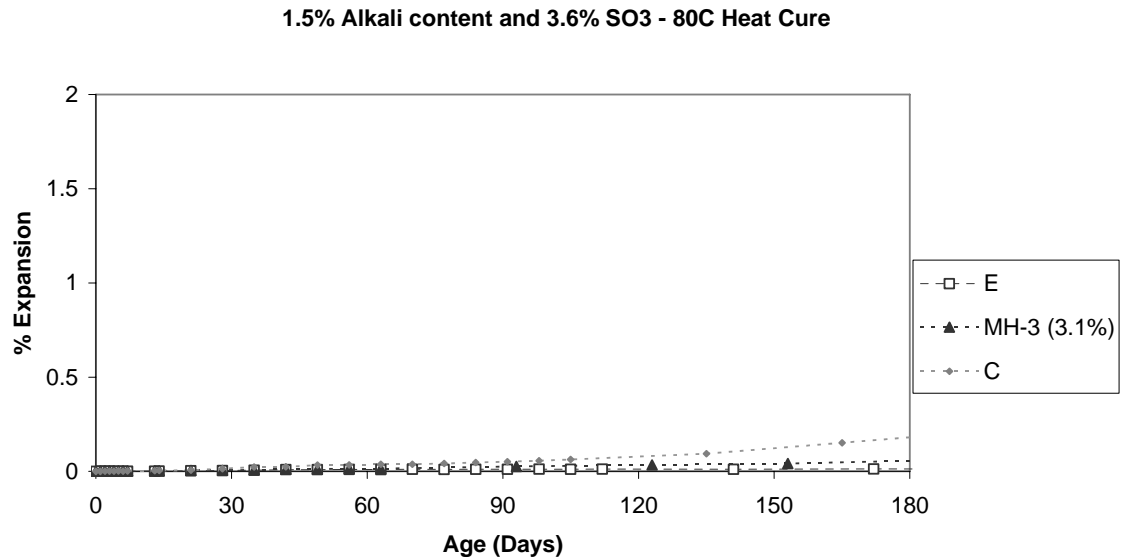


Figure 39: The effect of curing temperature on cement with 1.5% alkali and 3.6 % sulfate after 80°C heat cure

1.5% Alkali content and 3.6% SO3 - 60C Heat Cure

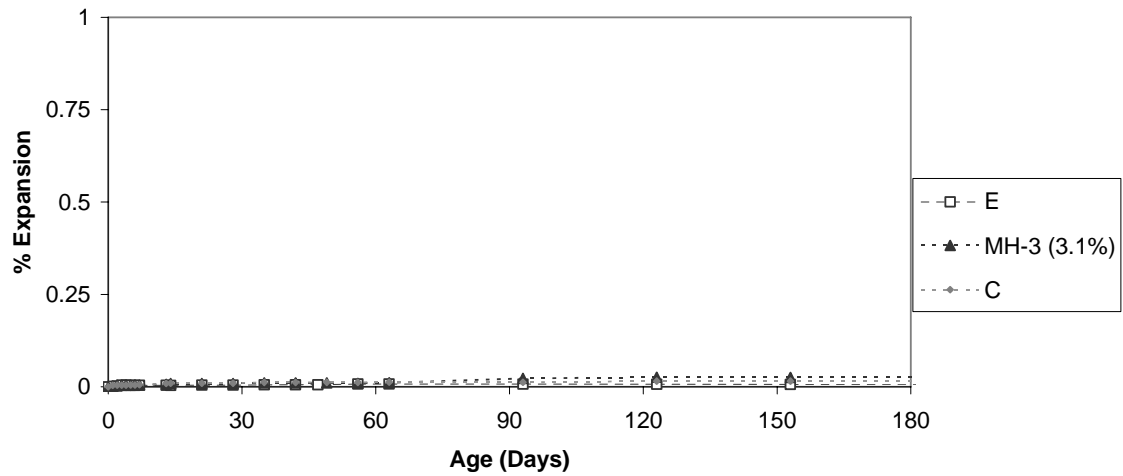


Figure 40: The effect of curing temperature on cement with 1.5% alkali and 3.6 % sulfate after 60°C heat cure

1.5% Alkali content and 3.6% SO3 - 23C Heat Cure

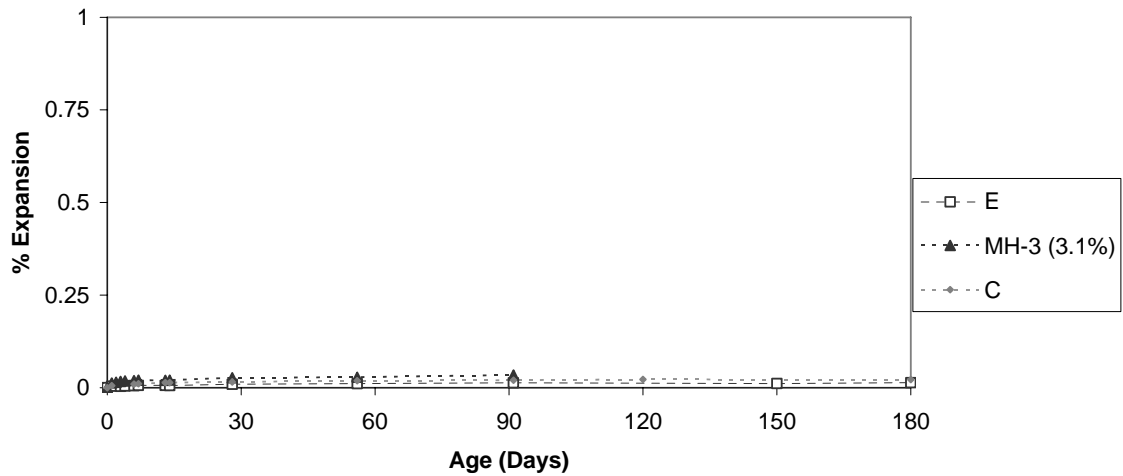


Figure 41: The effect of curing temperature on cement with 1.5% alkali and 3.6 % sulfate after 23°C heat cure

In Figures 42 thru 44 the rate of expansion for all three cements are presented at 1.5% Alkali and 5% Sulfate content. These graphs clearly show the effect of heat curing temperature on expansion. Higher the temperatures result in greater expansion over time.

E: 1.5% Alkali, 5% SO₃

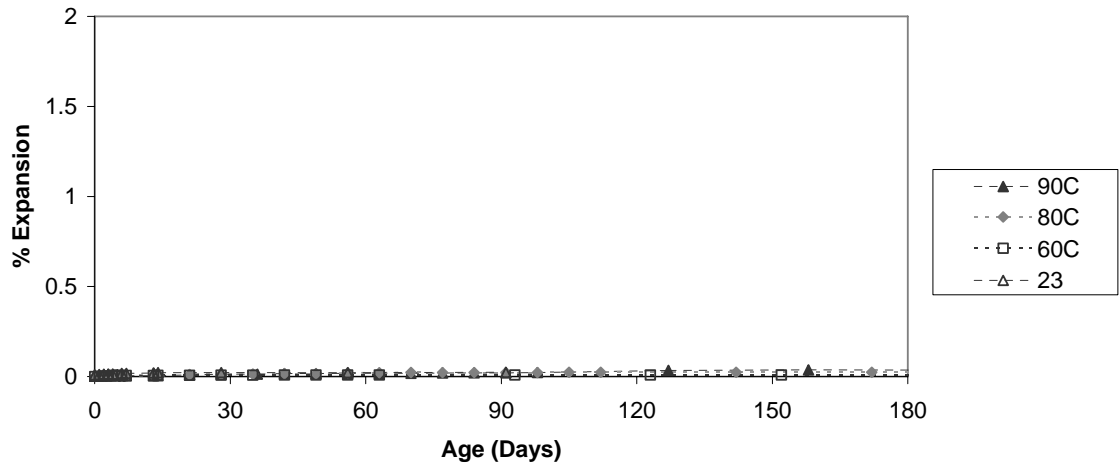


Figure 42: The effect of heat cure temperature on cement E with alkali = 1.5% and SO₃ = 5.0%

MH-3: 1.5% Alkali, 5% SO₃

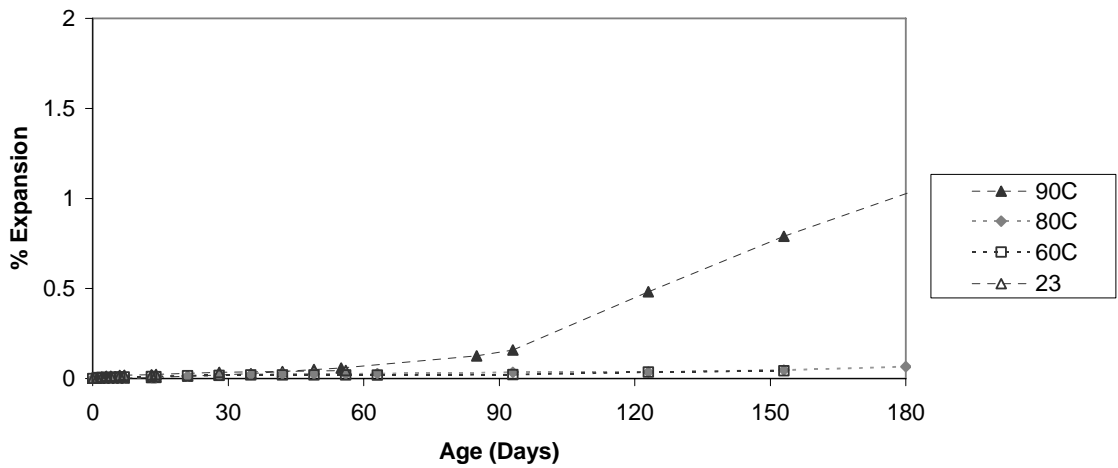


Figure 43: The effect of heat cure temperature on cement MH-3 with alkali = 1.5% and SO₃ = 5.0%

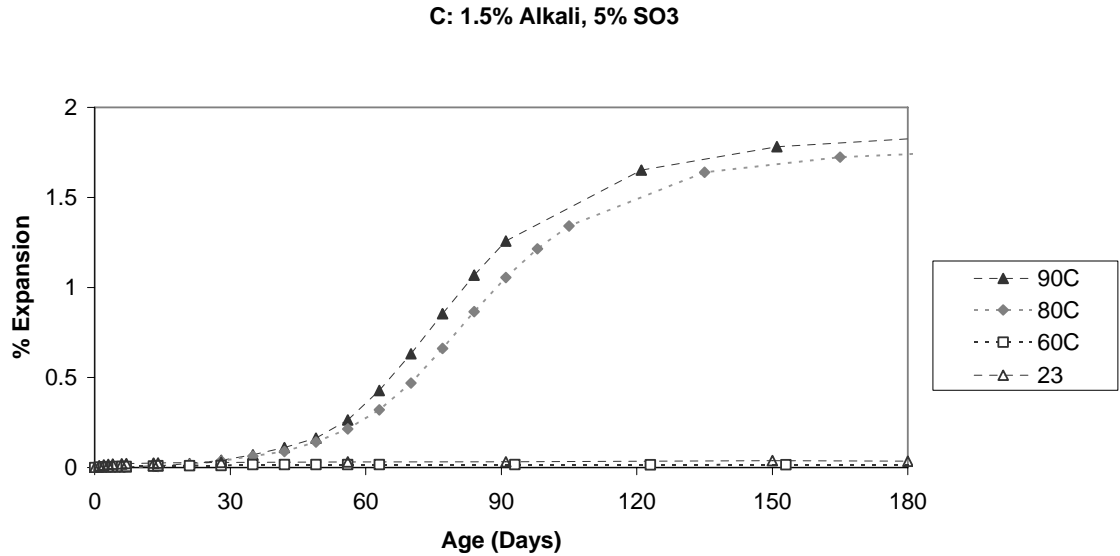


Figure 44: The effect of heat cure temperature on cement C with alkali = 1.5% and SO₃ = 5.0%

Before the results are discussed, let us consider the rate of expansion as measured in % expansion per day for all three cements. Figures 45 thru 48 show the rate of expansion for all three cements at an equalized chemistry of 5.0% sulfate and 1.5% alkali. At both 80°C and 90°C cement C has the greatest rate of expansion. After the 60°C and 23°C heat cure cement MH-3 expands at the greatest rate. This is another example showing that cement C has the greatest expansion after the high temperature heat cures.

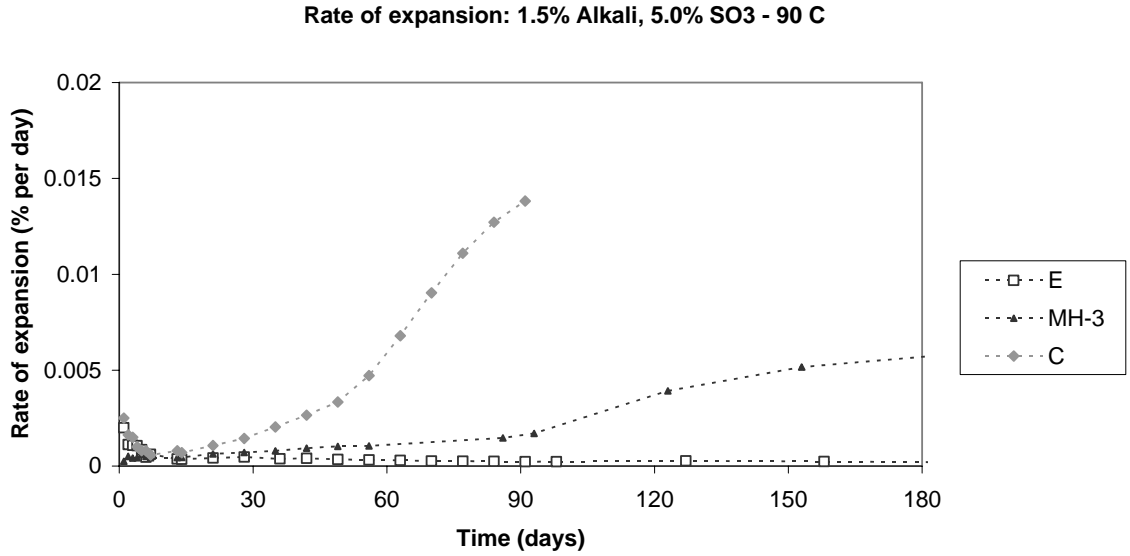


Figure 45: The rate of expansion for cements with SO₃ = 5% and alkali = 1.5% cured at 90°C. * Note: results on cement C terminated at 91 days due to bending

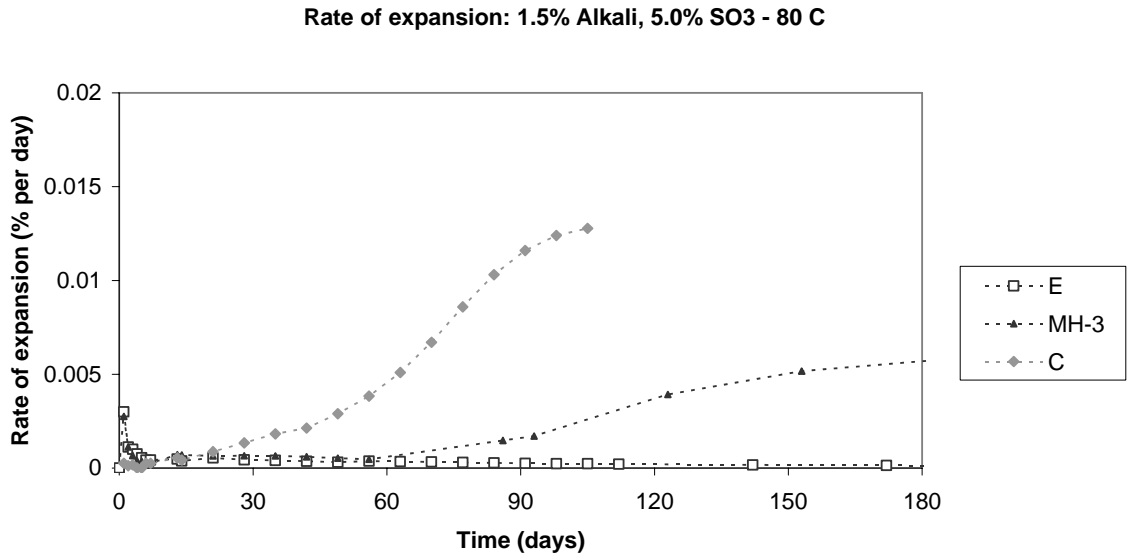


Figure 46: The rate of expansion for cements with SO₃ = 5% and alkali = 1.5% cured at 80°C. * Note: results on cement C terminated at 105 days due to bending

The same trend is shown at a sulfate level of 3.6%. Figures 49 thru 52 are graphs of cements at 3.6% sulfate and 1.5% alkali.

Rate of expansion: 1.5% Alkali, 5.0% SO3 - 60 C

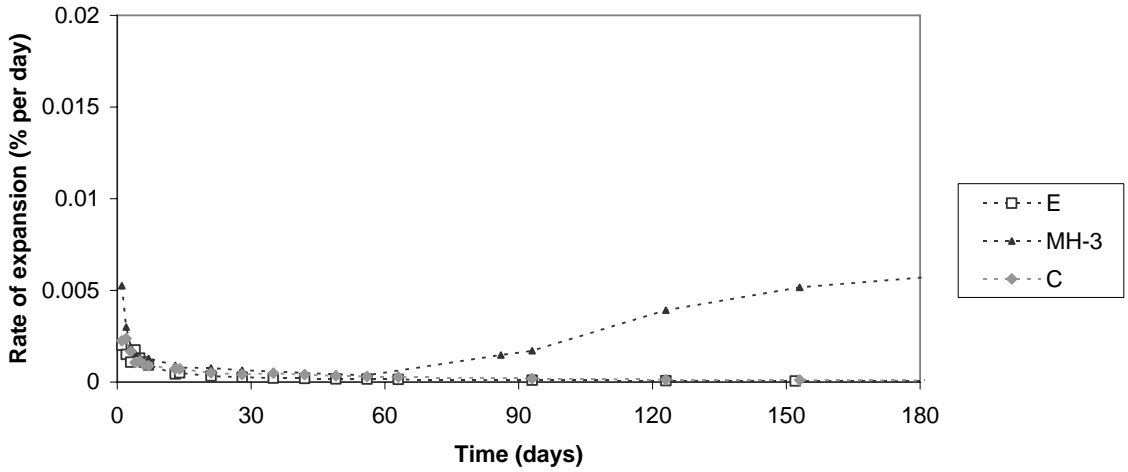


Figure 47: The rate of expansion for cements with $SO_3 = 5\%$ and alkali = 1.5% cured at $60^\circ C$

Rate of expansion: 1.5% Alkali, 5.0% SO3 - 23 C

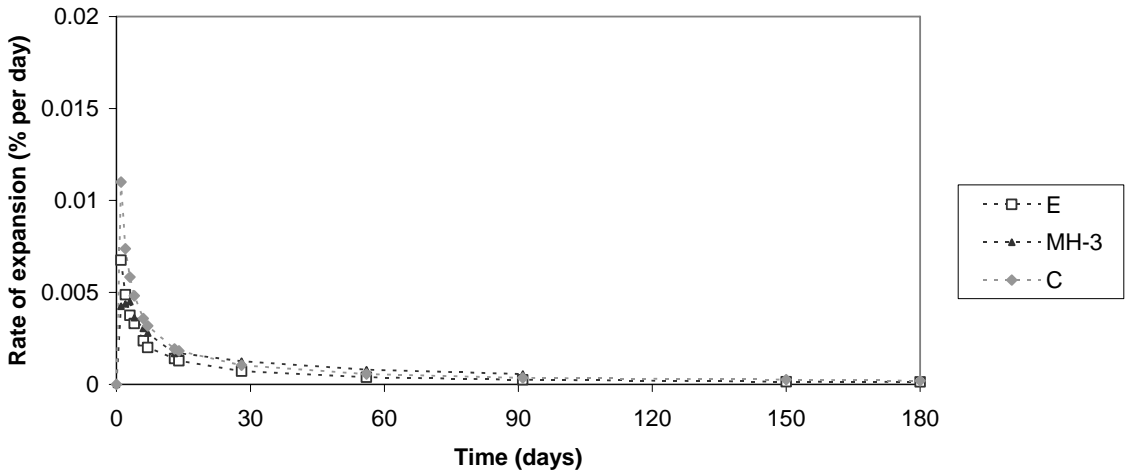


Figure 48: The rate of expansion for cements with $SO_3 = 5\%$ and alkali = 1.5% cured at $23^\circ C$

At a sulfate level of 5% and alkali level of 1.5%, cement and $60^\circ C$ heat cure, cement MH-3 is the only one of the three to have any meaningful level of expansion.

Although the level of expansion is far from that required to produce physical damage, the heat curing had some effect on this cement. There is little expansion for any of the cements when cured at 23°C.

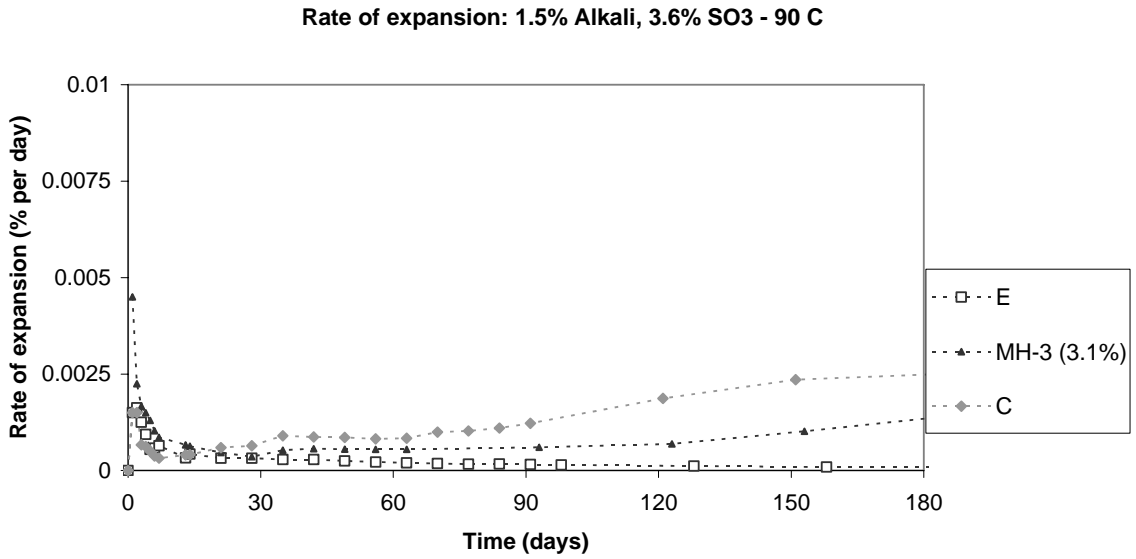


Figure 49: The rate of expansion for cements with SO₃ = 3.6% and alkali = 1.5% cured at 90 C

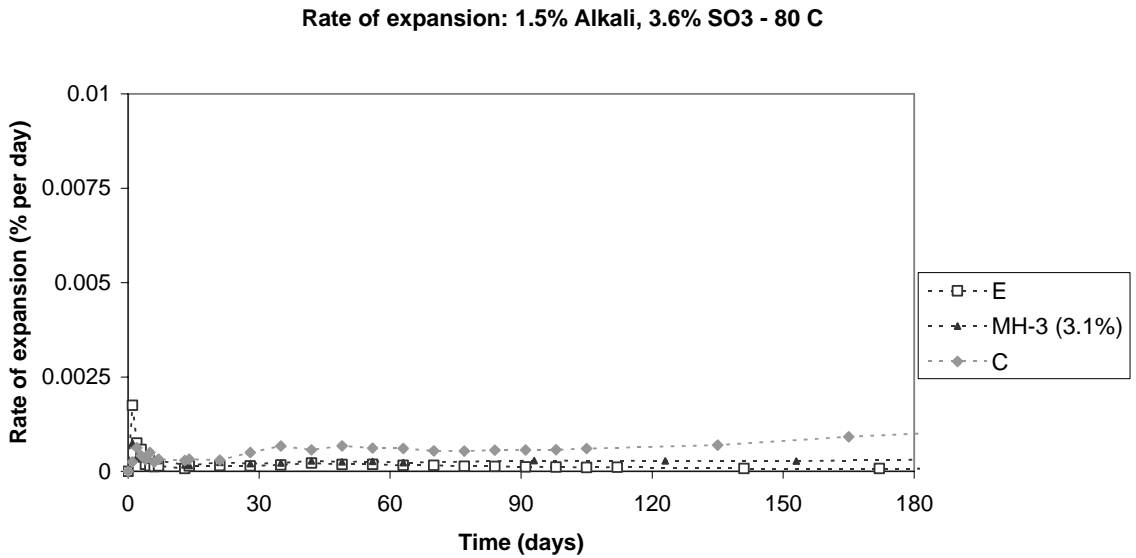


Figure 50: The rate of expansion for cements with SO₃ = 3.6% and alkali = 1.5% cured at 80°C

Rate of expansion: 1.5% Alkali, 3.6% SO₃ - 60 C

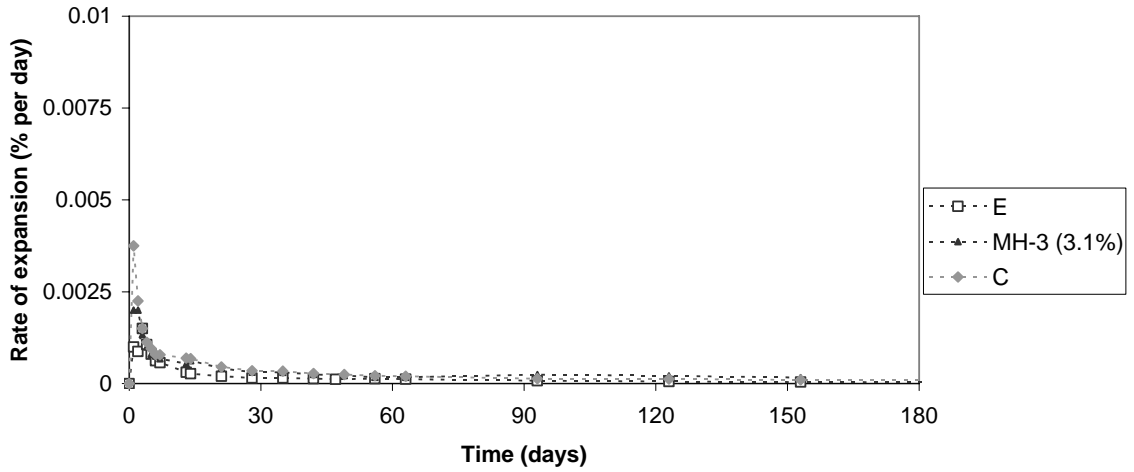


Figure 51: The rate of expansion for cements with SO₃ = 3.6% and alkali = 1.5% cured at 60°C

Rate of expansion: 1.5% Alkali, 3.6% SO₃ - 23 C

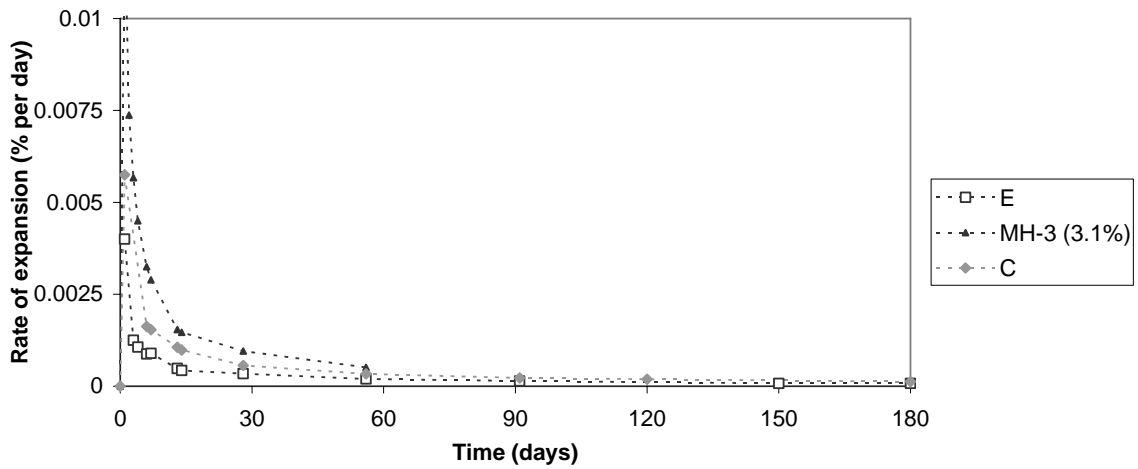


Figure 52: The rate of expansion for cements with SO₃ = 3.6% and alkali = 1.5% cured at 23°C

Charts 53 thru 56 show the expansion rate for cements with as received sulfate and 1.5% alkali content. Charts 57 thru 60 show the expansion rate for cements with as

received sulfate and as received Alkali content. At all three temperatures cement MH-3 shows the greatest expansion followed by cement C then cement E. These results correlate with the sulfate content.

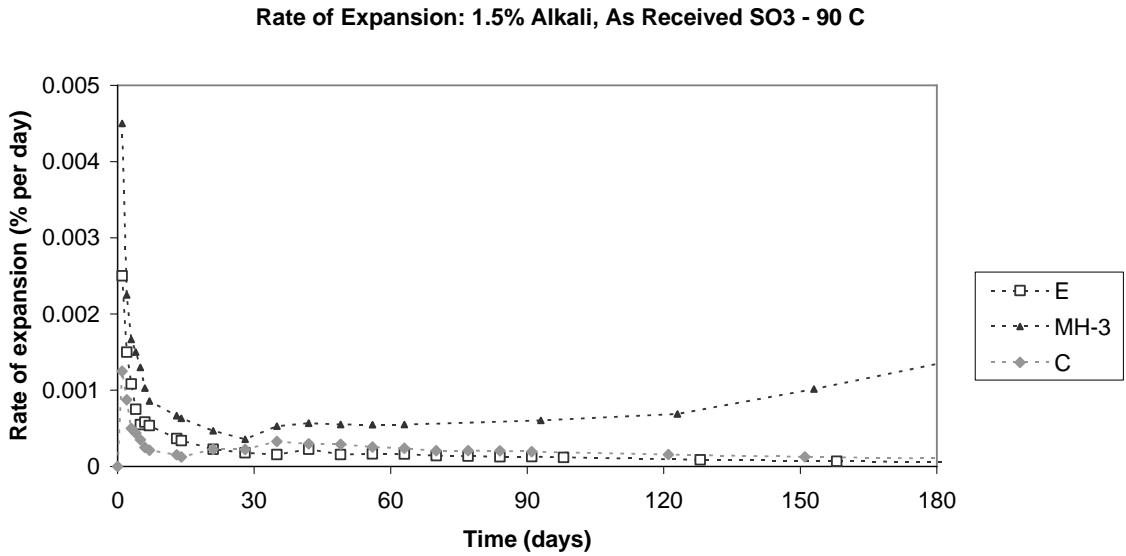


Figure 53: The rate of expansion for cements with as received SO₃ and alkali = 1.5% cured at 90°C

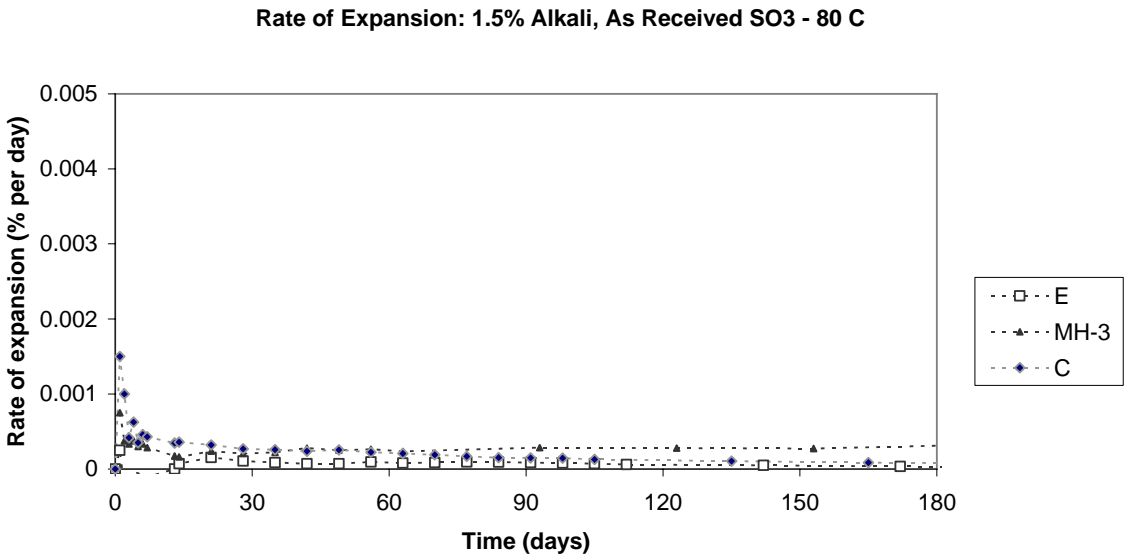


Figure 54: The rate of expansion for cements with as received SO₃ and alkali = 1.5% cured at 80°C

Rate of Expansion: 1.5% Alkali, As Received SO₃ - 60 C

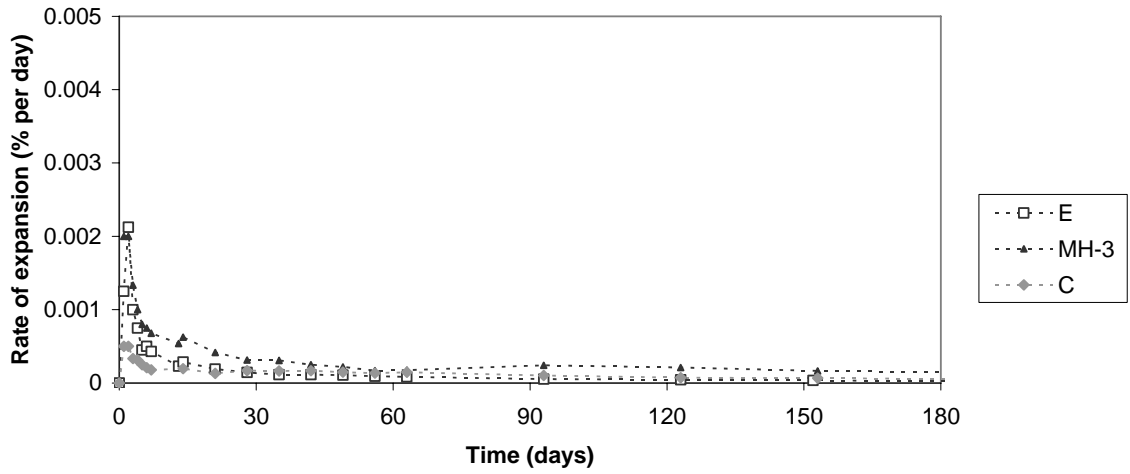


Figure 55: The rate of expansion for cements with as received SO₃ and alkali = 1.5% cured at 60°C

Rate of Expansion: 1.5% Alkali, As Received SO₃ - 23 C

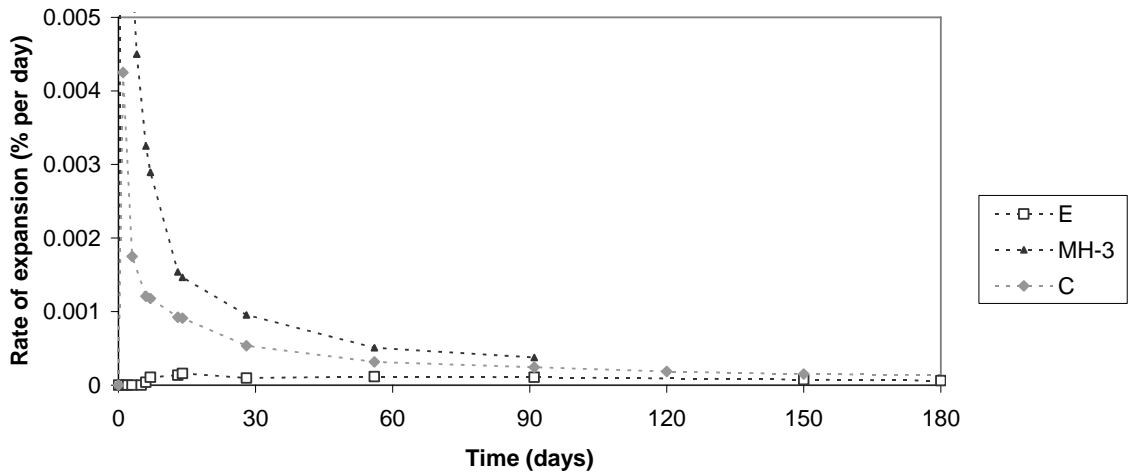


Figure 56: The rate of expansion for cements with as received SO₃ and alkali = 1.5% cured at 23°C

Rate of expansion: Alkali and SO₃ As Received - 90 C

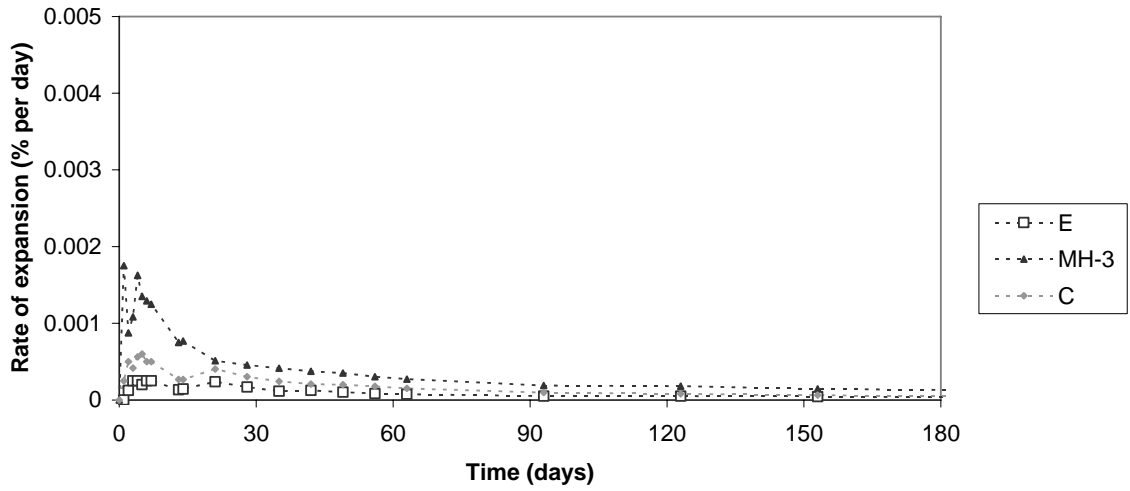


Figure 57: The expansion rate for cements with as received SO₃ and alkali cured at 90°C

Rate of expansion: Alkali and SO₃ As Received - 80 C

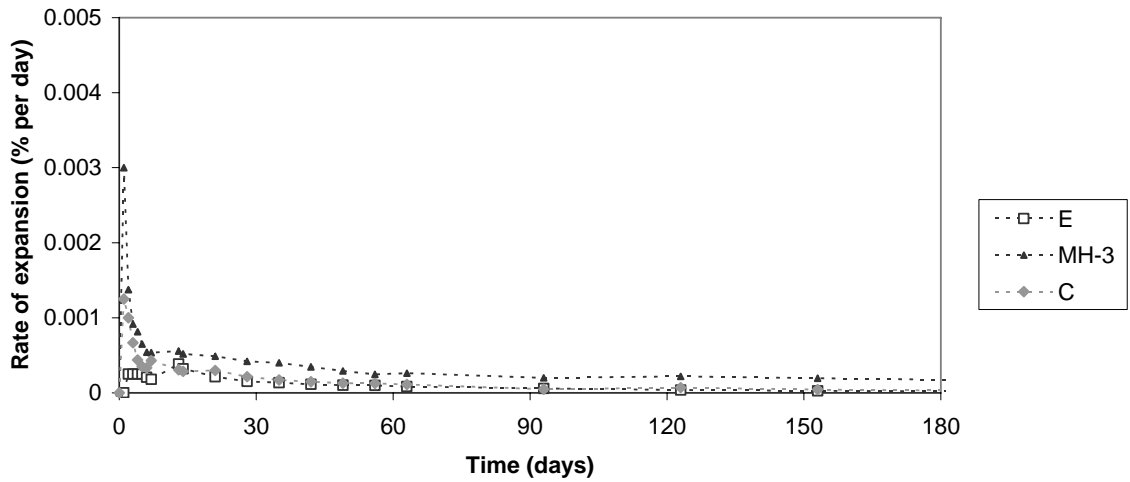


Figure 58: The expansion rate for cements with as received SO₃ and alkali cured at 80°C

Rate of expansion: Alkali and SO₃ As Received - 60 C

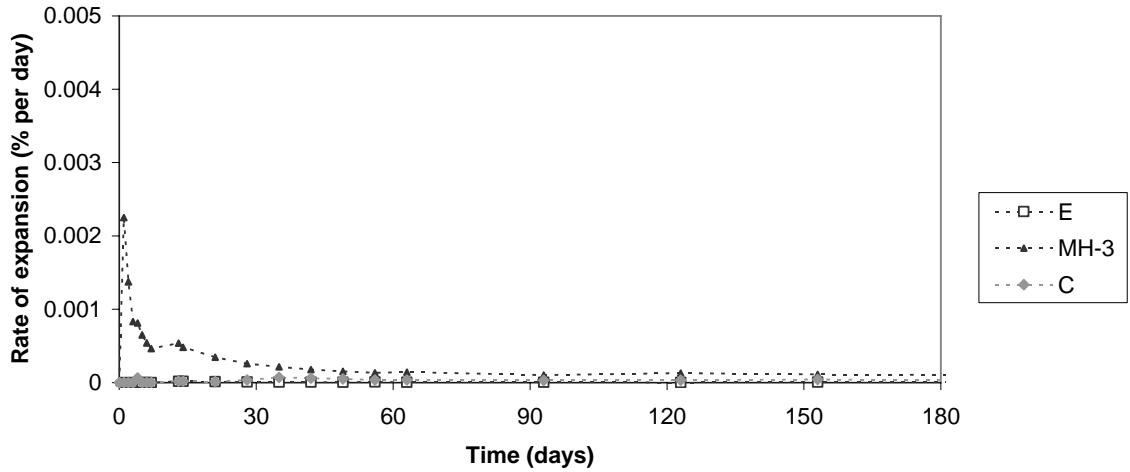


Figure 59: The expansion rate for cements with as received SO₃ and alkali cured at 60°C

Rate of expansion: Alkali and SO₃ As Received - 23 C

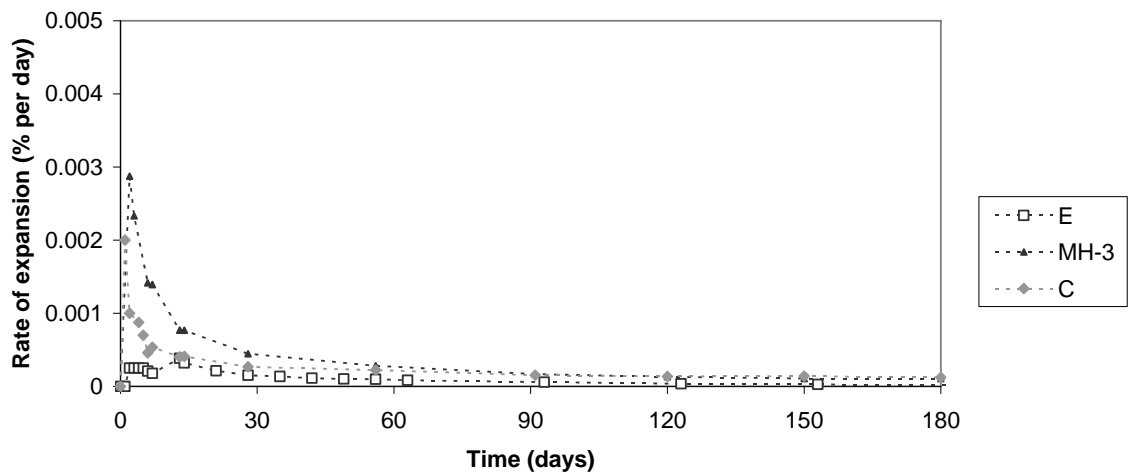


Figure 60: The expansion rate for cements with as received SO₃ and alkali cured at 23°C

A series of charts were made plotting the level of expansion (%) against the heat curing temperature for all three cements. All cements were plotted separately to show the

chemistry variations; the plots were done at specific ages. These charts tend to highlight the effect of heat curing temperatures upon the variation in chemistry. Figures 61 thru 63 are for cement E, and represent the time periods of 120, 180, and 270 days. Because the level of expansion for cement E was so small, the scale was reduced from 2% to 0.5%. Temperature, sulfate, and alkali levels had very little effect on the expansion levels for this cement. At 270 days the 5% sulfate and 1.5% alkali mortar bars that were cured at 90°C only expanded slightly more than the other mixes. It is to be remembered that this cement had the lowest C_3S and C_3S/C_2S ratio of all three cements.

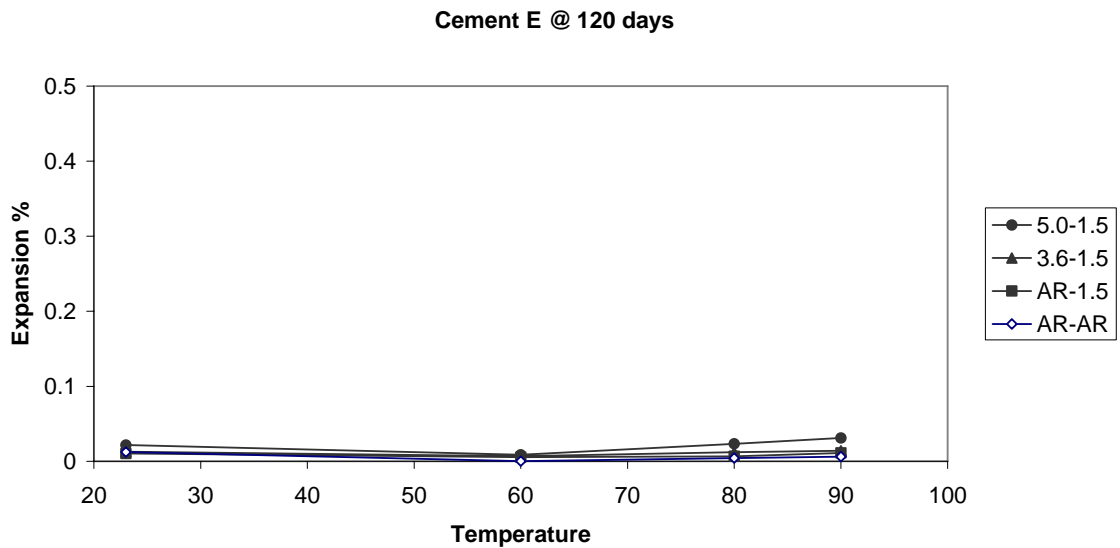


Figure 61: Expansion exhibited by cement E at one-hundred and twenty days

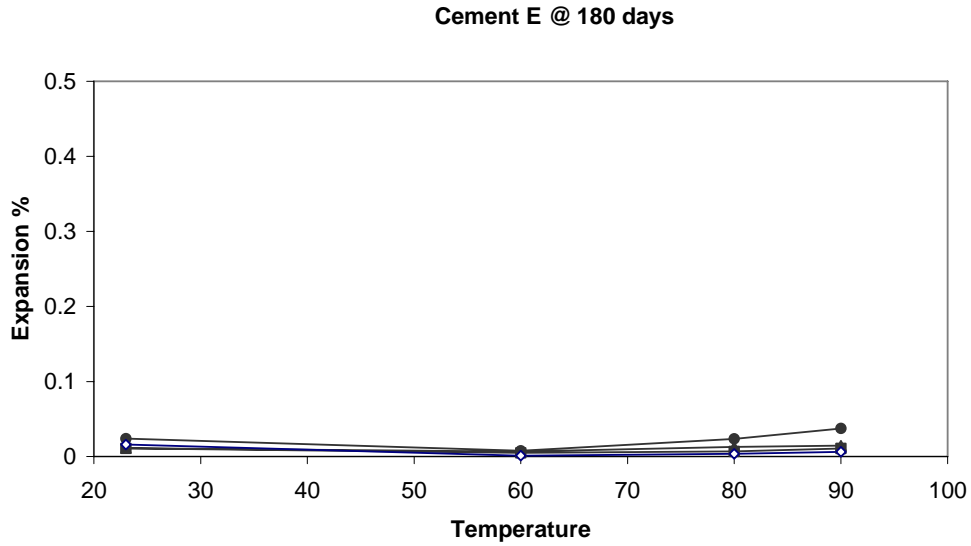


Figure 62: Expansion exhibited by cement E at one-hundred and eighty days

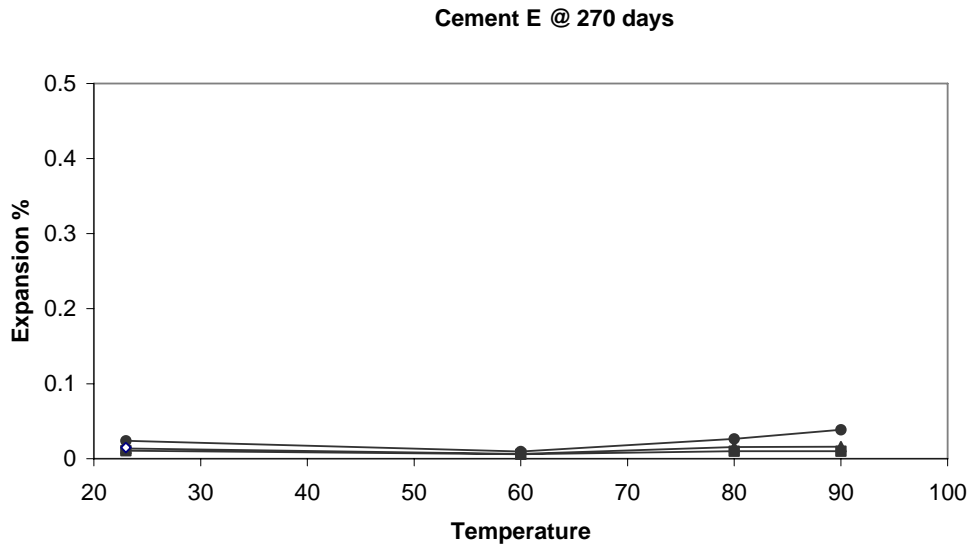


Figure 63: Expansion exhibited by cement E at two-hundred and seventy days

The same graphs were generated for cement MH-3. The effect of temperature, sulfate and alkali content are very apparent for this cement as well as cement C. The scale was set at a 2% expansion level to clearly show the effect of temperature and chemistry upon the level of expansion experienced by the mortar bar. The mixture with

5% sulfate and 1.5% alkali expanded at a much greater rate than the other mixes. With this mix, the heat curing temperature determines the level of expansion.

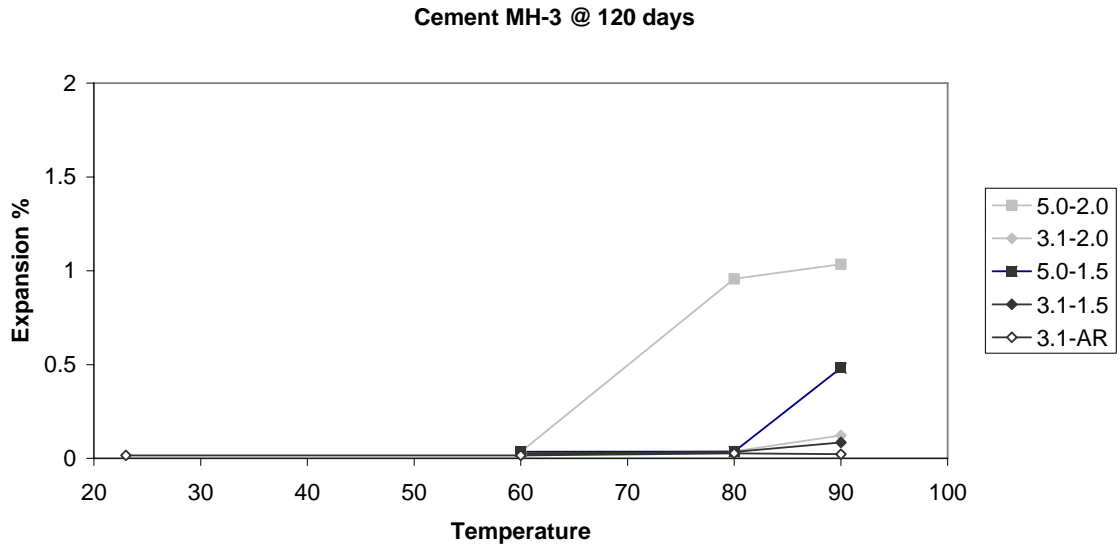


Figure 64: Expansion exhibited by cement MH-3 at one-hundred and twenty days

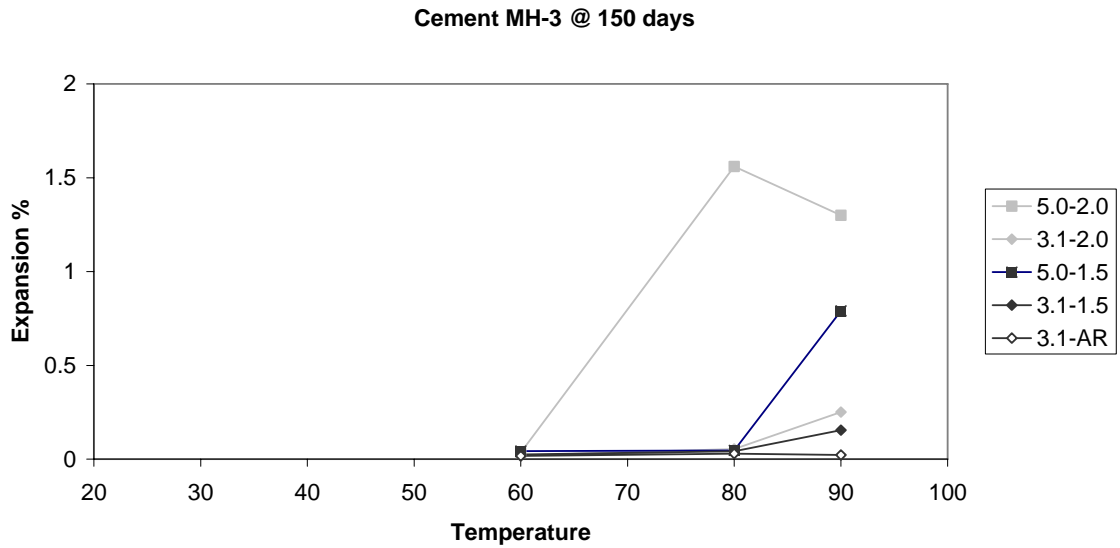


Figure 65: Expansion exhibited by cement MH-3 at one-hundred and fifty days.
 * The 5.0-2.0 data at 90°C is a bent bar and the expansion is higher than shown

The trends observed for cement E carry through the experiment. The heat cure temperature and cement chemistry determine the levels of expansion.

Cement MH-3 was mixed at three alkali levels. The expansion follows the increasing alkali content, with the 2.0% alkali mortar bars expanding at a much greater rate than those of lower alkali content. Figures 65 and 66 shows cement MH-3 at 120 and 150 days. No data is available at this time for the 180 and 270 day expansion levels.

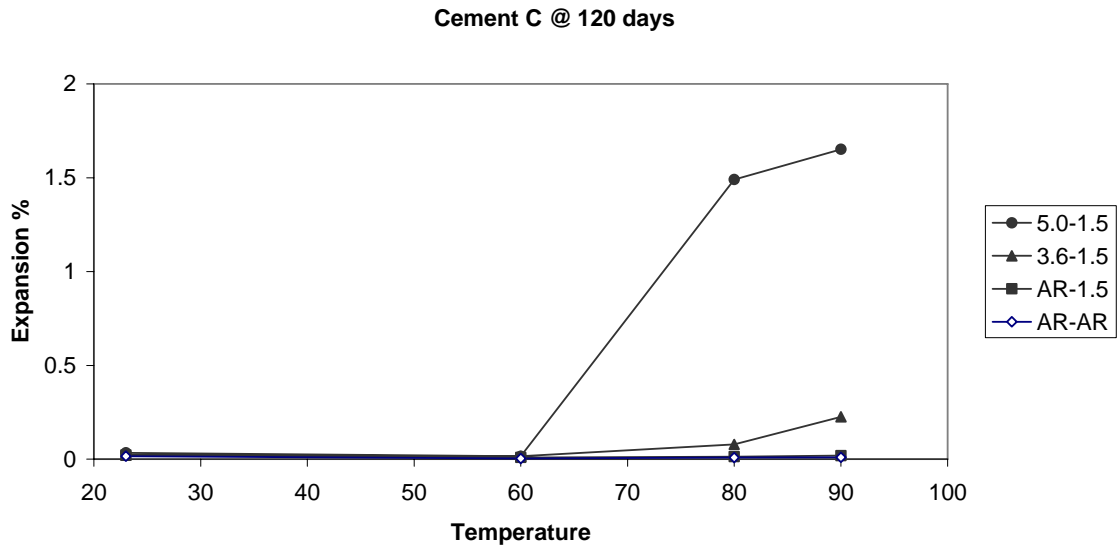


Figure 66: Expansion exhibited by cement C at one-hundred and twenty days

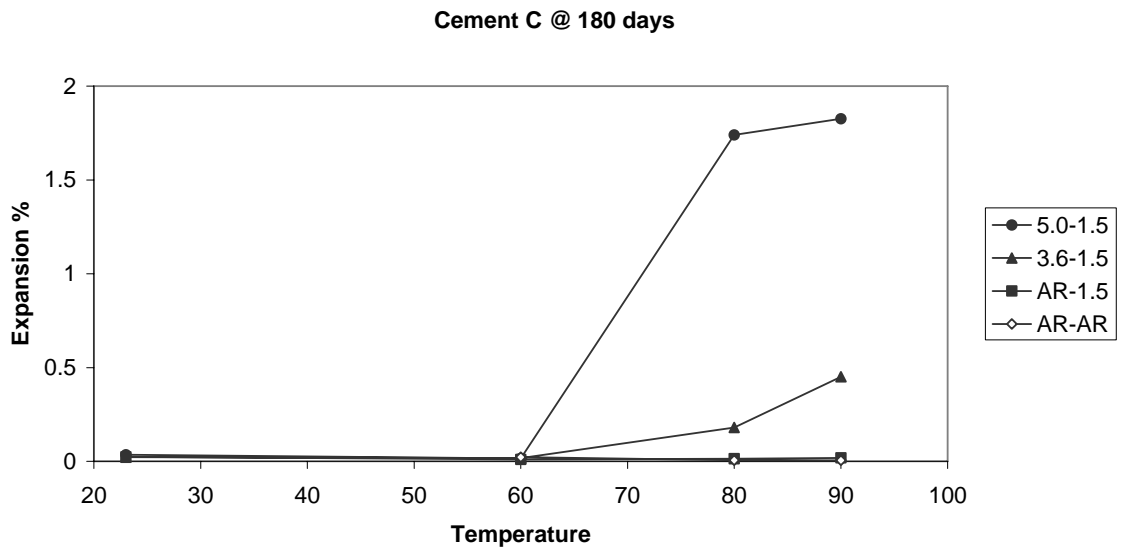


Figure 67: Expansion exhibited by cement C at one-hundred and eighty days

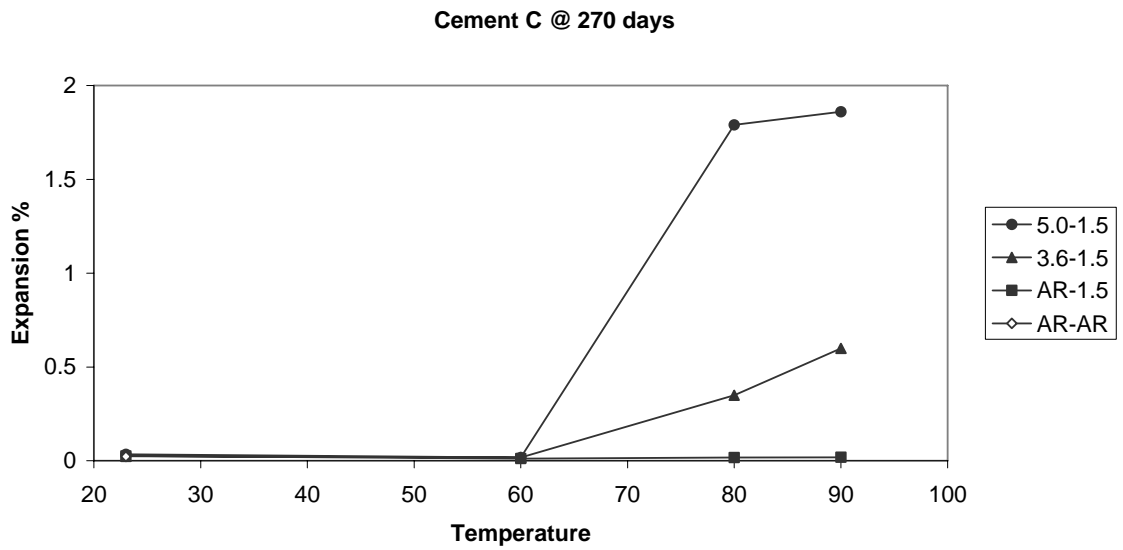


Figure 68: Expansion exhibited by cement C at two-hundred and seventy days

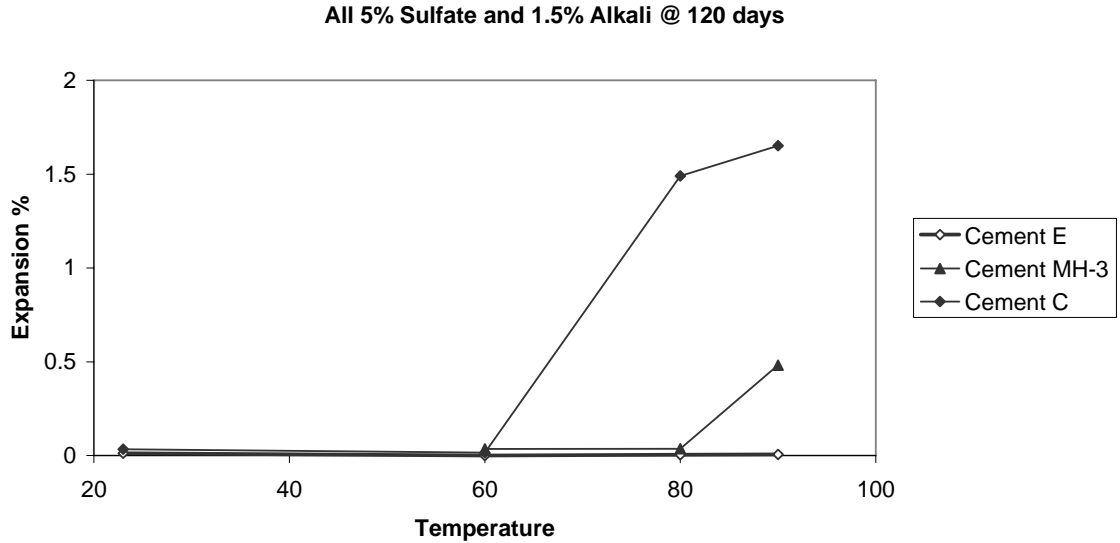


Figure 69: Comparison of expansion exhibited by all cements with a sulfate content of 5.0% and an alkali content of 1.5% at 120 days

At 120 days cement C exhibits the greatest expansion. The temperature effect shows for cement C above 60°C as opposed to cement MH-3 which shows little expansion after the 80°C heat cure. The same trends hold true at 180 days. Figures 70 and 71 show the same cements at the 3.6% sulfate level and 1.5% alkali level.

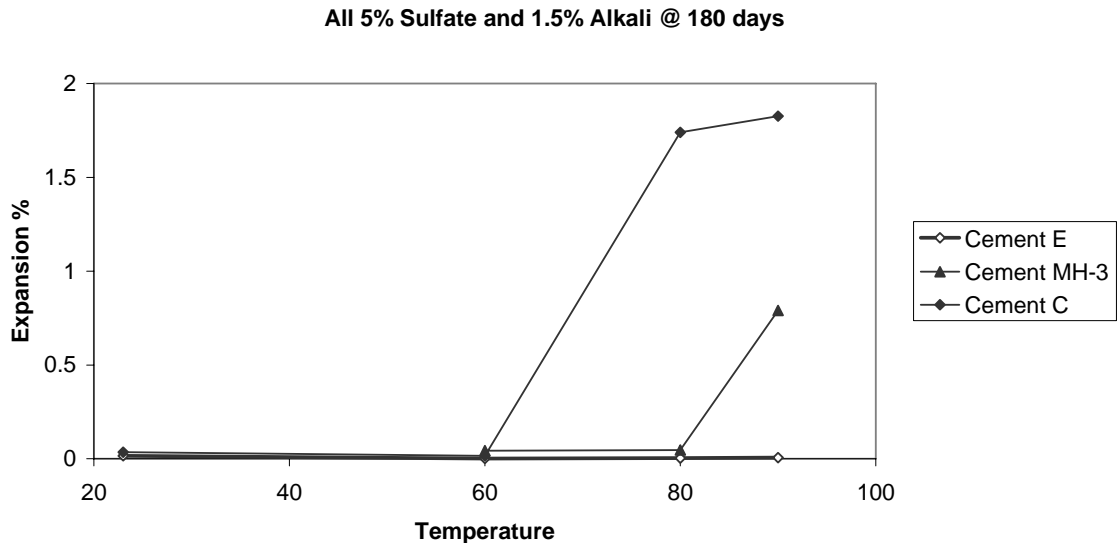


Figure 70: Comparison of expansion exhibited by all cements with a sulfate content of 3.6% and an alkali content of 1.5% at 180 days

All 3.6% Sulfate and 1.5% Alkali @ 120 days

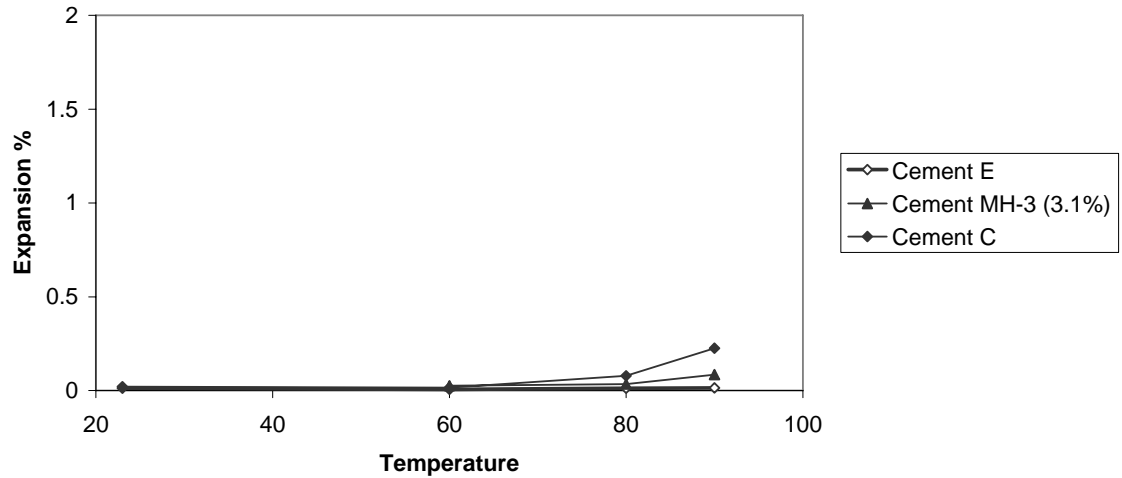


Figure 71: Comparison of expansion exhibited by all cements with a sulfate content of 3.6% and an alkali content of 1.5% at 120 days

The expansion levels are much lower at the 3.6% sulfate level. Cement C still shows a temperature effect above 60°C and MH-3 above 80°C as in the 5.0% sulfate charts. At 180 days the same trends continue for all cements with E having almost no expansion, while C and MH-3 continue to follow the same trends as the 5.0% sulfate mortar bars.

All 3.6% Sulfate and 1.5% Alkali @ 180 days

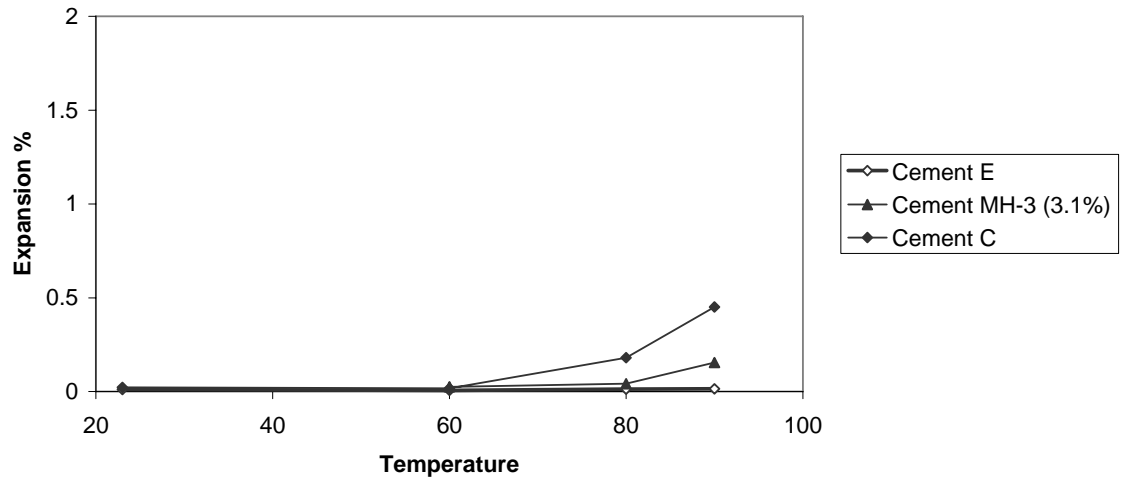


Figure 72: Comparison of expansion exhibited by all cements with a sulfate content of 3.6% and an alkali content of 1.5% at 180 days

3.2 XRD Results Using Reitveld Analysis

Bars that expanded to the level that there was noticeable bending present were run on the XRD machine to determine the levels of key components that included ettringite. Tables 6 thru 14 show the results of these runs. In every case, except one, ettringite was present in measurable quantities.

A series of XRD runs were also made on cement C heat cured at 90°C at two different chemistries. The cement was run in the as received condition and at 1.5% alkali and 5.0% sulfate level. The results of these runs are shown in Tables 15 thru 24. The results show how the phases present and their percentages change during the process and cover a time period that stretches from the initial mixing to sixty days. There were 9 different times considered, this paper will only show the tabled results for five time periods from each.

Table 6: XRD results from cement C with 5.0% sulfate content and 1.5% alkali content heat cured at 90°C after 102 days storage in a saturated lime solution

Cement: C SO3 = 5.0%, Alkali = 1.5% Cured @ 90 C 102dl 1.4% Expansion		
Phase	Diffraction angle	Intensity Ratio($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.258
Silica (SiO ₂)	26.6	0.092
C-S-H (gel)	50.0	0.258
Portlandite (Ca(OH) ₂)	34.1	0.983
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.205
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

Table 7: XRD results from cement C with 5.0% sulfate content and 1.5% alkali content heat cured at 80°C after 116 days storage in a saturated lime solution

Cement: C SO3 = 5.0%, Alkali = 1.5% Cured @ 80 C 116dl 1.4% Expansion		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.221
Silica (SiO ₂)	26.6	0.134
C-S-H (gel)	50.0	0.214
Portlandite (Ca(OH) ₂)	34.1	1.004
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.151
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

At higher heat curing temperatures the bars expand at a faster rate due to ettringite formation. The time required for the bars to show a noticeable bend was 102 days for the 90°C heat cure as compared to 116 days for the 80°C heat cure. The amount of ettringite present is much greater in the 90°C heat cured bars. Tables 6 and 7 represent the most expansive combination: 5.0% sulfate and 1.5% alkali cured at 80°C and 90°C.

Table 8: XRD results from cement C with 3.6% sulfate content and 1.5% alkali content heat cured at 90°C after 122 days storage in a saturated lime solution

Cement: C SO ₃ = 3.6%, Alkali = 1.5% Cured @ 90 C 122dl .2% Expansion		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.309
Silica (SiO ₂)	26.6	0.35
C-S-H (gel)	50.0	0.095
Portlandite (Ca(OH) ₂)	34.1	1.663
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.225
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

The lower sulfate level of 3.6% showed noticeable bending at 122 days in a saturated lime solution when heat cured at 90°C. The 80°C heat cure did not exhibit this level of expansion until 195 days.

Tables 9 thru 12 show cement MH-3 at 5.0% sulfate and 1.5% or 2.0% alkali. Although the ages are similar, the 2.0% alkali mixes run at both 80°C and 90°C show lower levels of ettringite.

Table 9: XRD results from cement MH-3 with 5.0% sulfate content and 1.5% alkali content heat cured at 90°C after 123 days storage in a saturated lime solution

Cement: MH-3 SO ₃ = 5.0%, Alkali = 1.5% Cured @ 90 C 123dl .5% Expansion		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.000
Silica (SiO ₂)	26.6	0.257
C-S-H (gel)	50.0	0.115
Portlandite (Ca(OH) ₂)	34.1	1.665
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.201
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

Table 10: XRD results from cement MH-3 with 5.0% sulfate content and 1.5% alkali content heat cured at 80°C after 121 days storage in a saturated lime solution

Cement: MH-3 SO ₃ = 5.0%, Alkali = 1.5% Cured @ 80 C 121dl 0.04% Expansion		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.197
Silica (SiO ₂)	26.6	0.740
C-S-H (gel)	50.0	0.316
Portlandite (Ca(OH) ₂)	34.1	1.487
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.235
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

The results are similar for both the above charts. The difference in the amount of ettringite present is probably due to the survival of primary ettringite after the 80°C heat cure.

Table 11: XRD results from cement MH-3 with a 5.0% sulfate content and 2.0% alkali content heat cured at 90°C after 125 days storage in a saturated lime solution

Cement: MH-3 SO ₃ = 5.0%, Alkali = 2.0% Cured @ 90 C 125dl 1.0% Expansion		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.057
Silica (SiO ₂)	26.6	0.102
C-S-H (gel)	50.0	0.087
Portlandite (Ca(OH) ₂)	34.1	1.564
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.140
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

Table 12: XRD results from cement MH-3 with a 5.0% sulfate content and 2.0% alkali content heat cured at 80°C after 120 days storage in a saturated lime solution

Cement: MH-3 SO ₃ = 5.0%, Alkali = 2.0% Cured @ 80 C 120dl 0.96% Expansion		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.271
Silica (SiO ₂)	26.6	0.165
C-S-H (gel)	50.0	0.155
Portlandite (Ca(OH) ₂)	34.1	1.511
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.159
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

Interestingly, both sets of data show the ettringite levels higher after the 80°C heat cure cycle than at the 90°C cycle. This may be due to the fact that primary ettringite exists at greater levels in the bars cured at 80°C than those done at 90°C.

Table 13: XRD results from cement E with 5.0% sulfate content and 1.5% alkali content heat cured at 90°C after 285 days storage in a saturated lime solution

Cement: E SO ₃ = 5.0%, Alkali = 1.5% Cured @ 90 C 285dl 0.04% Expansion		
Phase	Diffraction angle	Intensity Ratio (I _{phase} /I _{TiO₂})
Rutile (TiO ₂)	27.4	1
Calcite (CaCO ₃)	29.4	0.324
Silica (SiO ₂)	26.6	.540
C-S-H (gel)	50.0	0.146
Portlandite (Ca(OH) ₂)	34.1	0.915
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0
Gypsum (CaSO ₄ 2H ₂ O)	11.5	0

It is interesting to note the low levels of ettringite present in cement E after 300 days in lime water. In the bars heat cured at 90°C, no ettringite was found. This is in direct contrast to the other cements in which higher curing temperatures lead to greater amounts of delayed ettringite formation. Cement E has a very low expansion rate, and did not show any signs of bending during the experiment. Cement C was mixed in the as received condition and as doped to 1.5% alkali and 5.0% sulfate. The initial XRD runs were made directly after the paste nuggets were placed in the humid cabinet for their one hour age. Tables 14 and 15 show the results at this time.

Table 14: XRD results from cement C in the as received condition 20 minutes after the initial hydration

Cement: C SO3 = AR, Alkali = AR (20 minutes)		
Phase	Diffraction angle	Peak Height
Rutile (TiO ₂)	27.4	0
Calcium Silicate (Ca ₃ SiO ₂)	32.5	545
Portlandite Ca(OH) ₂	34.1	0
Calcite (CaCO ₃)	29.4	443
Anhydrite (CaSO ₄)	25.4	81
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0
Gypsum (CaSO ₄ •2H ₂ O)	11.6	20
Bassanite (CaSO ₄ •1/2 H ₂ O)	14.7	40

Table 15: XRD results from cement C as doped to a 1.5% alkali and 5.0% sulfate level 30 minutes after initial hydration

Cement: C SO3 = 5.0%, Alkali = 1.5% (30 minutes)		
Phase	Diffraction angle	Peak Height
Rutile (TiO ₂)	27.4	0
Calcium Silicate (Ca ₃ SiO ₂)	32.5	449
Portlandite Ca(OH) ₂	34.1	0
Calcite (CaCO ₃)	29.4	465
Anhydrite (CaSO ₄)	25.4	50
Calcium Silicate (Ca ₂ SiO ₂)	31	0
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	43
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	27
Gypsum (CaSO ₄ •2H ₂ O)	11.6	78
Bassanite (CaSO ₄ •1/2 H ₂ O)	14.7	44

Rutile was not added to the paste during the initial run because the sample was run as wet paste. It is hard to accurately compare the mixes at this point due to the time difference of ten minutes and the lack of an internal standard. After the one hour age in the humid cabinet the paste nuggets were prepared and mixed with 10% rutile which acted as an internal standard. Tables 16 and 17 show the results at this step. It is interesting to note in the time progression of the samples that ettringite was present before the heat curing process, and was destroyed during the heat curing process.

Table 16: XRD results from cement C with as received sulfate levels 75 minutes after the initial hydration

Cement: C SO3 = AR, Alkali = AR (75 Minutes)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.907
Portlandite Ca(OH) ₂	34.1	0.233
Calcite (CaCO ₃)	29.4	0.615
Anhydrite (CaSO ₄)	25.4	0.109
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.059
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.038
Bassanite (CaSO ₄ •1/2 H ₂ O)	14.7	0.054

Table 17: XRD results from cement C as doped to a 1.5% alkali and 5.0% sulfate level 75 minutes after initial hydration

Cement: C SO3 = 5.0%, Alkali = 1.5% (75 Minutes)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	1.026
Portlandite Ca(OH) ₂	34.1	0
Calcite (CaCO ₃)	29.4	0.916
Anhydrite (CaSO ₄)	25.4	0.092
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.073
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.104

From a comparison of the above two tables it is evident that the higher sulfate levels result in higher levels of ettringite. The paste nuggets were run at 6, 12, 16 and 17 hours. Sixteen hours from the start of the heat curing process the paste nuggets were once again at room temperature. Tables 18 and 19 show the results at this time.

Table 18: XRD results from cement C with as received sulfate levels 17 hours and 15 minutes after the initial hydration

Cement: C SO3 = AR, Alkali = AR Cured @ 90°C (17.25 Hours)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.543
Portlandite Ca(OH) ₂	34.1	0.662
Calcite (CaCO ₃)	29.4	0.348
Anhydrite (CaSO ₄)	25.4	0.087
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0.063
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.053
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.000

Table 19: XRD results from cement C as doped to a 1.5% alkali and 5.0% sulfate level 17 hours and 15 minutes after initial hydration

Cement: C SO3 = 5.0%, Alkali = 1.5% Cured @ 90°C (17.25 Hours)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.413
Portlandite Ca(OH) ₂	34.1	1.014
Calcite (CaCO ₃)	29.4	0.311
Anhydrite (CaSO ₄)	25.4	0.063
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0.079
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.000
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.000

At this point in the process, the phases that are present in each mix are at almost the same level. There is no measurable ettringite present in either mix. The 28 and 60 day measurements are presented in Tables 20 thru 23. Ettringite is reformed in the paste which contained 5.0% sulfate, and was at measurable levels within twenty-eight days. The paste that had the as received sulfate level still had no measurable ettringite after 60 days.

Table 20: XRD results from cement C with as received sulfate levels 28 days after the initial hydration

Cement: C SO3 = AR, Alkali = AR Cured @ 90°C (28 Days)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.046
Portlandite Ca(OH) ₂	34.1	1.129
Calcite (CaCO ₃)	29.4	0.000
Anhydrite (CaSO ₄)	25.4	0.061
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0.148
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.063
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.000

Table 21: XRD results from cement C with as received sulfate levels 60 days after the initial hydration

Cement: C SO3 = AR, Alkali = AR Cured @ 90°C (60 Days)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.042
Portlandite Ca(OH) ₂	34.1	1.160
Calcite (CaCO ₃)	29.4	0.110
Anhydrite (CaSO ₄)	25.4	0.000
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0.160
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.000
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.000

The hydration process was still taking place at 60 days. The levels of portlandite and calcite were increasing while anhydrite and calcium silicates were being consumed in the process. At 60 days there were no measurable quantities of ettringite. The same process was taking place in the doped cement as shown in Tables 22 and 23.

Table 22: XRD results from cement C as doped to a 1.5% alkali and 5.0% sulfate level 28 days after initial hydration

Cement: C SO3 = 5.0%, Alkali = 1.5% Cured @ 90°C (28 Days)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.232
Portlandite Ca(OH) ₂	34.1	1.171
Calcite (CaCO ₃)	29.4	0.146
Anhydrite (CaSO ₄)	25.4	0.061
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0.236
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.000
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.2	0.122

Table 23: XRD results from cement C as doped to a 1.5% alkali and 5.0% sulfate level 60 days after initial hydration

Cement: C SO3 = 5.0%, Alkali = 1.5% Cured @ 90°C (60 Days)		
Phase	Diffraction angle	Intensity Ratio ($I_{\text{phase}}/I_{\text{TiO}_2}$)
Rutile (TiO ₂)	27.4	1
Calcium Silicate (Ca ₃ SiO ₂)	32.5	0.000
Portlandite Ca(OH) ₂	34.1	0.986
Calcite (CaCO ₃)	29.4	0.000
Anhydrite (CaSO ₄)	25.4	0.075
Calcium Silicate (Ca ₂ SiO ₂)	31.0	0.207
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	12.2	0.000
Ettringite (Ca ₆ Al ₂ S ₃ •32H ₂ O)	9.09	0.185

In the higher sulfate paste nuggets ettringite has been found at measurable levels at 28 days. The relative amount of portlandite, calcite, and calcium silicates decreases in the 32 day time period from 28 to 60 days. Ettringite levels continue to increase as the aging process continues as shown in the chart below.

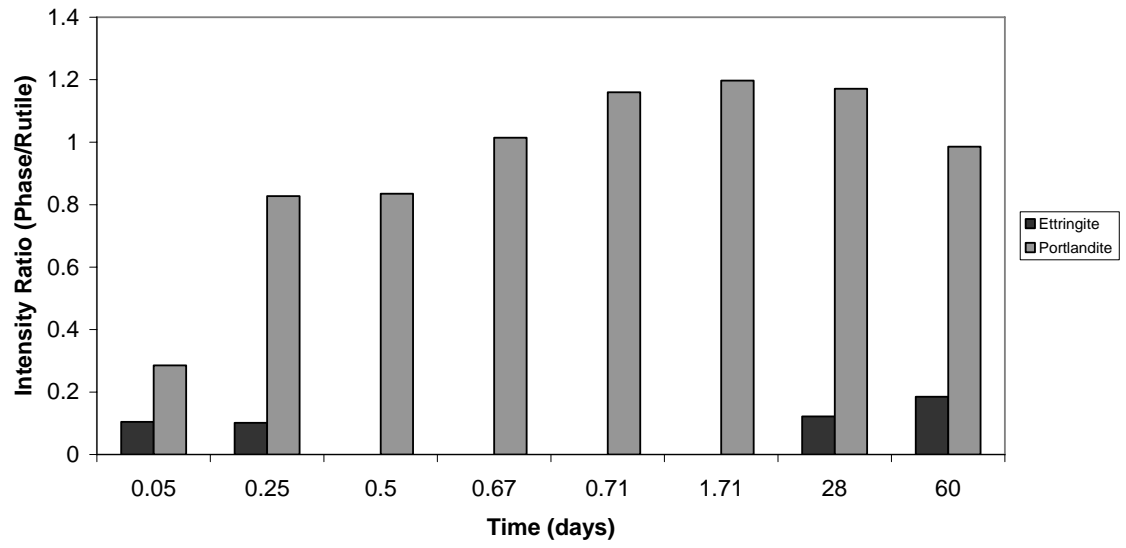


Figure 73: Ettringite and portlandite formation over time from XRD results of cement C with 1.5% alkali and 5.0% sulfate level

CHAPTER 4

CONCLUSIONS AND RECOMENDATIONS

The study indicated the significance of several variables in the ISA process. It confirmed the impact of sulfate and alkali levels along with the heat curing temperature. Equalization of the cement chemistries and fineness illustrated the impact of tricalcium silicate levels on the ISA process.

The chemistry of all three cements was shown in tables 2 thru 5. In the as received condition cement MH-3 has the highest SO_3 , $\text{Na}_2\text{O}_{\text{eq}}$ and MgO levels. This is reflected in the as received expansion results in figures 3 thru 6 and 53 thru 59. In the first four graphs and the last seven graphs, the expansion follows the SO_3 levels of the cements. Bars made with MH-3 expanded the greatest amount followed by C then E.

The expansion picture changes when the cements are equalized in alkali and sulfate content. At both 80°C and 90°C cement C bars expanded at a greater rate and experienced greater expansion levels than cement MH-3. This is what is to be expected when the only variable is the C_3S content of the cement. The effect of C_3S levels on expansion is a function of the alkali and sulfate content.

Research conducted by Rasheeduzzafar and others have come to the conclusion that the $\text{C}_3\text{S}/\text{C}_2\text{S}$ ratio has a bearing on ettringite formation and ultimately the level of expansion experienced by a particular cement over time. One problem with the experiments that were used to show this point was the variations in the alkali and sulfate

levels of the cements used in the studies. The cements used in this study were carefully chosen to represent a small range in sulfate levels and a wide variation in the alkali levels. Doping was used to both equalize the cement chemistries and to explore the effect of sulfate and alkali levels on cements with variable tricalcium silicate content. The conclusions reached by use of the experimental data are outlined below.

The heat curing temperature has a large effect on expansion experienced by the bars. In all cases the rate and level of expansion increased the higher the heat curing temperature. Divet and Randriambololona found that the high heat curing temperatures destroy the aluminosulfates initially formed during the early hydration stage, and have an effect on the structure of the C-S-H gel. The sulfates that were a constituent of the initially formed ettringite were adsorbed by the C-S-H gel or held in the pore waters. Reformation of ettringite takes place due to sulfate desorption by the C-S-H gel or sulfates in solution in the pore waters. The present study found that 60°C heat cure has little or no effect on the durability of the cement for ages up to 180 days. Even at high sulfate and alkali levels the cements exhibited little expansion for the duration of the experiment.

The sulfate level has a large impact on the durability of the cement paste. This is recognized by both ASTM and AASHTO and regulated accordingly. ASTM C-150 requirements were discussed under Section 1.3 “Chemistry of Portland Cement” and will not be restated here. It is of interest to note that in every case increasing the sulfate level lead to higher expansion rates.

The alkali levels present in the unhydrated cement have a large impact on the cements durability. According to F.P. Glasser, alkalis allow greater amounts of sulfate to

be held both in pore waters and adsorbed by the C-S-H gel. This sulfate is readily available through desorption from the C-S-H gel providing essential oxide for secondary ettringite formation. The experiments ran two different alkali levels in cements C and E, and three levels in MH-3. A review of Figures 10 thru 21 shows the effect of the alkali content on the overall expansion rates. These figures prove that increasing the alkali level will lead to a corresponding increase in both the level and rate of expansion.

Finally, the experimental data shows the effect of tricalcium silicate levels on expansion due to ettringite formation. High C_3S content is detrimental to durability. This is due to a combination of factors such that the effect of high alkalis and sulfates tend to be exaggerated at C_3S contents of 60% or more. Figure 73 shows the data for the worst case scenario tested: 5.0% sulfate and 1.5% alkali at 180 days.

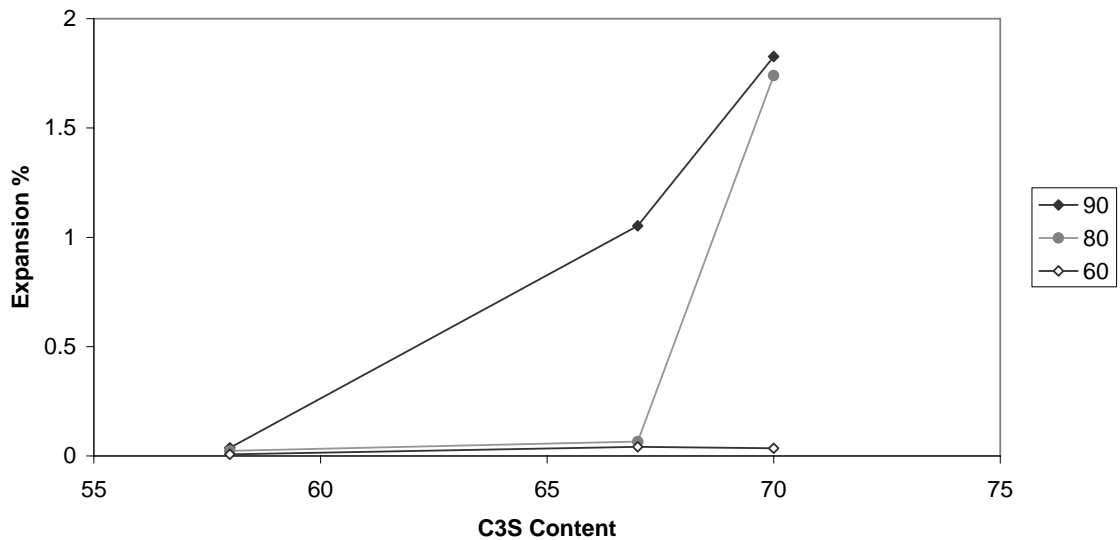


Figure 74: Effect of C_3S level upon expansion of bars with 5.0% sulfate and 1.5% alkali at 180 days in limewater

The best approach to cement durability issues would not be a limit on any single component, but the chemistry considered as a whole. The graphs show that the

expansion that a cement experiences can be directly related to interplay between the alkali, sulfate, and tricalcium silicate levels.

A discussion of the experimental conditions as they would compare to the field is warranted. Exposure to 90 C during curing is not out of line with the temperatures experienced in the field in thick sections. The sulfate level of 3.6% is also close to that of field concretes. The exposure of the bars to a lime water solution is far from field cements. This was done to stabilize the ettringite formed initially and through ISA. According to Brown and Bothe calcium has a large effect on the stability of ettringite. In the experiment, the pre-cure was limited to one hour. This is to speed up the process of expansion as proven in experiments by Fu, Ding, and Beaudoin in their 1997 paper. They found a dramatic increase in the rate of expansion if the moist curing time was reduced to one hour.

Further research is needed to confirm the results of this study and determine the effect of tricalcium silicate levels on the microstructure of the cement paste. It was apparent from the XRD data that the levels of ettringite present do not always correspond to the amount of expansion experienced by the mortar bars. Perhaps a link can be made between the cement chemistry and curing temperatures to the strength and expansion of the paste.

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